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(54) Title: PESTICIDAL FORMULATIONS			
(57) Abstract Pesticidal formulations are provided which allow incompatible pesticides to be incorporated in the same formulation. The formulations comprise a two-phase formulation, the first phase of which comprises a first active ingredient, a stabiliser and optionally an emulsifier or wetting or dispersing agent, and a carrier or solvent for the active ingredient; and a second phase immiscible with the first phase which comprises a second active ingredient and optionally an emulsifier or wetting or dispersing agent and a carrier or solvent for the second active ingredient. Methods for making such formulations and their use in controlling pests are provided.			

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PESTICIDAL FORMULATIONS

The present invention relates to formulations, particularly pesticidal formulations which contain two incompatible pesticides, to methods for making such formulations and their use in controlling pests.

It has been found that an anhydrous formulation of a pesticide, i.e. one which does not contain an aqueous phase, may be formulated with a second immiscible phase which contains a second pesticide. This has the advantage that incompatible pesticides may be incorporated in the same formulation.

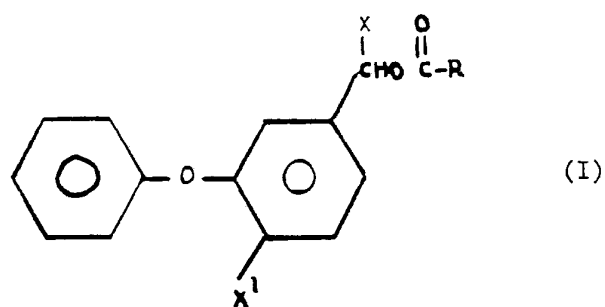
Accordingly, the present invention provides a two-phase formulation, the first phase of which comprises a first active ingredient, a stabiliser, and optionally an emulsifier or wetting or dispersing agent, and a carrier or solvent for the active ingredient; and a second phase immiscible with the first phase which comprises a second active ingredient and optionally an emulsifier or wetting or dispersing agent and a carrier or solvent for the second active ingredient.

Normally, the first active ingredient is dissolved or dispersed into the first phase but when the active ingredient is a liquid a solvent is not always required. The second phase which is immiscible with the first phase contains the second active ingredient either dissolved or dispersed in the second phase. Preferably, the first phase is a water immiscible phase and the second phase is a water phase.

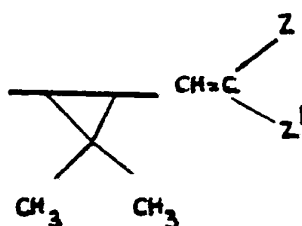
The first and second active ingredients are preferably physically and/or chemically incompatible when contained in a single phase, i.e. the presence of one of the actives in a formulation normally affects adversely the stability or utility of the other active. In addition, the active ingredient in the first phase may be one which has properties, for example irritancy or noxious vapour, which may be avoided by formulating it according to the present invention. Thus, it may have been possible previously to prepare stable but irritant

formulations of the active ingredients; formulations according to the present invention may avoid such irritancy. By active ingredient we mean both non-biologically and biologically active compounds. For example, the active ingredients may be selected from insecticides, acaricides, herbicides, fungicides, insect and plant growth regulators, pheromones, insect behaviour modifiers, biological control agents (e.g. viruses, bacteria and eggs of parasites), dyes, perfumes, flavours, bactericides, lubricants, medicaments, food supplements, paints, polishes, lacquers (including hair lacquer), textile treatments (including sizes), or other active ingredients which are limited in their use by their incompatibility with other active ingredients. Examples of incompatible actives include combinations of pesticides selected from arthropodicides (insecticides, acaricides), herbicides, fungicides or insect and plant growth regulators. Examples of incompatible pesticides are the pyrethroids and organophosphate insecticides, the pyrethroid and formamidine insecticides, α -cyano-pyrethroid insecticides and thiazole anthelmintics, and pyrethroids and tributyl tin fungicides.

