

PATENT SPECIFICATION

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(54) RESIN COMPOSITION CONTAINING O, O, O', O'-TETRAMETHYL O, O'-THIODI-*p*-PHENYLENE PHOSPHOROTHIOATE

(71) We, AMERICAN CYANAMID COMPANY, a coporation organized and existing under the laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, 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:-

This invention relates to a resin composition containing a pesticidal agent which is effective for the control of siphonaptera on dogs and cats, and other animals.

O, O, O', O'-Tetramethyl O, O'-thiodi-*p*-phenylene phosphorothioate is disclosed in United States Patents No. 3,317,636 and 3,459,856 as an insecticidal agent. It has been prepared as rubber pellets and plaster of paris cubes which were floated in water at breeding sites for mosquitoes. However, these latter preparations have not been especially effective for mosquito control.

This invention provides a dry blended extrudable and extruded polyvinyl chloride resin compositions containing as the essential active ingredient, a pesticidally effective amount of O, O, O', O'-tetramethyl O, O'-thiodi-*p*-phenylene phosphorothioate.

The compositions of the invention are generally prepared in the finished form of extruded flexible sheets, strips, swatches or the like, and are particularly well suited to use in the manufacture of pesticide, especially siphonapteracide, collars for pet companion animals, particularly dogs and cats, and farm animals.

The polyvinyl chloride resins which may be utilized in the preparation of compositions of this invention are solids at room temperature. They have a weight average molecular weight of from 60,000 to 280,000 as calculated from the inherent viscosity by the Staudinger equation, and an inherent viscosity of from 0.5 to 1.2 determined by the A.S.T.M. Method D-1243-58T - Method A. In this method inherent viscosity is determined on a solution of 0.2 g. of resin in 100 ml. of cyclohexanone at 30°C.

The resins which may be employed in the manufacture of the compositions of this invention are poly-vinyl chloride resins characterized by the above-indicated molecular weight and viscosity measurements.

In accordance with this invention, it has been found that dry blended resin compositions comprising a polyvinyl chloride resin having a weight average molecular weight of from 60,000 to 280,000 and preferably 80,000 to 230,000 and an inherent viscosity from 0.5 to 1.2 and preferably from 0.67 to 1.07 and from 13 to 50% by weight and preferably 18% to 50% by weight of O, O, O', O'-tetramethyl O, O'-thiodi-*p*-phenylene phosphorothioate, are effective for the control of insect pests, particularly siphonaptera, (fleas) such as (*Ctenocephalides canis*) and (*Ctenocephalides felis*) which infest companion and farm animals.

Surprisingly, we have found that O, O, O', O'-tetramethyl O, O'-thiodi-*p*-phenylene phosphorothioate is not only a superior pesticide, but also an excellent plasticizing agent and may be used exclusively as both the pesticidal agent and the plasticizing agent in the manufacture of the extruded and extrudable compositions of this invention. Preferred

