

PATENT SPECIFICATION

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(54) ACARICIDAL RESIN COMPOSITION

(71) We, AMERICAN CYANAMID COMPANY, a Corporation organised 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 polyvinyl chloride composition useful for forming articles having acaricidal properties, and to such articles formed from the composition.

Spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester is disclosed in United States Patent No. 3,962,458 as a systemic insecticidal and acaricidal agent for treatment of homothermic animals. U.S. Patent 3,966,959 discloses and claims the compound.

In accordance with this invention there is provided a dry blended polyvinyl chloride resin composition useful for forming articles having acaricidal properties, 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—1.2, and as an acaricidal agent from 15% to 40% by weight of the composition of spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid 3,3 - dimethyl - α - cyano - *m* - phenoxybenzyl ester.

The compositions of the invention are generally prepared in the finished form of extruded (and/or compression molded) flexible sheets, strips, swatches and the like, and are particularly well suited to use in the manufacture of acaricidal collars for companion animals, particularly dogs and cats, and farm animals.

The polyvinyl chloride (PVC) 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, preferably from 80,000 to 230,000, and an inherent viscosity of from 0.5 to 1.2, preferably from 0.67 to 1.07, as determined by 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.

In preferred embodiments, the present compositions also contain a plasticizer such as dioctylphthalate or octyl epoxystallate, and preferably in amount of from 15% to 30% by weight of the composition. The preferred concentration of spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester is from 20% to 30% by weight of the composition. The present compositions are effective for the control of insect pests, particularly acarina such as *Dermacentor variabilis* and *Rhipicephalus sanguineus* which infest companion and farm animals, and are characterized by extended residual pesticidal activity and low mammalian toxicity.

Particularly preferred compositions comprise from 18% to 35% by weight of spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester, 15% to 25% by weight of dioctylphthalate, such as di - *n* - octylphthalate or di - (2 - ethylhexyl)phthalate, plasticizing agent, 0.1% to 0.5% by weight of stearic acid lubricant, 0.5% to 1.5% by weight of "Thermolite" 831 - di - *n* - octyltin maleate polymer (a PVC heat stabilizing agent — "Thermolite" is a registered Trade Mark), and 38% to 66% by weight of Diamond Alkali PVC 40 resin with an inherent viscosity of about 0.80 (A.S.T.M. D-1243-58T (A)) and with an approximate weight average molecular weight of 120,000 (approximate number average molecular weight: 50,000).

Other particularly preferred compositions of this invention contain 18% to 35% by weight of spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester, 15% to 25% by weight of octyl epoxystallate (FLEXOL[®] EP-8; a product of Union Carbide) plasticizing agent, 0.1% to 0.5% by weight of stearic acid lubricant, 0.8% to 1.2% by weight of "Thermolite" 831 - di - *n* - octyltin maleate polymer (as PVC heat stabilizing agent), and 38% to 66%

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by weight of Diamond Alkali PVC 40 resin with an inherent viscosity of about 0.80 (A.S.T.M. D-1243-58T(A)) and with an approximate weight average molecular weight of 120,000 (approximate number average molecular weight: 50,000).

Colorants, selected from inorganic and organic pigments, may be added to the above compositions, if desired, to achieve a more pleasing eye appeal. Usually 0.1% to 2% by weight of a pigment suffices to impart the desired effect to the compositions. Addition of a pigment colorant is compensated for by adjusting the resin content accordingly. Suitable inorganic pigments may be selected from carbon black, titanium dioxide, cadmium yellow and the like, organic pigments may be selected from a large group of quinacridone, anthraquinone, alizarine and phthalocyanine type of pigments and mixtures thereof.

The preferred dry blended extrudable (and/or compression molded) compositions of the invention are converted into sheets, strips, ribbons and the like, by dry blending the finely divided, solid, low molecular weight PVC resin with the stabilizer, plasticizer and lubricant (and a pigment colorant if desired) and incorporating the desired amount of spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester as the acaricidal agent.

When the mixture is thoroughly dry blended, it is charged to the extruder, and extruded (or compression molded) at a stock temperature of about 160°C at the exit. In operation we have found it most desirable to operate at a relatively low temperature to avoid thermal degradation of the spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester acaricidal agent. The preferred stock extrusion (or compression molding) temperature is between about 150°C to 180°C.