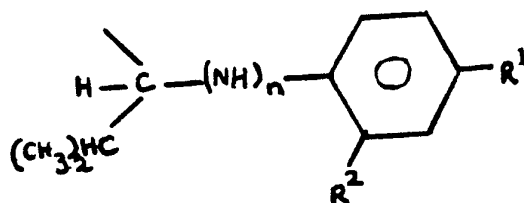
Examples of pyrethroid insecticides include those of the formula (I)



where R is



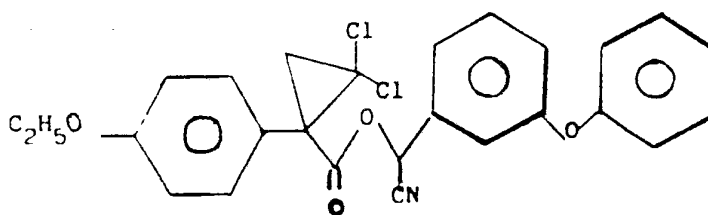
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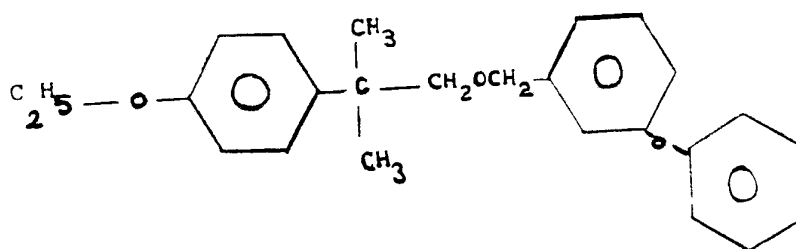
and n is 0 or 1,

R^1 is halo, CF_3 or CHF_2O , R^2 is hydrogen or halo, and Z and Z^1 are each independently selected from halo, CF_3 and methyl, X is hydrogen or halo, and X is H, CN or $C\equiv CH$

or



or



Examples of pyrethroids are 3-phenoxybenzyl-(1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-1-carboxylate (permethrin), (RS)- α -cyano-3-phenoxybenzyl-(1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-1-carboxylate (cypermethrin) and its indivi-

dual isomers such as the (1RS) cis isomer (alphamethrin), (S)- α -cyano-3-phenoxybenzyl-(IR)-cis-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropane-1-carboxylate (deltamethrin), or a reaction mixture comprising two enantiomeric pairs in approximately ratio 2:3 (S)- α -cyano-3-phenoxybenzyl-(IR)-cis-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and (R)- α -cyano-3-phenoxybenzyl (IS)-cis-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate with (S)- α -cyano-3-phenoxybenzyl (IR)-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and (R)- α -cyano-3-phenoxybenzyl (IS)-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (beta-cypermethrin), (RS)- α -cyano-3-phenoxybenzyl-(Z)-(IRS)-cis-3-(2-chloro-3,3,3-trifluoro propenyl)-2,2-dimethylcyclopropanecarboxylate (cyhalothrin) and a mixture of its (S)(Z)-(IR)-cis and (R)(Z)-(IS)-cis-isomers;

(RS)- α -cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methylbutyrate (fenvalerate) and the single (S), (S) isomer (esfenvalerate) (RS)- α -cyano-3-phenoxybenzyl (S)-2-(4-difluoromethoxyphenyl)-3-methylbutyrate (flucythinate), (RS)- α -cyano-3-phenoxybenzyl N(2-chloro- α,α,α -trifluoro-p-tolyl)-D- valinate (fluvalinate), (RS)- α -cyano-4-fluoro-3-phenoxybenzyl (IRS)-cis-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (cyfluthrin), (RS)- α -cyano-4-fluoro-3-phenoxybenzyl (IRS)-cis-trans-3-(2-chloro-2(4-chlorophenyl)vinyl)-2,2-dimethylcyclopropanecarboxylate (flumethrin), 2-methylbiphenyl-3-yl-methyl(Z)-(IRS,3RS)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl cyclopropane carboxylate (Bifenthrin);