- compositions comprise from 36% to 50% by weight of O, O,O',O'-tetra-methyl O,O'ce
thiodi-*p*-phenylene phosphorothioate, from 45% to 63% by weight of the polyvinyl
chloride resin, from 1% to 3% by weight of a heat stabilizing agent for the resin and
optionally up to 2.0% by weight of a lubricant. These preferred compositions are preferably
free of additional and/or secondary plasticizing and pesticidal agents; however, said prefer-
red compositions may optionally contain a small amount up to 2.0% by weight, for example
0.1% to 2.0% by weight, of an organic or inorganic pigment. Where pigments are employed,
the percentage of resin in the compositions can be adjusted to compensate for the added
pigment.
- Other preferred extrudable compositions of this invention contain from 13% to 40% and
preferably 18% to 40% by weight of O, O,O',O'-tetramethyl O,O'-thiodi-*p*-phenylene
phosphorothioate, from 22.5% to 7.6% by weight of a plasticizing agent having a molecular
weight of from 400 to 1000 and preferably selected from the group consisting of epoxidized
soybean oil, octyl epoxystallate (e.g. sold under the trade name Flexol E.P.-8, product of
Union Carbide Co.), epoxidized linseed oil, epoxidized tall oil ester and epoxidized butyl
ester of linseed oil acids, from 1% to 3% by weight of a heat stabilizing agent for the resin,
optionally up to 2.0% by weight of a lubricant and from 47.4% to 63.5% and preferably
47.4% to 58.5% by weight of the polyvinyl chloride resin. These compositions may likewise
also contain up to 2.0% by weight of an organic or inorganic pigment. As with the other
preferred compositions, addition of pigment is compensated for by adjusting the resin
content accordingly.
- Still other preferred compositions of this invention contain 32% to 40% by weight of
O, O,O',O'-tetra-methyl O,O'-thiodi-*p*-phenylene phosphorothioate, from 6.5% to 2.75%
by weight of a dioctylphthalate, such as di-*n*-octylphthalate or di-(2-ethylhexyl) phthalate,
from 1% to 3% by weight of a heat stabilizing agent for the resin, optionally up to 2.0% by
weight of a lubricant, and from 52.25 to 60.5% by weight of the polyvinyl chloride resin.
Optionally, up to 0.5% by weight of a pigment, either organic or inorganic, may also be
added with appropriate compensation of the resin concentration.
- Among the heat stabilizing agents which may be employed in the compositions of the
present invention are the organo metal stabilizers conventionally used in the preparation of
extrudable polyvinyl chloride resins. These include organotin stabilizers; organo barium,
cadmium, and lead stabilizers; zinc and calcium salts and mixtures of organo barium and
cadmium stabilizers.
- Exemplary of the lubricants which may be used in the compositions of this invention are
calcium stearate, stearic acid, paraffin waxes, magnesium stearate, aluminum stearate,
amide waxes, low molecular weight polyethylene and where a lead stabilizer is used, lead
stearate.
- Pigments which may be added to the extrudable compositions of this invention include
inorganic pigments such as carbon black and titanium dioxide and organic pigments such as
quinacridones, anthraquinones, lithol reds and alizarine maroon.
- Exemplary of the polyvinyl chloride resins which can be used in the preparation of the
resin compositions of this invention are the Diamond Alkali Company's polyvinyl chloride
resins CR80A, FCR, PVC 30, PVC 33, PVC 35, PVC 40, PVC 7-44 and characterized as
follows:

Resins	Inherent Viscosity ASTM D-1243-58T (A)	Approximate Weight Average Molecular Weight
Diamond FCR	0.55	60,000
Diamond PVC 30	0.57	60,000
Diamond PVC 35	0.70	85,000
Diamond PVC 40	0.80	120,000
Hooker Rucon B-34	1.07	230,000
Hooker Rucon B-38	1.19	280,000

The dry blended extrudable compositions of this invention may be converted into extruded sheets, strips, ribbons or other extruded forms by dry blending the finely divided, solid, low molecular weight polyvinyl chloride resin with, if desired, the heat stabilizer and/or the lubricant, and incorporating into the blended material the desired amount of O,O,O',O'-tetramethyl-O,O'-thiodi-*p*-phenylene phosphorothioate as the pesticidal agent, selected from those mentioned above, may, if desired, be added to prepare the desired extruded composition and where desired, pigment or dye may be incorporated in the blend. When the mixture is thoroughly dry blended it is charged to an extruder, and extruded, most preferably at a stock temperature of about 160°C at exit; in operation we have found it most desirable to operate at a relatively low temperature in order to avoid thermal degradation of the phosphorothioate pesticidal and plasticizing agent, and therefore the preferred stock extrusion temperature is from 150°C to 180°C.

The extrudate from this process may be obtained in the form of a flexible plastic strip or sheet which is readily fashioned into collars for pet companion animals or farm animals. Extruded strips simply require the addition of a buckle or other fastening means to complete the collar. Sheets may, of course, be cut into strips to which a buckling device may be appended and a collar prepared; or they may be cut into strips and coated on one side with adhesive such that the strips can be secured to the inside of a conventional animal collar.

Unlike many of the pest control collars and devices presently available which rely on the high vapor pressure of the pesticide to achieve pest control by fumigant action, the phosphorothioate of the present compositions has a very low vapor pressure and achieves control of insect pests, especially fleas, by topical action.

Advantageously, the compositions of this invention have a very low mammalian toxicity. They have not been found to cause dermatitis on cats, dogs or the like, when used in contact with the animals coat for an extended period of 9 months or more. Moreover, they have been found to be effective for the control of fleas on cats and dogs for this period.

In one of its aspects the present invention provides a method for the control of siphonaptera on dogs and cats comprising attaching to the dogs or cats a flexible collar formed from a flexible strip extruded from the novel pesticidal composition.

This invention is illustrated by the following examples.