The extrudate (or mold) from this process is obtained in the form of a flexible plastic strip or sheet, which is readily fashioned into collars for 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 collar.

Advantageously, the compositions of this invention have a very low mammalian toxicity. They have not been found to cause dermatitis on dogs, cats and the like when used in contact with the animals coat for an extended period of time. Moreover, they have been found to be effective up to 12 weeks for the control of ticks on the animals, and

do not show diminished activity over this period of time.

Although the novel resin-acaricide compositions of the present invention provide lasting control only for ticks infesting companion animals, it is of further advantage that they may be combined physically with resin-siphonaptericidal compositions such as a PVC - O,O,O',O' - tetramethyl - O,O' - thiodi - *p* - phenylene phosphorothioate to achieve simultaneous control of fleas such as *Ctenocephalides canis* and *Ctenocephalides felis*.

Thus animal collars may be prepared by laminating two PVC resin strips side by side, one containing the acaricide and the other the siphonaptericide, respectively; and attaching a buckle or some other suitable fastening device thereto. Alternatively, strands of the resin strips may be woven into ribbons of suitable widths, and formed into animal collars. Animal collars thus prepared, would, obviously provide lasting and effective protection for companion animals against ticks and fleas, in addition, such a collar would have substantial aesthetic value.

The following examples serve to illustrate the invention.

Example 1.

*Preparation of a PVC - Spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester composition*

Diamond PVC 40 resin (48.9 g), inherent viscosity approximately 0.80 as determined by A.S.T.M. D-1243-58T (Method A), approximate weight average molecular weight 120,000 (approximate number average molecular weight 50,000), stearic acid (0.24 g), octyl epoxystallate (FLEXOL EP-8; 20.0 g), 1.0 g "Thermolite" 831 - di - *n* - octyltin maleate polymer PVC heat stabilizing agent and technical spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester (30.0 g—82.5% pure, 24.75 g real) are mixed and thoroughly blended; and sheeted on a 143°C two-roll rubber mill. The stock is mixed for 5 minutes by cutting vinyl sections loose and retrieving these sections to the mill nip. The stock is then sheeted off thicker than 0.32 cm.

The stock is then press-molded in a 27.9 cm x 27.9 cm x 0.32 cm picture-frame mold to remove bubbles; the stock is first molded at 154°C (1.5 minutes preheat, 1 minute of pressure 50 tons; 1 minute in cold press). The molded slab is cut in 4 parts, stacked, and remolded 166°C to achieve a smooth surface.

The sheets are cut into 0.86 cm strips and made into collars approximately 53.5 cm long, weighing about 20 grams.

Example 2.

Preparation of PVC - Spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - m - phenoxybenzyl ester composition

By the procedure of Example 1, the following composition is prepared. The ingredients and amounts are listed below.

Diamond PVC 40	43.9 g
Diocetyl phthalate	25.0 g
"Thermolite" 831-	
di-n-octyltin maleate polymer	0.9 g
Spiro[cyclopropane-1,1'-indene]-	
2-carboxylic acid, 3,3-dimethyl-,	
α -cyano-m-phenoxybenzyl	
ester; 82.5% pure	30.0 g
	(24.75 g real)

Example 3.

Evaluation of the efficacy of tick collars containing spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - m - phenoxybenzyl ester

Animals

Nine mongrel dogs are randomly distributed into three groups of three dogs each. The animals are housed in cages fitted with a grated floor. "Purina" (registered Trade Mark) High Protein Dog Meal is fed once daily and water offered *ad libitum*.

Materials and Methods

One group of three dogs serves as un-medicated infested controls.

The dogs in the other groups are fitted with

PVC collars 0.86 cm wide, 0.32 cm thick by 50.8 cm long, prepared from the compositions of Examples 1 and 2.

Each dog is infested with 10 male and 10 female adult *Dermacentor variabilis* and *Rhipicephalus sanguineus* on days one, four and seven pretreatment. The collar and the dog are weighed separately to determine the total mg/kg dose rate.