the allethrins, for example (1RS)-3-allyl-2-methyl-4-oxocyclopent-2-enyl (1R,3R)-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate (bioallethrin), (1S)-allyl-2-methyl-4-oxocyclopent-2-enyl (1R,3R)-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate (S-bioallethrin), and mixtures of allethrin isomers (esbiothrin);

the resmethrins, for example 5-benzyl-3-furylmethyl (IRS, 3RS; IRS, 3SR)-2,2-dimethyl-3-(2-methyl-prop-1-enyl)cyclopropanecarboxylate (resmethrin) and 5-benzyl-3-furylmethyl (1R,3R)-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate (bioresmethrin).

Examples of organophosphate insecticides are:

0,0-dimethyl-0-3,5,6-trichloro-2-pyridylphosphorothioate (Chloropyrifos-methyl)

Examples of formamidine insecticides include N-methyl bis(2,4-xyl-aminomethyl)amine (Amitraz). Examples of thiazole anthelmintics include 2,3,5,6-tetrahydro-6-phenylimidazo[2,1-b]thiazole(levamisole). Examples of fungicides include tributyl tin oxide.

Particularly preferred examples of incompatible actives in the formulations of the present invention include deltamethrin and chlorpyrifos methyl in an aqueous system.

The first phase is preferably dispersed within the second phase. The stabiliser forms a barrier at the interface between the dispersed first phase and the second phase. The stabiliser is preferably a film-forming alkanol eg. an alkanol which can act as an evaporation retardant in an aqueous spray system as described in European Patent Specification 331474. It is preferably a primary alcohol; preferably with no more than one or two side substitutions selected from methyl, ethyl, trifluoromethyl and halo (e.g. fluoro or chloro), with such substitutions preferably remote from the alcohol group (preferably at least 7 carbon atoms away from the hydroxyl group), and preferably the alkanol is not substituted at all; preferably C₁₆₋₂₀; preferably saturated; and preferably a solid at 27°C, Octadecan-1-ol and, particularly, hexadecan-1-ol are preferred. Hexadecan-1-ol (also known as cetyl alcohol) is usually available commercially as a mixture with a minor proportion of octadecan-1-ol (stearyl alcohol) and such "cetostearyl alcohol" is quite satisfactory. Heptadecan-1-ol performs adequately but is much more expensive. Other highly effective film-forming agents include 1-hexadecylamine, 1-heptadecylamine and 1-octadecylamine. Less preferred film-forming agents include hexadecan-2-ol, 1,2-hexadecandiol, methyl stearate, stearyl acetate, methyl palmitate and 1,2-octadecandiol. N-alkoxyalkanols may be used,

for example $\text{CH}_3(\text{CH}_2)_{21}\text{OC}_2\text{H}_4\text{OH}$, $\text{CH}_3(\text{CH}_2)_{21}\text{OC}_3\text{H}_6\text{OH}$, $\text{CH}_3(\text{CH}_2)_{17}\text{OC}_2\text{H}_4\text{OH}$ or $\text{CH}_3(\text{CH}_2)_{15}\text{OC}_2\text{H}_4\text{OH}$, as may oxyethylene-docosanol and mixtures of any of the said film-forming compounds.

The emulsifier may be any suitable compound or mixture of compounds. Cationic emulsifiers can be used, but they tend to irritate the user's eyes. Anionic emulsifiers such as calcium dodecyl benzene sulphate (CDBS) or sodium d-isopropyl naphthalene sulphonate (SDNS) can also be used, but these are not as effective at stabilising the emulsion whilst maintaining evaporation retarding properties. Preferably, the emulsifier is a non-ionic compound, or mixture of non-ionic compounds, having an HLB (hydrophilic/lipophilic balance) of 6-20 and preferably 8-18. Suitable compounds include polyoxyethylene stearyl ethers (PSE), polyoxyethylene monolaurates (PEM), polyoxyethylene mono-oleates (PMO), sorbitan mono-oleate (SMO), nonylphenol ethoxylate (NPE), polyethylene glycol (PEG) and blends of oleyl ethoxylate (10 mole), and PEG20 glyceryl oleate (OE/PGO).

