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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

An Insecticidal Composition

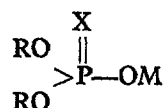
We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to an insecticidal composition, and a shaped article wholly or partly comprising such an insecticidal composition.

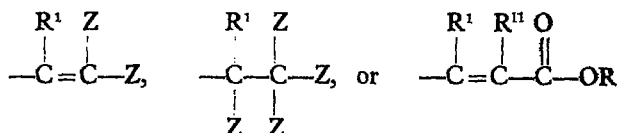
Organophosphorus compounds, particularly certain phosphate esters having a structure defined below, are well known as systemic insecticides. These compounds are functional as general poisons on contact, by ingestion or by inhalation. Because of their efficacy, they are widely used as sprays, dusts and baits. In general, they are characterised by a relatively high vapour pressure, and thus rapidly dissipate from crops and treated surfaces. While they are generally stable in dry storage, they hydrolyse when in contact with moisture, and as a consequence must be formulated, sorted and used under conditions

where their contact with water does not inhibit their utility. Such phosphate esters have been conventionally used in solid formulations on inert dusts, for example lime, dolomite, gypsum, talc, pumice, diatomaceous earths, kaolins, bentonites and attapulgite. However, because the surfaces of these carriers may be acidic or basic, and because these surfaces absorb moisture, the esters are generally not stable on the dusts for long periods and tend to undergo decomposition.

According to the invention, there is provided a solid insecticidal composition comprising a solid organic polymeric macromolecular substance having a molecular weight above 1000 and an organophosphorus compound having the general formula



(wherein R is an alkyl group; X is oxygen or sulphur; and M is a group having the structure



wherein R¹ is hydrogen or an alkyl group; Z is halogen; and R¹¹ is hydrogen, an alkyl group or halogen).

A composition of the invention has superior resistance to hydrolysis, and has a dry stable form which lends itself readily to storage and to use in the form of dust, powder, pellets or similar solid shapes. It can be used to generate vapours of the insecticides at controlled rates. It is easily prepared and handled, and affords a stable moisture-resistant formulation whereby the

efficacy of the organophosphorus insecticide is retained for extended periods.

The solid polymeric organic macromolecular substance present in a composition of the invention has a molecular weight of above 1000. The polymeric macromolecular substance may be thermosetting or thermoplastic, although the latter is more readily employed in the formulation of a composition of the invention. Examples of suitable macromolecular substances are the polyolefins (for example polyethylene, polypropylene and co-

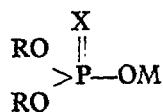
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described, both the cis- and trans-isomers are intended.

It is an important feature of the invention that the insecticidal organophosphorus compounds are also superior plasticizers for solid organic macromolecular substances, particularly for the polymers of vinyl compounds.

A composition of the invention preferably contains up to approximately 70% by weight of the insecticidal organophosphorus compound. The amount should preferably be sufficient to plasticize the macromolecular substance to yield a composition dry and solid to the touch. The total amount of phosphate ester which can be held in the composition as a plasticizer depends both on the nature of the particular phosphate ester and on the nature of the macromolecular substance with which it is mixed. In general, however, less than 5% w of the phosphate ester has no substantial plasticizing effect, while in compositions wherein the ester content is greater than 75% w, the limit of solubility of the ester in the solid macromolecular substance is exceeded, and the resulting mixture is wet or gummy.

While the organophosphorus compounds described are generally sufficiently soluble in the macromolecular substance, the phosphorus compounds having the general formula:



(wherein X is oxygen) have somewhat greater compatibility in the macromolecular substances, particularly in the polyvinyl compounds, and for this reason these organophosphorus compounds are preferred as plasticizers.

The preparation of a composition of the invention is achieved by conventional methods. Because of the great compatibility of the phosphate esters in the macromolecular substances, the compositions may be prepared merely by mechanical mixing of the ester with the powdered macromolecular substance. When the resulting powder is dry, it may then be used as it stands. Fluid pastes, or "plastisols", can be made which can be moulded, extruded, cast, or otherwise formed into such other shapes as sheets, rods, granules and foams. In some cases, the mixture of the organophosphorus compound and the macromolecular substance must be heated, preferably in a closed vessel up to 100°C. or higher to achieve solidification, or "fusion" of the macromolecular substance. Alternatively, the phosphorus compound may be incorporated in the macromolecular substance by milling, by the use of mutual solvents, and by other similar blending methods. The phosphate esters may also be incorporated in a liquid monomer (for

example styrene or methyl methacrylate) or in a liquid resin (for example an epoxy resin) before polymerisation or curing.