Example 1

Preparation of PVC-O,O,O',O'-Tetramethyl O,O'-thiodi-p-phenylene phosphorothioate Extrudable Resin Composition

One thousand grams of Diamond 40 PVC resin, inherent viscosity 0.80 determined by A.S.T.M. D1243-58T (Method A), weight average molecular weight 120,000 (number average molecular weight 50,000), is charged to a Prodexhenschel mixer along with 5 g. stearic acid, 2 g. of carbon black and 20 g. of "Thermolite" 831-di-*n*-octyltin maleate polymer PVC heat stabilizing agent ("Thermolite" is a registered Trade Mark). The mixer is run at high speed (3600 rpm) until the temperature of the mixture is 175°F, 930 g. of O,O,O',O'-tetramethyl O,O'-thiodi-*p*-phenylene phosphorothioate (90% potency) is then added and mixing is continued.

When addition of the phosphorothioate is complete and the temperature of the mixture reaches 200°F, the speed of mixing is reduced to 1800 rpm and the batch discharged. The hot dry blend is then cooled and ready for extrusion.

The extrusion composition is then charged to the feed hopper of the extruder and extruded through a horizontal ribbon die having a 3/8 inch wide slot 1/8 inch thick.

Extrusion is accomplished with the mixture heated from 250°F at the rear feed to 330°F at the die zone and an extruded stock temperature of 163°C (326°F). This extrusion is conducted with a head pressure of 300 psi. Circulating water is used to cool the feed throat under the feed hopper as well as the extrudate exiting the die.

The extruded strip is then cut into 2 foot lengths to which a buckle is attached.

The animal collars thus prepared are free of secondary plasticizing and insecticidal agents other than the above-mentioned phosphorothioate which amounts to 47.5% (42.8% real) by weight of the composition.

The above procedure is repeated using 1000 g. of the above-identified PVC resin (inherent viscosity 0.80), 20 g. of di-*n*-octyltin, maleate polymer, 750 or 800 g. of the above said phosphorothioate, O or 2 g. of carbon black, and either 50 g. of dioctyl phthalate or 150 g. of epoxidized soybean oil.

The above compositions, all of which provide effective, easy to process, siphonapteracidal animal collars, are reported in parts by weight of composition and % w/w technical and real for the phosphoro-thioate.

Table I

Siphonapteracidal Compositions

Compound	Parts by Weight			
Polyvinyl chloride (Inherent Viscosity 0.80)	100	100	100	100
Di-n-Octyltin maleate polymer	2	2	2	2
Stearic acid	0.5	0.5	0.5	0.5
0, 0, 0', 0'-Tetramethyl 0, 0'-thiodi-p-phenylene phosphorothioate (Technical 90% potency)	93	80	80	75
Di (2-ethylhexyl) phthalate	—	—	—	5
Octylepoxytallate	—	15	15	—
Carbon black	0.2	0.2	—	0.2
% 0, 0, 0', 0'-Tetramethyl 0, 0'-thiodi-p-phenylene phosphorothioate	47.5*	40*	40*	40*
	42.8**	36**	36**	36**
% Plasticizer (secondary)	0	7.6	7.6	2.75

* = % Technical

** = % Real

Example 2

Effective levels of 0,0,0', 0'-Tetramethyl 0,0'-thiodi-p-phenylene phosphorothioate as a Plasticizing Agent for Polyvinyl Chloride Resin

Following the procedure of Example 1, resin compositions are prepared which are free of any secondary plasticizing agent. Materials used are reported as parts by weight. Data obtained are reported in Table II below. In the preparations reported the above-mentioned phosphoro-thioate is technical material 90% potency.

Table II
Plasticizing Effect of O, O', O'-Tetramethyl O, O'-thiodi-p-phenylene phosphorothioate on Polyvinyl Chloride Resin

Compound									
Polyvinyl Chloride (Inherent Viscosity 0.80)	100	100	100	100	100	100	100	100	100
	2	2	2	2	2	2	2	2	2
Di-n-Octyltin maleate polymer	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
O, O', O'-Tetramethyl O, O'-thiodi-p-phenylene phorothioate (Technical 90% potency)	10	20	70	100	120	150			
% O, O', O'-Tetramethyl -thiodi-p-phenylene phosphorothioate	8* 7.2**	16.3* 14.7**	40.6* 36.5**	49.4* 44.5**	53.9* 48.5**	59.4* 53.5**			
Comments	Hard to process	Very hard and very brittle	Easy to process	Easy to process flexible	Easy to process very	Hard to process soupy			

* = % Technical

** = % Real

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(13)

*Example 3**Effect of Secondary Plasticizing Agents on PVC - O,O, - O',O'-Tetramethyl O,O'-thiodi-p-phenylene phosphorothioate Extrudable Resin Compositions*