These emulsifiers are available as follows:

<u>Abbrev.</u>	<u>Trade name</u>	<u>Supplier</u>
OE/PGO	Tegoplant	Th.
	EM11	Goldschmidt Ltd.
PSE	Brij 72, Brij 76,	ICI Speciality
	Brij 78	Chemicals
PEM	Tween 20	ICI Speciality
		Chemicals
SMO	Span 80	ICI Speciality
		Chemicals
PMO	Tween 80	ICI Speciality
		Chemicals

NPE	Ethylan	Lankro
	KEO, 55, BV	Chemicals
		Limited
CDBS	Arylan CA	Lankro
		Chemicals
		Limited
SDN	Aerosol OS	Cyanamid GB
		Ltd.

The solvent, for the first phase, preferably has a low relative molecular mass, namely less than about 200. Suitable compounds include aromatic hydrocarbons, lower alkyl esters, lower ketones, lower alkanols and lower alkanes, the term "lower" meaning C₁₋₁₂, preferably C₁₋₁₀ and more preferably C₁₋₈.

Particular solvents include the following, all available from Exxon Chemicals Limited;

"Solvesso 150" - An aromatic hydrocarbon solvent (C₉ to C₁₁) with a distillation range 190 to 210°C.

"Solvesso 200" - An aromatic hydrocarbon solvent (C₁₀ to C₁₂) with a distillation range 226 to 290°C.

"Exxate 700" - Heptyl acetate 99% pure, or

Odourless kerosene - A mixture of high boiling non-aromatic hydrocarbons consisting of paraffins and naphthenes with a distillation range of 180 to 270°C.

The first phase may comprise more than one active ingredient (optionally with a synergist or potentiator, which is regarded as an active ingredient for the purpose of the Formula below), more than one solvent, more than one emulsifier and/or more than one stabiliser, together with other ingredients such as perfumes and dyes.

In a preferred aspect, the first phase of the formulation satisfies the formula :

$$\frac{\text{mass of oil phase}}{\text{mass of stabiliser}} \leq \frac{M_{\text{oil}}}{M_{\text{stabiliser}}} \times \text{Exp} \left[\frac{\ln(L/4) + C \ln(AX^B)}{C} \right]$$

where L is less than or equal to 15, A = 700376, B = -1.51, C = 0.8472

M_{oil} is the weighted average relative molar mass of the oil phase

$M_{\text{stabiliser}}$ is the average molar mass of the stabiliser, and

$$X = \frac{(M_{\text{oil}})^{1.8}}{Y}$$

where Y is the molar solubility ratio of the formulation, defined as the minimum number of moles of oil phase which will dissolve the stabiliser, divided by the number of moles of stabiliser, provided that, in the Formula above, any solvent which has no liquid phase at 27°C at atmospheric pressure is excluded.

The "oil phase" is the liquid non aqueous phase and will comprise one or more of the active ingredient, the solvent therefor and in some cases the emulsifier.

For the avoidance of doubt, and to clarify any ambiguities which may arise in the printing or copying of this specification, it is to be noted that the relational symbol in the Formula is "less than or equal to", "Exp" means the exponential of what follows in brackets, "ln" means the natural logarithm, i.e. $\log_e$, L is divided by 4, X is raised to the power B, B is a negative value (minus 1.51) and, in the definition of X, M_{oil} is raised to the power 1.8.

Preferably L is less than 12, 10, or 8 and is most preferably less than 5. A distilled water spray has an "L" value of about 26, and most conventional diluted formulations have a value of about 22-30.

In the formulations of the invention, "L" can be set at a desired value in order to calculate the required ratios of the ingredients.

M_{oil} , the average molecular weight of the oil phase, is the weighted average, i.e. taking into account the relative proportions of the ingredients.