The resulting composition contains the organophosphorus compound in solid solution but substantially in chemically unchanged form. The composition is dry to the touch, dimensionally stable, and may be formed into useful shapes by conventional methods. For example, a paste of polyvinyl chloride containing 30% w dimethyl dichlorovinyl phosphate may be extruded with simultaneous application of heat to form strands which may be chopped into desired lengths as extruded to afford solid cylindrical pellets. Alternatively, the composition may be extruded into sheets which may be cut into strips. Polyvinyl chloride containing 20% w dimethyl dichlorovinyl phosphate, in admixture with an additional plasticizer and a blowing agent, can be made into foams of the material. The shape of the product desired will be determined by the use to which the composition is to be put. It will thus be clear that the invention also relates to shaped articles wholly or partly comprising an insecticidal composition as described above.

A composition of the invention acts as a generator of vapour - phase insecticide. Because the phosphorus compound is volatile, it tends to evaporate from the surface of the composition into the surrounding atmosphere. Since the phosphate esters described are characterized by high insecticidal activity in the vapour phase, only small amounts of the ester need to be released at any given time to render the compositions highly effective. For example, a concentration of only 0.03 to 0.04 µg/litre of dimethyl dichlorovinyl phosphate in air is lethal to mosquitoes.

The rate of release of the phosphate ester from any given mass of the composition into free air at any given time will depend on the temperature, the concentration of the phosphorus compound in the composition, the amount of free surface, and the rate of diffusion of the phosphate ester to the surface, the latter being the rate-controlling step. Because the phosphate ester is protected from moisture by the macromolecular substance until it reaches the surface, a composition of the invention serves as a long-lived continuous generator of fresh unhydrolyzed ester, even under conditions of high relative humidity. Furthermore, when kept in sealed containers wherein the atmosphere quickly becomes saturated with phosphate ester, the composition may be stored for extended periods without appreciable decrease in ester content.

Vapour pressures of some insecticidal phosphate esters are presented in the following table:

Ester	Temperature, °C	Vapour Pressure mm Hg
Dimethyl-2,2-dichlorovinyl phosphate	60	0.296
	32	0.032
2-Carbomethoxy-1-methylvinyl dimethyl phosphate	21	0.0029

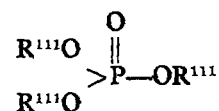
5 The dialkyl vinyl phosphate esters, particularly the dimethyl vinyl esters, are the most volatile and for that reason are particularly useful in compositions of the invention.

10 In general, when phosphate esters of the type described are dispersed under field conditions, for example as dusts or sprays, they dissipate at an undesirably rapid rate. Because of this lack of persistence, repeated applications of the phosphate ester must be employed in order to obtain lasting protection in a given area. When the esters are dispersed in the form of solids prepared from compositions of the invention, the persistence of the esters is, however, materially extended without risk of hydrolysis of the unevaporated material.

15 Because of its enhanced persistence and superior resistance to hydrolysis, a composition of the invention may be used for soil and sub-soil applications. In this way, it may be used against ants, beetles, termites, worms and larvae.

20 In order to prepare a composition of the invention containing smaller amounts of the insecticidal organophosphorus compound and nevertheless having a long persistence, a mixture of the insecticidal volatile dialkyl phosphate ester and a non-insecticidal plasticizer (for example an inert phosphate ester) may be included in the macro-molecular substance. The total amount of the insecticide and non-insecticidal phosphate ester must be sufficient to plasticize the resin. No more than approximately 70% w of total phosphate ester is required, and for best results at least 5% w of the insecticidally effective phosphate ester should be used.

30 Examples of insecticidally inert esters which may be used as inert diluents are triaryl phosphates (for example tri-cresyl phosphate, triphenyl phosphate, tri(p-tertbutylphenyl) phosphate, tri(biphenyl) phosphate, α-biphenyl diphenyl phosphate and cresyl diphenyl phosphate); trialkyl phosphates (for example tri-n-butyl phosphate, tri-2-ethylhexyl phosphate, tri-n-octyl phosphate and tri-lauryl phosphate); and mixed phosphates (for example 2-ethylhexyl diphenyl phosphate). These compounds may be generally described by the formula



(wherein R¹¹¹ is an aryl, aralkyl or alkaryl group, or an alkyl group preferably having at least four carbon atoms). They are virtually non-volatile, and, because of their similar structure, are readily compatible with the insecticidal phosphate esters in compositions of the invention.