Each dog is observed daily for signs of tick mortality and/or repellency. Numbers of adult ticks falling from treated and control dogs are recorded on an individual basis and oviposition and hatch rates are checked.

Each dog is reinfested weekly after the initial treatment to determine the effective control period for each set of collars.

Results

One week after wearing the collars, both treated and control groups are still infested with ticks, although the treated dogs had reduced tick populations.

All dogs are reinfested with ticks one week after wearing the collars. The tick population on all the treated dogs is low and only one of the treated dogs (fitted with a collar prepared from the Experiment 2 formulation) has a significant population of young adults four days after reinfestation.

All dogs are reinfested with ticks at one week intervals. Collars prepared from Experiment 1 composition gave complete tick control. Collars from Experiment 2 composition were highly effective but failed to give complete control.

The data obtained are summarized in Table I below.

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TABLE I

Evaluation of the Efficacy of PVC Animal Collars, Containing Spiro[cyclopropane-1,1'-indene]-2-carboxylic acid, 3,3-dimethyl-, α -cyano-*m*-phenoxybenzyl ester, for the Control of Ticks of Dogs.

Treatment	Dog	Duration of Effectiveness (in Weeks)											
		1	2	3	4	5	6	7	8	9	10	11	12
Infested, untreated Controls	a	N	N	N	N	N	N	N	N	N	N	N	N
	b	N	N	N	N	N	N	N	N	N	N	N	N
	c	N	N	N	N	N	N	N	N	N	N	N	N
Example 1	d	P	P	C ₂	C	C	P ₃	P ₃	C	P	N	N	N
	e	P	P	C	*P	N	N	N	N	N	N	N	N
	f	P	P	P	P	C	C	C	C	C	P	C	P
Example 2	g	Deceased											
	h	P	N	P	N	N	P ₃	C	P	P	C ₃	C	P
	i	P	P	P	C ₄	C ₅	C ₆	P	C ₃	P	C ₃	C	C

N = no control.

P = partial control

C = Control

* = Collar destroyed

Subscript (e.g. C₂; P₃) indicates the number of days past reinfestation, after which the degree of controls indicated, is regained.

Example 4.

Preparation of PVC - O,O,O',O' - tetramethyl O,O' - thiodi - *p* - phenylene phosphorothioate resin composition

Diamond 40 PVC resin (1000 g), 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 Henschel mixer along with stearic acid (5 g), carbon black (2 g) and "Thermolite" 831 - di - *n* - octyltin maleate polymer PVC heat stabilizing agent (20 g). The mixer is run at high speed (3600 rpm) until the temperature of the mixture is 79°C, O,O,O',O' - tetramethyl O,O' - thiodi - *p* - phenylene phosphorothioate (930 g; 90% real) is then added and mixing is continued.

When addition of the phosphorothioate is completed and the temperature of the mixture reaches 93°C, 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 9.52 mm (3/8") wide slot 3.17 mm (1/8") thick.

Extrusion is accomplished with the mixture heated from 121°C at the rear feed to 165°C at the die zone and an extruded stock temperature of 163°C. This extrusion is conducted with a head pressure of 21 kg cm⁻². 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 61 cm (2') lengths to which a buckle is attached.

The animal collars thus prepared contain only the above-mentioned phosphorothioate which amounts to 42.8% (47.5% as is) by weight of composition.

Example 5.

O,O,O',O' - Tetramethyl O,O' - thiodi - *p* - phenylene phosphorothioate Flea collar activity against *Ctenocephalides felis* on dogs

Two groups of 4 dogs each are infested with 100 adult *Ctenocephalides felis* three days prior to placing a flea collar around the neck of each dog in one of the groups. The dogs in the second group serve as infested untreated controls. Each dog is systematically examined daily for fleas presence or absence. Complete flea control observed within one week from the time the collar is placed on the dog is considered effective control. Each