The value "Y", namely the molar solubility ratio of the formulation, may be derived empirically by making up at 40°C a series of mixtures with different ratios of oil phase to alkanol, allowing the mixtures to cool to 27°C, leaving the cool mixtures for at least 48 hours at 27°C, and determining the amount, in moles, of the oil phase which is needed to dissolve completely a given amount of retardant, in moles. The former is then divided by the latter to give Y.

Preferred film-forming compounds include C_{16-20} saturated alkanols such as hexadecan-1-ol and C_{16-18} saturated amines.

Preferred emulsifiers and solvents for the first phase are as described hereinbefore for European Patent Specification 331474, which is incorporated herein by reference.

The use of the formulations of the present invention will be dependent upon the nature of the active ingredients included within the formulation but the formulations will commonly be used to control pesticial infestations such as insect, acarine or helminth or microbial infestations. The application rate of the active ingredients will correspond to the application rates of these actives when applied conventionally for that particular use.

A preferred formulation of the present invention contains 20% chlorpyrifos methyl and 1% deltamethrin, cetyl alcohol being the stabiliser. This formulation is useful for the treatment of stored crops such as grain, in particular against insect pests, of the orders Coleoptera (e.g. Anobium, Ceutorhynchus, Rhynchophorus, Cosmopolites,

Lissorhoptrus, Meligethes, Hypothenemus, Hylesinus, Acalymma, Lema,
Psylliodes, Leptinotarsa, Gonocephalum, Agriotes, Dermolepida,
Heteronychus, Phaedon, Tribolium, Sitophilus, Oryzaephilus,
Rhyzopertha, Prostephanus, Cryptolestes, Trogoderma, Typheae,
Diabrotica, Anthonomus or Anthrenus spp.), Lepidoptera (e.g. Ephestia,
Mamestra, Earias, Pectinophora, Ostrinia, Trichoplusia, Pieris,
Plodia, Sitotroga, Corcyra, Laphygma, Agrotis, Amathes, Wiseana,
Tryporysa, Diatraea, Sporganothis, Cydia, Archips, Plutella, Chilo,
Heliothis, Spodoptera or Tineola spp.), Diptera (e.g. Musca, Aedes,
Anopheles, Culex, Glossina, Simulium, Stomoxys, Haematobia, Tabanus,
Hydrotaea, Lucilia, Chrysomia, Callitroga, Dermatobia, Gasterophilus,
Hypoderma, Hylemyia, Atherigona, Chlorops, Phytomyza, Ceratitis,
Liriomyza and Melophagus spp.), Phthiraptera (Malophaga e.g. Damalina
spp. and Anoplura e.g. Linognathus and Haematopinus spp.), Hemiptera
(e.g. Aphis, Bemisia, Phorodon, Aeneolamia, Empoasca, Parkinsiella,
Pyrilla, Aonidiella, Coccus, Pseudococcus, Helopeltis, Lygus,
Dysdercus, Oxycarenus, Nezara, Aleurodes, Triatoma, Psylla, Mysus,
Megoura, Phylloxera, Adelyes, Niloparvata, Nephrotetix or Cimex spp.),
Orthoptera (e.g. Locusta, Gryllus, Schistocerca or Acheta spp.),
Dictyoptera (e.g. Blattella, Periplaneta or Blatta spp.) Hymenoptera
(e.g. Athalia, Cephus, Atta, Solenopsis or Monomorium spp.), Isoptera
(e.g. Odontotermes and Reticulitermes spp.), Siphonaptera (e.g.
Ctenocephalides or Pulex spp.), Thysanura (e.g. Lepisma spp.),
Dermaptera (e.g. Forficula spp.), Psocoptera (e.g. Peripsocus spp.) and
Thysanoptera (e.g. Thrips tabaci),. Acarine pests include ticks, e.g.
members of the genera Boophilus, Ornithodoros, Rhipicephalus,
Amblyomma, Hyalomma, Ixodes, Haemaphysalis, Dermacentor and Anocentor,
and mites and manges such as Acarus, Tyrophagus, Glycyphagus,
Tetranychus, Psoroptes, Notoednes, Sarcoptes, Psorergates, Chorioptes,
Eutrombicula, Demodex, Panonychus, Bryobia, Eriophyes, Blaniulus,
Polyphagotarsonemus, Scutigera, and Oniscus spp. and Periplaneta,
Blatta, Blattella and Lepisma.