Examples of other materials which are effective to plasticize the macromolecular substance are phthalates (for example dioctyl phthalate, diphenyl phthalate, dicyclohexyl phthalate, dimethyl phthalate and dihexyl phthalate); sebacates (for example dipentyl sebacate, n-butyl benzyl sebacate and dibenzyl sebacate); and adipates (for example dioctyl adipate, dicapryl adipate, diisobutyl adipate and dinonyl adipate). Other compatible plasticizers are, for example, hydrogenated polyphenols; alkylated aromatic hydrocarbons; and polyester plasticizers, for example polyesters of polyols such as hexanediol, and polycarboxylic acids such as sebacic or adipic acid, having molecular weights of about 2000.

Other materials (for example dyes, pigments, lubricants, fillers, anti-oxidants and ultraviolet stabilizers) may be included in a composition of the invention. For example, it has been found that the stability of both the macromolecular substance and the phosphorus compounds is extended if a stabilizing amount, preferably 0.1% w to 10% w, of a phenol is included in the composition; for example, phenol, p-cresol, m-cresol, hydroquinone, resorcinol and pyrogallol are effective as stabilisers. The phenols are preferably unsubstituted and alkyl-substituted mono- and dihydroxybenzenes wherein the alkyl groups have not more than eight carbon atoms. Particularly preferred phenols are phenolic anti-oxidants, for example mononuclear phenols having a phenolic hydroxyl group which is hindered by one or more ortho alkyl groups (for example 2,6-dialkyl phenols, for instance 2,6-di-tert.butyl-4-methyl phenol; 2,4,6-tri-tert.butyl phenol; 2,6-di-

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tert.butyl phenol; 2 - methyl - 6 - tert.butyl phenol; 2,4 - dimethyl - 6 - tert.butyl phenol and 2,6 - diisopropyl - 4 - methyl phenol). Also preferred are, for example, bisphenolic and biphenolic stabilizers (for example bis-(3,5 - di - tert.butyl - 4 - hydroxyphenyl)-methane; bis - (2 - hydroxy - 3 - tert.butyl-5-methylphenyl) methane and 3,3',5,5'-tetra-tert.butyl - 4,4' - dihydroxy biphenyl); naphthols (for example beta-naphthol) and benzyl alcohols (for instance 3,5-di-tert.butyl-4-hydroxy-benzyl alcohol; 3,5 - diisopropyl-4-hydroxybenzyl alcohol and 3 - methyl-5-tert.butyl-4-hydroxybenzyl alcohol).

The following examples illustrate the invention, in which, unless otherwise indicated, proportions are in parts by weight. The mesh sizes referred to in these examples are based on the United States Standard mesh sizes.

EXAMPLE I

To samples of powdered polyvinyl chloride (Bakelite QYNV) were added various amounts of dimethyl 2,2 - dichlorovinyl phosphate, and the mixtures were mechanically mixed for 15 minutes. At the end of this time, the mixtures were examined and the following results were obtained:

% w of Phosphate Ester	Nature of the mixture
10	dry
15	dry
20	dry
25	wet
30	paste
35	fluid
40	fluid

30 These results indicated that polyvinyl chloride could absorb up to about 20% w of the ester without further treatment.

Each of the wet and fluid mixtures was heated to 90° C. to 100° C. for ten minutes.

35 In each case, a firm dry solid was obtained in this manner.

40 Solvent extraction of the ester from these materials with chloroform showed that the ester was not chemically altered by the treatment and could be recovered unchanged.

EXAMPLE II

A solid foam was prepared having the following composition:

	% w
45 Polyvinyl chloride	62.5
Dimethyl 2,2-dichlorovinyl phosphate	12.5
Tricresyl phosphate	25.0
	100.0

50 This foam was hung in a duct through which passed a moving column of room-temperature air. The foam was removed at intervals to determine the rate at which the foam was generating the ester in vapour form. The following results were obtained:

Exposure Time,
days

Vaporization Rate,
μg/cm²/hour

0	32
7	13
23	9
32	8
51	1

The foam was generating ester vapour long after an equivalent amount of the ester in liquid form would have evaporated.