5 Following the procedure of Example 1, resin compositions containing polyvinyl chloride resin, O,O,O',-O'-tetramethyl O,O'-thiodi-p-phenylene phosphorothioate as the primary plasticizing agent and the siphapteracidal agent and a secondary plasticizing agent, are prepared to determine the effect of said seconary plasticizing agent on the composition. Compositions and physical observations relating thereto are reported in Table III below, where it can be seen that compositions containing 18% to 40% by weight of the above-said phosphorothioate and 22.5% to 7.6% of a plasticizing agent having a molecular weight of 10 400 to 1000 and selected from epoxidized oils such as soybean oil, linseed oil, tall oil ester and butyl ester of linseed oil acids are extrudable compositions, useful as siphonapteracidal animal collars. 10

15 These data also demonstrate that compositions containing 32% to 40% by weight of the above-named phosphorothioate and from 6.5% to 2.75% of dioctylphthalate, are also extrudable compositions useful in the manufacture of siphonapteracidal animal collars. 15

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Table III
Effect of 0, 0', 0''-Tetramethyl 0, 0'-thiodi-p-phenylene phosphorothioate With and Without
Secondary Plasticizers On Flexibility of Extruded PVC Resin Compositions.

Compound	Parts by Weight				
Polyvinyl Chloride Resin (Inherent Viscosity 0.80)	100	100	100	100	100
Di-n-Octyltin Maleate Polymer	2	2	2	2	2
Stearic Acid	0.5	0.5	0.5	0.5	0.5
0, 0', 0'' - Tetramethyl 0, 0'- thiodi-p-phenylene phos- phorothioate (Technical)	75	51.75	49.0	49	29.5
Di (2-ethylhexyl) phthalate	5	17.25	11.5	10.5	15.1
Carbon Black	-	-	-	-	-
Octylepoxytallate	-	-	-	-	-
Above-mentioned Phosphoro- thioate					
% Technical	40	30	30	30	20
% Real	36	27	27	27	18
% Plasticizer	2.75	10	7.1	6.5	10.3
Comments	Flexible	Overly Flexible	Overly Flexible	Flexible	Too Stiff

Table III -- (continued)

[illegible]

*Example 4**O,O,O', O'-Tetramethyl O,O'-thiodi-p-phenylene phosphoro-thioate Flea Collar Activity Against Ctenocephalides Felis on Dogs*

- Twelve groups of 3 to 4 dogs each are infested with 100 adult *Ctenocephalides felis* 3 days prior to placing a flea collar around the neck of each dog. Each dog is systematically examined daily for fleas presence or absence. *Complete* flea control observed within 1 week from the time the collar is placed on the dog is considered effective control. Each dog is reinfested weekly with 100 adult *C. felis* and examined daily thereafter for fleas. Effective control is considered *complete* control of *C. felis* on all dogs within 1 week of reinfestation.
- All dogs are fed Purina High Protein Dog meal once daily and all are provided water *ad libitum*. The dogs are housed in individual cages with grate bottom floors.
- Compositions of extruded collars tested are reported in Table IV below in parts by weight and % w/w of the phosphorothioate.
- Observations are reported in Table V.
- From the data in Table V it can be seen that collars 1,2,4,7,8,9,10 and 11 are highly effective for the control of fleas on dogs for an extended period up to 30 weeks or more.

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Table IV
Flea Collar Compositions

Compound	1	2	3	4	5	6	7	8	9	10	11
Collar Number	100	100	100	100	100	100	100	100	100	100	100
Polyvinyl Chloride Resin (Inherent Viscosity 0.80)	2	2	2	2	2	2	2	2	2	2	2
Di-n-Octyltin Maleate Polymer	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Stearic Acid	93	75	50	35	33	35	80	93	80	75	45
0, 0', 0'-Tetramethyl 0, 0'-thiodi-p-phenylene phosphorothioate (Technical)	45.7	40	30	20	20	20	40	47.5	40	40	24.63
% Technical	42.8	36	27	18	18	18	36	42.8	36	36	22.2
% Real	—	5	15	—	25	—	—	—	—	5	—
Di (2-ethylhexyl) Phthalate	—	—	—	40	—	—	15	—	15	—	35
Octylepoxystallate	—	—	—	—	—	—	—	—	—	—	—
Emery Plastalein 9750 (Polyester plasticizer - based on azelaic acid)	—	—	—	—	—	40	—	—	—	—	—
Carbon Black	—	—	—	—	—	—	0.2	0.2	—	0.2	0.2