The formulations of the present invention may be prepared as follows:

- 1) The first active is dissolved in a solvent to form, or is itself, the first phase.
- 2) The stabiliser is dissolved into the first phase.
- 3) The second active ingredient is dispersed in part of the second phase.
- 4) The surfactants are dispersed either into the first phase or into the part of the second phase containing the second active ingredient.
- 5) The first phase is then dispersed into that part of the second phase that does not contain the second active ingredient.
- 6) The remainder of the second phase containing the second active ingredient is mixed with the mixture of the first phase and the other part of the second phase.

Step (6) is not carried out under high sheer conditions. Therefore the second portion of the second phase simply combines with the first portion of the second phase and the end result is a first-phase-in-second-phase dispersion or emulsion.

The present invention will now be described in more detail by way of the following examples. Example 1 describes formulations according to the present invention containing pyrethroid and an organophosphorus insecticide. Example 2 shows the result of tests to demonstrate the stability of formulations according to the present invention. Example 3 shows the results of biological tests on various insect pests.

Example 1 - Formulations

Ingredients	% w/w
chlorpyrifos methyl	19.15
solvesso 150	19.15
water (deionised)	51.40
emulsifiers	2.00
Deltamethrin (20% SC)	5.20

The deltamethrin (20% SC) contains deltamethrin (20%) in water with surfactant, thickening agents and biological preservative.

The oil phase was prepared by dissolving cetyl alcohol in a solution of chlorpyrifos methyl in Solvesso 150 at a temperature up to 50°C.

The emulsifiers were added to the water at 60°C and the resultant aqueous solution cooled to 50°C (aqueous phase).

The oil phase was added to the aqueous phase at 50°C with vigorous mixing and the resultant emulsion cooled to 20°C.

A 20% aqueous suspension of deltamethrin was added with stirring at 20-25°C

Example 2 - Stability testing

Tests were carried out on the stability of active ingredients in a formulation according to the present invention (A) and in a two-phase formulation that does not contain stabiliser (B).

Formulation A Results

A chlorpyrifos methyl/Deltamethrin Formulation with film forming agent was prepared in a similar manner to Example 1 above.

Typical Stability Data: chlorpyrifos methyl (CPMe) tests (figures $\pm$ 10%)

Time in months (M)	25°C	38°C	50°C
Initial	100	100	100
3 M or 4 M	101	103	103
6 M	102	100	103
12 M	101	94	101

Typical Stability Data : Deltamethrin (DLTM)

Time in months (M)	25°C	38°C	50°C
Initial	100	100	100
3 M or 4 M	96	99	98
6 M	97	103	103
12 M	98	94	76

Formulations B - results

A chlorpyrifos methyl/Deltamethrin Formulation without film forming agent.

Typical Stability Data : CPME

Time in months (M)	25°C	38°C	50°C
Initial	100	100	100
3 M	112	106	71

Typical Stability Data : DLTM

Time in months (M)	25°C	38°C	50°C
Initial	100	100	100
3 M	75	75	16

The results show formulations (B) without film forming agent are relatively unstable.

Example 3 - Biological testing

Protocol: Appropriately water-diluted formulation was sprayed on to 400 tonnes of grain at Wail, Victoria. It was applied to the grain stream during turning at one litre spray per tonne. Treated grain was sampled at intervals by means of a vacuum probe. Bioassays were conducted by holding 100 adult insects on 150g or 300g grain. After 3 weeks incubation at 25°C, 55-60% relative humidity the insects were sieved off and mortality counted. The grain was further sieved at 7, 9, and 11 weeks to remove and mortality count adult progeny.