EXAMPLE III

Granules of 9/24-mesh having the following composition were prepared:

	% w
Polyvinyl chloride	70
Dimethyl 2,2-dichlorovinyl phosphate	30
	100

Samples of the above granules and also of granules containing Pikes Peak 9H66 (an inorganic carrier material consisting mainly of silica and alumina), DDVP and 2,6-di-tert.butyl - 4 - methylphenol in Dacron mesh

bags were placed in a conduit through which and the rate of phosphate ester vapour passed a moving column of room temperature air. The bags were removed at intervals, generation determined. The following results were obtained:



Carrier	Quantity of Granules, g	Mesh Size	Initially	DDVP Insecticide Vaporized/hr, mg after Exposure (Days)						
				7	14	21	28	35	42	56
PVC (a)	15	10/24	1.49	1.55	1.91	1.24	0.74	0.52	—	—
PVC	15	10/24	1.05	1.37	1.13	0.45	0.64	0.31	0.25	0.32
PVC	60	10/24	1.08	1.63	1.37	—	—	0.41	—	—
PVC	60	10/24	4.54	2.40	0.79	—	—	—	—	—
PVC	60	10/24	—	2.26	1.90	—	—	—	—	—
PVC	60	24/60	2.52	—	1.26	—	—	—	—	—
PVC	60	24/60	—	1.25	1.49	—	—	—	—	—
Pikes Peak 9H66 (b)	15	20/40	1.31	0.87	—	0.24	—	—	—	—

(a) In this experiment, the bag of granules was lying flat during the vaporization test. In all other experiments, the bag was suspended in the chamber.

(b) In this experiment, the granules had the following composition:

	%w
Pikes Peak 9H66 (0.5% H ₂ O)	75
DDVP	20
2,6-Di-tert.butyl-4-methylphenol	5
	100

10 The plastic granules were producing appreciable amounts of vapour long after an equivalent amount of liquid ester would have evaporated.

EXAMPLE IV
The storage stability of dimethyl-2,2-dichlorovinyl phosphate formulated on conventional clays was compared with that of various polyvinyl chloride compositions containing the phosphate ester. The following results were obtained:

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On Granular Clay Carriers

Type of Clay	Water Content of Clay, % w	% of Ester		% Decomposition
		Initial	After 2 wks. at 130°F.	
Attapulgate	normal (a)	18.4	5.9	68
Montmorillonite	normal (a)	19.1	9.3	51
Montmorillonite	0.5 (specially dried)	18.9	12.7	33

(a) The water contents were normal for stored clays, being between 6 and 10% w.

Polyvinyl Chloride Formulations

Sample	% of Ester		% Decomposition
	Initial	After 2 wks. at 130°F	
9/24 mesh granules	27.0	25.6	5
24/60 mesh granules	26.8	23.3	13
Powder	18.3	15.6	15
Foam	11.3	10.5	7

The results of the stability tests show that the polyvinyl chloride compositions were much more stable than the formulations on clays.

EXAMPLE V

Monomeric methyl methacrylate was thermally polymerized by benzoyl peroxide with 0.1% w dimethyl - 2,2 - di - chlorovinyl phosphate in the mixture. The product was a tough dry solid resin. In another preparation, monomeric methyl methacrylate containing 0.1% w dimethyl - 2,2 - dichlorovinyl phosphate was heated on a steam bath until its viscosity had increased markedly. At that point, sufficient dimethyl 2,2 - dichlorovinyl phosphate was added to render the mixture 10% w in the phosphate. This mixture was allowed to polymerize at 50°—168°C. until a hard, tough dry polymeric product was obtained. The product was mixed with attaclay and dispersing agents and hammer-milled three times. A finely divided powder was obtained in this manner.

A solid polystyrene resin containing dimethyl 2,2 - dichlorovinyl phosphate was prepared in the same way.

EXAMPLE VI

A solid insecticidal composition was prepared by mixing Resinous Polyol X-450 (a polymerized styrene-allyl alcohol resin) with 3.6% w of dimethyl 2,2-dichlorovinyl phosphate. From this composition a smooth dry flowable powder was formed.

A similar result is obtained when the phosphate ester employed is 5% w dimethyl 1,2-dibromo-2,2-dichloroethyl phosphate.

EXAMPLE VII

A solid insecticidal composition was prepared by mixing disacryl resin (polyacrolein) with an equal weight of dimethyl 2,2 - dichlorovinyl phosphate. From this mixture a smooth dry flowable powder was formed.