	dog is reinfested weekly with 100 adult <i>C. felis</i> and examined daily thereafter for fleas. Effective control is considered complete control of <i>C. felis</i> on all dogs within one week of reinfestation.	
5	All dogs are fed "Purina" High Protein Dog meal once daily and all are provided with water <i>ad libitum</i> . The dogs are housed in individual cages with grate bottom floors.	
10	The data obtained in this example indicate that the flea collar prepared from Example 4 PVC resin-siphonaptericide composition provides complete (100%) control of <i>Ctenocephalides felis</i> for at least 52 weeks.	
15	Example 6. <i>Evaluation of the efficacy of tick and flea collars in physical combination for simultaneous control of ticks and fleas</i>	
20	Animals Four mongrel dogs are used in the test. The animals are housed in cages fitted with grated floor. "Purina" High Protein Dog Meal is fed once daily and water offered <i>ad libitum</i> .	
25	Material and Methods One group of two dogs serves as unmedicated infested controls (dogs A & B).	
	One dog is fitted with two PVC collars, one containing 30% by weight of spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - <i>m</i> - phenoxybenzyl ester (prepared by the process of Example 1) and the other containing 40.7% by weight of O,O,O',O' - tetramethyl O,O' - thiodi - <i>p</i> - phenylene phosphorothioate (prepared by the process of Example 4) (dog C); and one dog is fitted with a Hartz "2 in 1" collar, containing 9.5% by weight of 2 - chloro - 1 - (2,4,5 - trichlorophenyl)vinyl dimethyl phosphite (dog D).	30
	Each dog is infested with 10 male and 10 female <i>Dermacentor variabilis</i> and <i>Rhipicephalus sanguineus</i> and with 100 <i>Ctenocephalides felis</i> on days one, four and seven pretreatment.	35
	Each dog is observed daily for signs of tick and flea mortality and/or repellency. Number of adult ticks falling from treated and control dogs are recorded on an individual basis and oviposition and hatch rates are checked.	40
	Each dog is reinfested weekly after the initial treatment to determine the effective control period for each set of collars.	45
	The data obtained are summarized in Table II below.	50
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TABLE II
Evaluation of the Efficacy of Tick and Flea Collars in Physical Combination for the Simultaneous Control of Ticks and Fleas on Dogs, Compared to a Commercial Tick and Flea Collar.

Treatment	Dog	Insect Tested	Duration of Effectiveness (in Weeks)													
			1	2	3	4	5	6	7	8	9	10	11	12	13	14
Infested, untreated controls	A	Flea Tick	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	B	Flea Tick	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Spiro cyclopropane-1,1'-indene]-2-carboxylic acid, 3,3-dimethyl-, α -cyano- <i>m</i> -phenoxybenzyl ester in combination with O,O',O'-tetramethyl O,O'-thiodi- <i>p</i> -phenylene-phosphorothioate	C	Flea	+	+	+	+	+	+	+	+	+	+	+	+	+	+
		Tick	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Hartz 2" in 1" R Collar	D	Flea Tick	+	+	+	+	+	+	+	+	+	+	+	+	+	+

+ = Few, if any dead ± = Some dead (about 50%+) - = All dead, or moribund

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(14)

It can be seen from the above Table, that the physical combination of two collars, one containing spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester, and the other O,O,O',O' - tetramethyl O,O' - thiodi - *p* - phenylene phosphorothioate, respectively, offers positive control of fleas and ticks on dogs for 8 weeks. The commercial dog collar, on the other hand, offers only 5 weeks of positive control of fleas and 4 weeks of partial control of ticks, on dogs.

WHAT WE CLAIM IS:—

1. A dry blended polyvinyl chloride composition useful for forming articles having acaricidal properties, 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 an acaricidal agent from 15% to 40% by weight of the composition of spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester.
2. A composition according to Claim 1, 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.
3. A composition according to Claim 1 or Claim 2, wherein the polyvinyl resin has an approximate weight average molecular weight of 120,000 and an inherent viscosity of about 0.80.
4. A composition according to any preceding claim, wherein said acaricidal agent is present in a concentration of from 20% to 30% by weight of the composition.
5. A composition according to any preceding claim, containing also a plasticizer.
6. A composition according to any preceding claim, containing also a lubricant.
7. A composition according to any preceding claim, containing also a stabilizing agent.
8. A composition according to claims 1—7, comprising from 38% to 66% by weight of a polyvinyl chloride resin having an approximate weight average molecular weight of 120,000 and an inherent viscosity of about

0.80, from 18% to 35% by weight of spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester, from 15% to 25% by weight of a plasticizer selected from dioctyl phthalate, octyl epoxystallate and di - (2 - ethylhexyl)phthalate, from 0.1% to 0.5% by weight of stearic acid lubricant, and from 0.5% to 1.5% by weight of di - *n* - octyltin maleate polymer stabilizing agent, said percentages being by weight based on the total weight of the composition.