(1) 0.24:4.9mg/kg deltamethrin:chlorpyrifos-methyl

Insects tested	Months of post-treatment storage	% Mortality	Progeny numbers living dead		Progeny suppression %
Sitophilus oryzae	0	100	0	4	99.8
	1.5	100	0	0	100
	3	100	0	0	100
	4.5	100	0	0	100
	6	100	0	0	100
	9	100	0	0	100

Rhyzopertha	0	100	0	0	100
dominica	1.5	100	0	0	100
	3	100	0	0	100
	4.5	100	0	0	100
	6	100	0	0	100
	9	100	0	0	100
 Tribolium	0	100	0	0	100
castaneum	1.5	100	0	1	99.7
	3	100	0	0	100
	4.5	100	0	1	99.5
	6	100	0	4	99.0
	9	100	0	0	100
 Queensland	0	100	0	0	100
Tribolium	1.5	100	0	2	97
castaneum	3	99	0	0	100
279	4.5	99	0	1	99.7
	6	100	0	4	99.0
	9	95	0	0	100
 Oryzaephilus	0	100	0	0	100
surinamensis	1.5	100	0	0	100
	3	100	0	2	99.7
	4.5	99	0	0	100
	6	95	0	1	99.9
	9	100	0	0	100

Results show good control of insect pests for post-treatment storage up to 9 months.

CLAIMS

1. A pesticidal formulation comprising a two-phase formulation, the first phase of which comprises a first active ingredient, a stabiliser, and optionally an emulsifier or wetting or dispersing agent, and a carrier or solvent for the active ingredient; and a second phase immiscible with the first phase which comprises a second active ingredient and optionally an emulsifier or wetting or dispersing agent and a carrier or solvent for the second active ingredient.
2. A pesticidal formulation according to claim 1 wherein the first phase is a water immiscible phase.
3. A pesticidal formulation according to claim 2 wherein the second phase is a water phase.
4. A pesticidal formulation according to any preceding claim wherein the first and second active ingredients are physically and/or chemically incompatible when contained in a single phase.
5. A pesticidal formulation according to claim 4 wherein the incompatible actives include the pyrethroids and organophosphate insecticides.
6. A pesticidal formulation according to claim 5 wherein the insecticides are deltamethrin and chlorpyrifos methyl in an aqueous system.
7. A pesticidal formulation according to any preceding claim wherein the first phase of the formulation satisfies the formula:

$$\frac{\text{mass of oil phase}}{\text{mass of stabiliser}} \leq \frac{M_{\text{oil}}}{M_{\text{stabiliser}}} \times \text{Exp} \left[\frac{\ln(L/4) + C \ln(AX^B)}{C} \right]$$

where L is less than or equal to 15, A = 700376, B = -1.51, C = 0.8472

M_{oil} is the weighted average relative molar mass of the oil phase
 $M_{stabiliser}$ is the average molar mass of the stabiliser, and

$$X = \frac{(M_{oil})^{1.8}}{Y}$$

where Y is the molar solubility ratio of the formulation, defined as the minimum number of moles of oil phase which will dissolve the stabiliser, divided by the number of moles of stabiliser, provided that, in the Formula above, any solvent which has no liquid phase at 27°C at atmospheric pressure is excluded.

8. A pesticidal formulation according to claim 7 wherein L is less than 5.
9. A pesticidal formulation according to claim 7 or 8 wherein the stabiliser is a C₁₆₋₂₀ saturated alkanol, or C₁₆₋₁₈ saturated amine.
10. Use of a pesticidal formulation according to any preceding claim to control pesticidal infestations such as insect, acarine or helminth or microbial infestations.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 91/01413