EXAMPLE VIII

Samples of polyvinyl chloride containing dimethyl 2,2-dichlorovinyl phosphate were each hung in a mesh bag in the centre of separate substantially square huts having a volume of at least about 500 ft³. At the end of times specified in the following table, mosquitoes were introduced into the huts for 30-minute exposure. The knockdown and mortality rates of the mosquitoes at each time in each hut were determined; the results are presented in the following table:

	% Knockdown and Mortality				
	2 Hrs	24 Hrs	48 Hrs	7 Days	15 Days
24/60 mesh polyvinyl chloride granules, 30% w DDVP	100% 100%	100% 100%	100% 100%	100%* 100%	100% 100%
9/24 mesh polyvinyl chloride granules, 30% w DDVP	100% 100%	100% 100%	100% 100%	100%** 100%	100% 70%

* Hut was aired for 5 hours at end of 7 days.

** Hut was aired for 8 hours at end of 7 days.

EXAMPLE IX

The following insecticidal powder compositions were prepared and their effectiveness on mosquitoes evaluated by bringing the powder in 8' x 8' x 8' huts. The results obtained are presented in the following table:

Residual Toxicity of Plastic Powders to Adult *Anopheles Albimanus* Mosquitoes Exposed to Deposits for 1 Hour.

Formulation	Dosage mg/ft ²	Surface	Ave. % 24 Hr. Mortality at Interval Indicated		
			Fresh	1 day	7 days
25% DDVP — 75% Disacryl	100	Glass	100	100	100
25% DDVP — 75% Disacryl	100	Plywood	100	100	100
25% DDVP — 75% Disacryl	100	Mud	100	100	0
25% DDVP — 75% Disacryl	200	Mud	100	100	0
7.6% DDVP— 15.2% Aroclor(I) 5460 (polychlorinated polyphenyl)	100	Mud	100	100	10
7.6% DDVP— Novolac	100	Mud	100	0	20
7.6% DDVP— PBF Resin, (formaldehyde-hydrocarbon resin)	100	Mud	100	60	15

(I) "Aroclor" is a Registered Trade Mark.

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EXAMPLE X

A liquid Epon (polyepoxide) resin containing a chlorofluoroalkane blowing agent (Freon 11) was mixed with dimethyl 2,2-dichlorovinyl phosphate, and to the mixture was added an ethylene glycol solution of boron trifluoride sufficient to make the mixture 0.1% w in the trifluoride. The mixture was stirred until heat was evolved, and it began to expand.

In this way, solid polyepoxide foam

samples containing 5%, 10%, 20% and 30% by weight of the insecticide were prepared. Portions of these samples were ground to powder in the hammer mill without difficulty.

A sample of the polyepoxide foam containing 20% of the insecticide was held at 55° C. for an extended period. The concentration of the phosphate in the foam as a function of time was as follows:

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Time, Days	% of the original content
0	100%
4	90%
7	85%
14	72%

Similar results are obtained when the phosphate used is dimethyl 1,2-dibromo-2,2-dichloroethyl phosphate.

14 parts of a chlorofluoroalkane blowing agent (Freon 11) was prepared, and with samples of this was mixed varying amounts of dimethyl 2,2-dichlorovinyl phosphate.

EXAMPLE XI

A pre-cured mixture of 40 parts Epon 828 (diglycidyl ether of bis(hydroxyphenyl)propane), 40 parts of Epon 1001 (a high-molecular weight polyepoxide resin), 10 parts of the diglycidyl ester of mixed unsaturated dimer-trimer acids (a mixture of the dimer and trimer of linoleic acid), and

Small amounts of an ethylene glycol solution containing boron trifluoride were then mixed with the epoxy mixture. Heat from the curing expanded the foam, and a solid white foam, expanded by a factor of 7-8 in volume over the original mixture, was obtained. Foams having the following compositions were obtained.

Sample	DDVP	% w	
		Epon-Freon Mixture	Boron Trifluoride
1	0.5	97.5	2.0
2	1.0	97.0	2.0
3	9.2	89.0	1.8
4	4.8	93.3	1.9
Control	—	98.0	2.0

At the two higher concentrations of toxicant, the foam structure was being altered owing to the presence of DDVP. The expansion ratio was lowered somewhat, and the structure seemed to be slightly coarser than that of the two foams containing lower concentrations of toxicant.

The foams were tested on adult mosquitoes by placing twenty-five *Anopheles Albimanus* mosquitoes with the foam in a quart carton

with both ends screened. A pad of sugar water was provided for food. The mosquitoes were confined for 24 hours when the mortality counts were taken.