Table V
 Temephos Flea Collar Activity Against Ctenocephalides felis on Dogs
 Dogs with Complete Control/Dogs Treated

Collar No.	0	1	2	3	4	5	6	7	9	10	11	17	20	21	22	23	30
1	4/4	4/4	4/4	4/4	4/4	4/4				4/4		2/2	2/2	2/2			2/2
2	3/3	3/3	3/3	3/3	3/3	3/3	3/3				3/3	2/2	1/1	1/1	1/1		Terminated
3	2/4	3/4	3/4	4/4	3/4	3/4	Terminated										
4	1/3	3/3	3/3	3/3	3/3	3/3	3/3				3/3	2/2	2/2	1/2	2/2		Terminated
5	0/3	2/3	3/3	1/3	1/3	2/3	2/3	Terminated									
6	0/3	2/3	1/3	2/3	2/3	3/3	3/3	Terminated									
7	2/3	3/3	3/3	3/3	3/3	2/2	2/2		2/2	2/2	2/2	Terminated					
8	3/3	3/3	3/3	3/3	3/3	3/3	3/3		3/3	3/3	3/3	2/3*	2/2				
9	3/3	3/3	3/3	3/3	3/3	2/2	2/2		2/2	2/2	2/2	Terminated					
10	2/3	3/3	3/3	3/3	3/3	3/3	3/3		3/3	3/3	3/3	Terminated					
11	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3							
Untreated Animals	0/3	0/5	0/5	0/5	0/5	0/5	0/5	0/5	0/5	0/5	0/5	0/5	0/5	0/5	0/5	0/5	0/5

*Severe Case of Mange: No Hair Left: Dog Sacrificed

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WHAT WE CLAIM IS:-

1. A pesticidal dry blended polyvinyl chloride resin composition comprising, a polyvinyl chloride resin having a weight average molecular weight of from 60,000 to 280,000 and an inherent viscosity of from 0.5 to 1.2, and as the essential active pesticidal agent from 13% to 50% by weight of O,O,O',O'-tetramethyl O,O'-thiodi-*p*-phenylene phosphorothioate.
2. A composition according to Claim 1, comprising from 45% to 63% by weight of the polyvinyl chloride resin, from 36% to 50% by weight of the O,O,O',O'-tetramethyl O,O'-thiodi-*p*-phenylene phosphorothioate, from 1% to 3% by weight of a heat stabilizing agent for the resin, optionally up to 2.0% by weight of a pigment.
3. A composition according to Claim 1, comprising 47.4% to 63.5% by weight of the polyvinyl chloride resin, from 13% to 40% by weight of the O,O,O',O'-tetramethyl O,O'-thiodi-*p*-phenylene phosphorothioate, from 22.5% to 7.6% by weight of a plasticizing agent having a molecular weight of from 400 to 1000, from 1% to 3% by weight of a heat stabilizing agent, optionally up to 2% by weight of a lubricant, and optionally up to 2.0% by weight of a pigment.
4. A composition according to Claim 3, wherein the plasticizing agent is epoxidized soybean oil.
5. A composition according to Claim 1, comprising from 52.5% to 60.5% by weight of the polyvinyl chloride resin, from 32% to 40% by weight of the O,O,O',O'-tetramethyl O,O'-thiodi-*p*-phenylene phosphorothioate, from 6.5% to 2.75% of a dioctylphthalate, from 1% to 3% by weight of a heat stabilizing agent, optionally up to 2.0% by weight of a lubricant, and optionally up to 0.5% by weight of a pigment.
6. A composition according to any one of Claims 2 to 5, wherein the heat stabilizing agent is an organo metal stabilizer, the lubricant, if present, is selected from metal stearates, stearic acid, paraffin waxes, amide waxes and low molecular weight polyethylene, and the pigment, if present, is selected from carbon black, titanium dioxide, quinacridones, anthraquinones, litholreds and alizarine maroon.
7. A composition according to any preceding claim, wherein the polyvinyl chloride resin has a weight average molecular weight of from 80,000 to 230,000 and an inherent viscosity of from 0.67 to 1.07.
8. A composition according to any preceding claim, wherein said composition is in the form of an extruded flexible strip useful for the control of siphonaptera on dogs and cats.
9. A pesticidal composition, according to Claim 1 and substantially as described in any one of the Examples herein.
10. A method for the control of siphonaptera on dogs and cats comprising attaching to the dogs or cats a flexible collar formed from a composition according to Claim 8.

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