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 IPC5: A 01 N 25/22/(A 01 N 25/22, 25:00, 25:02, 25:04, 53:00 57:08)		
II. FIELDS SEARCHED Minimum Documentation Searched⁷		
Classification System IPC5	Classification Symbols A 01 N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	WO, A1, 8607525 (ROBERT YOUNG & COMPANY LIMITED) 31 December 1986, see the whole document --	1-10
X	GB, A, 2095109 (THE WELLCOME FOUNDATION LIMITED) 29 September 1982, see the whole document --	1-10
X	WO, A1, 8807326 (NC DEVELOPMENT INC) 6 October 1988, see page 11, line 31 - page 12, line 11; page 16, lines 5-22; page 30, lines 10-29; page 31, line 16 - page 32, line 3 --	1-10
* 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 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "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 21st November 1991		Date of Mailing of this International Search Report 17 DEC 1991
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer Mme N. KUIPER

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	EP, A1, 0331474 (THE WELLCOME FOUNDATION LIMITED) 6 September 1989, see the whole document --	1-10
X	EP, A1, 0304492 (SUMITOMO CHEMICAL COMPANY, LIMITED) 1 March 1989, see the whole document --	1-10
X	Patent Abstracts of Japan, Vol 13, No 115, C578, abstract of JP 63-290803, publ 1988-11-28 SUMITOMO CHEM CO LTD --	1-10
X	WO, A1, 9003112 (NC DEVELOPMENT, INC.) 5 April 1990, see page 12, 2:nd paragraph; page 16, 17, 29, 31 --	1-10
X	WO, A1, 9003111 (NC DEVELOPMENT, INC.) 5 April 1990, see page 9, line 13; page 13, line 28 - page 15, line 1 --	1-10
X	WO, A1, 8903176 (DOW CHEMICAL COMPANY LIMITED) 20 April 1989, see claims 1, 9, 10 --	1-10
X	WO, A1, 8903175 (DOW CHEMICAL COMPANY LIMITED) 20 April 1989, see claims 1, 8, 11; page 16, lines 1-29; page 18, lines 9-11 -- -----	1-10

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/GB 91/01413

SA 50701

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 8607525	31/12/86	AU-B- 595225 AU-D- 6126386 EP-A- 0259340 GB-A-B- 2176706	29/03/90 13/01/87 16/03/88 07/01/87
GB-A- 2095109	29/09/82	NONE	
WO-A1- 8807326	06/10/88	AU-B- 605855 AU-D- 1493488 EP-A- 0354212 JP-T- 2502821 US-A- 5037653 WO-A- 90/03111 WO-A- 90/03112	24/01/91 02/11/88 14/02/90 06/09/90 06/08/91 05/04/90 05/04/90
EP-A1- 0331474	06/09/89	AU-B- 610717 AU-D- 3291489 WO-A- 89/07888	23/05/91 22/09/89 08/09/89
EP-A1- 0304492	01/03/89	WO-A- 88/06842	22/09/88
WO-A1- 9003112	05/04/90	AU-B- 605855 AU-D- 1493488 EP-A- 0354212 JP-T- 2502821 US-A- 5037653 WO-A- 88/07326 WO-A- 90/03111 EP-A- 0439477	24/01/91 02/11/88 14/02/90 06/09/90 06/08/91 06/10/88 05/04/90 07/08/91
WO-A1- 9003111	05/04/90	AU-B- 605855 AU-D- 1493488 EP-A- 0354212 JP-T- 2502821 US-A- 5037653 WO-A- 88/07326 WO-A- 90/03112 EP-A- 0436651	24/01/91 02/11/88 14/02/90 06/09/90 06/08/91 06/10/88 05/04/90 17/07/91
WO-A1- 8903176	20/04/89	EP-A- 0381691 JP-T- 3501845 JP-T- 3501846 WO-A- 89/03175	16/08/90 25/04/91 25/04/91 20/04/89
WO-A1- 8903175	20/04/89	EP-A- 0381691	16/08/90

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 8903175	20/04/89	JP-T- 3501845	25/04/91
		JP-T- 3501846	25/04/91
		WO-A- 89/03176	20/04/89

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