The foams were all toxic to mosquitoes when tested the same day they were prepared. The foams containing 4.8 and 9.2% DDVP maintained their residual effectiveness for four weeks. Results of these experiments are presented in the following table:

Toxicity of DDVP foams to Adult <i>Anopheles Albimanus</i> Mosquitoes								
Sample	% DDVP	Per Cent Mortality at Weeks Indicated						
		Fresh	1	2	3	4	8	16
Control	0	0	0	0	0	—	—	—
1	0.5	92	0	8	0	—	—	—
2	1.0	100	8	44	0	—	—	—
3	9.2	100	100	100	100	100	100	100
4	4.8	100	100	100	100	100	100	100

5 Similar results are obtained when 2-carbo-
methoxy - 1 - methylvinyl dimethyl phos-
phate is used in place of the dimethyl 2,2-
dichlorovinyl phosphate.

EXAMPLE XII

10 An EPON Resin foam containing di-
methyl 2,2 - di - chlorovinyl phosphate
(DDVP) was prepared. The materials used
in this preparation were as follows:

90 g EPON-FOAM Resin X-30 (a poly-
glycidyl ether of bis(hydroxyphenyl)-
propane containing Freon 11)
10 g DDVP
15 2.5 g Curing Agent G (1.5 parts boron
trifluoride dihydrate in 14.25 parts
of polyethylene glycol).

20 The DDVP was added to the liquid
EPON-FOAM Resin X-30 and well mixed.
The Curing Agent G was added, and the
mixture vigorously agitated for one minute.
The mixture was then allowed to stand until
the curing and foaming had stopped. A sig-
25 nificant amount of heat was evolved in this
step, and apparently a large amount of the
toxicant vaporized or was decomposed.

EXAMPLE XIII

30 A granular polyvinyl chloride formulation
containing dimethyl 2,2-dichlorovinyl phos-
phate (DDVP) was prepared. The materials
used were as follows:

23 g DDVP
77 g Polyvinyl Chloride powder (Bakelite
QYNV)

35 While the powdered polyvinyl chloride was
being mixed in a small tumbler blender, the
DDVP was added as a fine spray. During
the tumbling action, the resin formed soft
beads coated with powder. After the addi-
40 tion of the toxicant, the material was

screened through a nine-mesh screen. Those
lumps that failed to pass were gently
brushed through the screen. The soft beads
were spread in a thin layer, and heat cured
in an oven at 130° C. for three minutes.
45 Fairly hard firm granules resulted. These
were mechanically screened into fractions of
9 to 24 mesh and 24 to 60 mesh. About
80—85% of the blend was between 9 and
60 mesh. 50

EXAMPLE XIV

Plastic pellets containing polyvinyl chloride
and dimethyl 2,2 - dichlorovinyl phosphate
(DDVP) were prepared. The materials used

6 g Polyvinyl Chloride powder (Bakelite
QYNV) 55
4 g DDVP

A plastisol was formed by mixing the
resin and the DDVP. The paste formed was
moulded into pellets on a pill board. While
in the mould, the pellets were gelled by plac-
ing the board on a steam bath and heating
ten minutes on each side. A final fusion was
accomplished by heat curing the gelled
pellets in an oven at 130° C. for four
65 minutes. Mechanically stable plastic pellets
resulted.

EXAMPLE XV

A powder containing polyvinyl chloride
(PVC) and dimethyl 2,2-dichlorovinyl phos-
phate (DDVP) as the toxicant was prepared.
The following materials were used: 70

24 g Polyvinyl Chloride powder (Bakelite
QYNV)
6 g DDVP 75

The DDVP was added dropwise to the
resin while the latter was being constantly
agitated. Many small, soft lumps were
formed which were broken up by grinding
in a mortar and pestle. The powder was 80

then screened through a 40 mesh screen, affording a dry stable powder.

EXAMPLE XVI

- 5 Plastic pellets consisting of polyvinyl chloride and 2-carbomethoxy-1-methylvinyl dimethyl phosphate (CMDP) were prepared. The materials used were:

- 6 g Polyvinyl Chloride powder (Bakelite QYNV)
10 4 g CMDP

- A plastisol was formed by mixing together the PVC and the CMDP. The paste formed was moulded into pellets on a pill board. While in this mould, the pellets were gelled by heating the board on a steam bath for ten minutes on each side. Hard mechanically-stable plastic pellets resulted.

EXAMPLE XVII

- 20 A plastic material containing dimethyl 2,2-di-chlorovinyl phosphate (DDVP) and having a large surface area was prepared.

The ingredients used in this formulation are as follows:

- 25 20 g Polyvinyl Chloride powder (Bakelite QYNV)
8 g Tricresyl phosphate
4 g DDVP
12 g Freon 11

- 30 The DDVP and tricresyl phosphate were mixed together and added slowly with agitation to the PVC powder. This plastisol was well mixed to ensure good distribution. Following this, the F-11 was added and mixed into the plastisol. The mixture was poured into a petri dish, 9 cm in diameter, and placed on a steam bath. At this temperature, the Freon 11 volatilized as the gellation of the

plastisol took place. A solid cake resulted that possessed a porous, irregular surface of considerable surface area.

Following the fusion of this porous cake, portions of it were formed into clear films.

EXAMPLE XVIII

- Using the methods of the previous Examples, a solid resinous composition was prepared having the following composition:

- Coumarone-indene resin 90%
2 - Carbomethoxy-1-methylvinyl-dimethyl phosphate 10%

- Another preparation had the following composition:

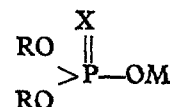
- Piccolastic D-150 (Polystyrene resin) 80%
2 - Carbomethoxy-1-methyl-vinyl dimethyl phosphate 20% 55

Both of these compositions were characterized by insecticidal activity.

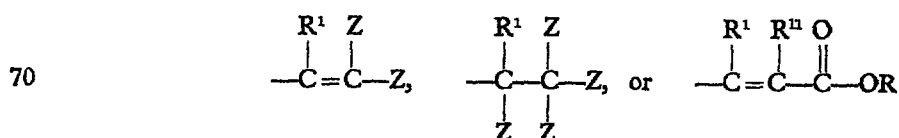
The words "Bakelite", "Dacron" and "Freon" used in the above examples are Registered Trade Marks.

WHAT WE CLAIM IS:—

1. A solid insecticidal composition comprising a solid organic polymeric macromolecular substance having a molecular weight above 1000 and an organophosphorus compound having the general formula:



(wherein R is an alkyl group, X is oxygen or sulphur, and M is a group having the structure



wherein R¹ is hydrogen or an alkyl group, Z is halogen; and R¹¹ is hydrogen, an alkyl group or halogen).

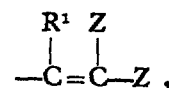
2. A composition as claimed in claim 1, wherein the macromolecular substance is thermoplastic.

3. A composition as claimed in claims 1 or 2, wherein the macromolecular substance is a polymer or a copolymer of a vinyl compound.

4. A composition as claimed in claim 3, wherein the macromolecular substance is a polymer or a copolymer of vinyl chloride.

5. A composition as claimed in any one of claims 1 to 4, wherein the group M contains not more than 8 carbon atoms.

6. A composition as claimed in any one of claims 1 to 5, wherein the group M has the structure



and each alkyl group has not more than 4 carbon atoms.

7. A composition as claimed in claim 6,

then screened through a 40 mesh screen, affording a dry stable powder.

EXAMPLE XVI

5 Plastic pellets consisting of polyvinyl chloride and 2-carbomethoxy-1-methylvinyl dimethyl phosphate (CMDP) were prepared. The materials used were:

10 6 g Polyvinyl Chloride powder (Bakelite QYNV)
4 g CMDP

15 A plastisol was formed by mixing together the PVC and the CMDP. The paste formed was moulded into pellets on a pill board. While in this mould, the pellets were gelled by heating the board on a steam bath for ten minutes on each side. Hard mechanically-stable plastic pellets resulted.

EXAMPLE XVII

20 A plastic material containing dimethyl 2,2-di-chlorovinyl phosphate (DDVP) and having a large surface area was prepared.

The ingredients used in this formulation are as follows:

25 20 g Polyvinyl Chloride powder (Bakelite QYNV)
8 g Tricresyl phosphate
4 g DDVP
12 g Freon 11

30 The DDVP and tricresyl phosphate were mixed together and added slowly with agitation to the PVC powder. This plastisol was well mixed to ensure good distribution. Following this, the F-11 was added and mixed into the plastisol. The mixture was poured
35 into a petri dish, 9 cm in diameter, and placed on a steam bath. At this temperature, the Freon 11 volatilized as the gellation of the

plastisol took place. A solid cake resulted that possessed a porous, irregular surface of considerable surface area.

Following the fusion of this porous cake, portions of it were formed into clear films.

EXAMPLE XVIII

Using the methods of the previous Examples, a solid resinous composition was prepared having the following composition:

Coumarone-indene resin	90%
2 - Carbomethoxy-1-methylvinyl-dimethyl phosphate	10%

Another preparation had the following composition:

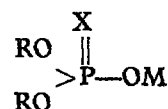
Piccolastic D-150 (Polystyrene resin)	80%
2 - Carbomethoxy-1-methyl-vinyl dimethyl phosphate	20%

Both of these compositions were characterized by insecticidal activity.

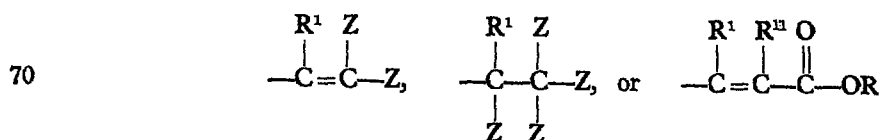
The words "Bakelite", "Dacron" and "Freon" used in the above examples are Registered Trade Marks.

WHAT WE CLAIM IS:—

1. A solid insecticidal composition comprising a solid organic polymeric macromolecular substance having a molecular weight above 1000 and an organophosphorus compound having the general formula:



(wherein R is an alkyl group, X is oxygen or sulphur, and M is a group having the structure



wherein R¹ is hydrogen or an alkyl group, Z is halogen; and R¹¹ is hydrogen, an alkyl group or halogen).

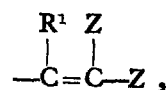
2. A composition as claimed in claim 1, wherein the macromolecular substance is thermoplastic.

3. A composition as claimed in claims 1 or 2, wherein the macromolecular substance is a polymer or a copolymer of a vinyl compound.

4. A composition as claimed in claim 3, wherein the macromolecular substance is a polymer or a copolymer of vinyl chloride.

5. A composition as claimed in any one of claims 1 to 4, wherein the group M contains not more than 8 carbon atoms.

6. A composition as claimed in any one of claims 1 to 5, wherein the group M has the structure



and each alkyl group has not more than 4 carbon atoms.

7. A composition as claimed in claim 6,

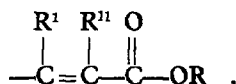


wherein the organophosphorus compound is beta, beta-di-chlorovinyl dimethyl phosphate.

- 5 8. A composition as claimed in any one of claims 1 to 5, wherein the organophosphorus compound is a dialkyl 1,2-dibromo-2,2-dichloroethyl phosphate.

- 10 9. A composition as claimed in claim 8, wherein the organophosphorus compound is 1,2-dibromo-2,2-dichloroethyl dimethyl phosphate.

10 10. A composition as claimed in any one of claims 1 to 5, wherein the group M has the structure



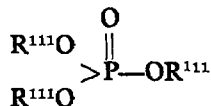
- 15 each alkyl group has not more than 4 carbon atoms, and the halogen is chlorine or bromine.

- 20 11. A composition as claimed in claim 10, wherein the organophosphorus compound is 2-carbomethoxy-1-methylvinyl dimethyl phosphate.

12. A composition as claimed in any one of claims 1 to 11, wherein the amount of organophosphorus compound is between 5 and 75% by weight of the composition.

- 25 13. A composition as claimed in any one of claims 1 to 12, which also contains a non-insecticidal plasticizer.

- 30 14. A composition as claimed in claim 13, wherein the non-insecticidal plasticizer has the structure



(wherein R¹¹¹ is an alkyl, aryl, aralkyl or alkaryl group).

- 35 15. A composition as claimed in claim 14, wherein R¹¹¹ is an alkyl group having at least four carbon atoms.

40 16. A composition as claimed in claim 14 or 15, wherein the sum of the amounts of the insecticidal and non-insecticidal phosphate ester is not more than 70% by weight of the composition and the amount of the insecticidal phosphate ester is at least 5% by weight.

45 17. A composition as claimed in any one of claims 1 to 16, which also contains a phenol as stabilizer.

18. A composition as claimed in claim 17, wherein the amount of phenol is between 0.1% and 10% by weight of the composition.

50 19. A composition as claimed in claim 17 or 18, wherein the phenol is a mono- or dihydroxybenzene or an alkyl-substituted mono- or dihydroxybenzene having not more than eight carbon atoms in the alkyl group.

55 20. A composition as claimed in any one of claims 17 to 19, wherein the phenol is a mononuclear phenol having a phenolic hydroxyl group which is hindered by one or more ortho alkyl groups.

60 21. An insecticidal composition as claimed in claim 1, substantially as hereinbefore described.

65 22. An insecticidal composition as claimed in claim 1, substantially as hereinbefore described with reference to any one of the Examples.

23. A shaped article wholly or partly comprising an insecticidal composition as claimed in any one of claims 1 to 22.

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