9. A composition according to Claim 5, wherein the plasticizing agent is dioctyl phthalate, octyl epoxystallate or di - (2 - ethylhexyl)phthalate, and is present in a concentration of from 15% to 25% by weight, based on the weight of the composition.

10. An article useful for the control of acarina on animals and formed by molding a dry blended polyvinyl chloride composition according to any preceding claim.

11. An article according to Claim 10 in the form of a collar for placing around the neck of an animal.

12. A method for the control of acarina on dogs and cats, comprising placing a collar according to Claim 11 around the neck of the animal to be protected.

13. A method according to Claim 12, wherein control of fleas on said animal is simultaneously obtained by placing a second PVC collar containing O,O,O',O' - tetramethyl O,O' - thiodi - *p* - phenylene phosphorothioate around the neck of the animal.

14. A dry blended polyvinyl chloride composition, according to Claim 1 and substantially as described in any one of Examples 1, 2 and 4 herein.

15. An acaricidal collar for an animal moulded from a composition according to Claim 14.

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5 It can be seen from the above Table, that
the physical combination of two collars, one
containing spiro[cyclopropane - 1,1' - indene] -
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10 *m* - phenoxybenzyl ester, and the other
O,O,O',O' - tetramethyl O,O' - thiodi - *p* -
phenylene phosphorothioate, respectively, offers
positive control of fleas and ticks on dogs for
8 weeks. The commercial dog collar, on the
other hand, offers only 5 weeks of positive
control of fleas and 4 weeks of partial control
of ticks, on dogs.

WHAT WE CLAIM IS:—

- 15 1. A dry blended polyvinyl chloride composition useful for forming articles having acaricidal properties, 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 an acaricidal agent from 15% to 40% by weight of the composition of spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester.
- 20 2. A composition according to Claim 1, 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.
- 30 3. A composition according to Claim 1 or Claim 2, wherein the polyvinyl resin has an approximate weight average molecular weight of 120,000 and an inherent viscosity of about 0.80.
- 35 4. A composition according to any preceding claim, wherein said acaricidal agent is present in a concentration of from 20% to 30% by weight of the composition.
- 40 5. A composition according to any preceding claim, containing also a plasticizer.
6. A composition according to any preceding claim, containing also a lubricant.
7. A composition according to any preceding claim, containing also a stabilizing agent.
- 45 8. A composition according to claims 1—7, comprising from 38% to 66% by weight of a polyvinyl chloride resin having an approximate weight average molecular weight of 120,000 and an inherent viscosity of about

0.80, from 18% to 35% by weight of spiro[cyclopropane - 1,1' - indene] - 2 - carboxylic acid, 3,3-dimethyl-, α - cyano - *m* - phenoxybenzyl ester, from 15% to 25% by weight of a plasticizer selected from dioctyl phthalate, octyl epoxystallate and di - (2 - ethylhexyl)phthalate, from 0.1% to 0.5% by weight of stearic acid lubricant, and from 0.5% to 1.5% by weight of di - *n* - octyltin maleate polymer stabilizing agent, said percentages being by weight based on the total weight of the composition.

9. A composition according to Claim 5, wherein the plasticizing agent is dioctyl phthalate, octyl epoxystallate or di - (2 - ethylhexyl)phthalate, and is present in a concentration of from 15% to 25% by weight, based on the weight of the composition.

10. An article useful for the control of acarina on animals and formed by molding a dry blended polyvinyl chloride composition according to any preceding claim.

11. An article according to Claim 10 in the form of a collar for placing around the neck of an animal.

12. A method for the control of acarina on dogs and cats, comprising placing a collar according to Claim 11 around the neck of the animal to be protected.

13. A method according to Claim 12, wherein control of fleas on said animal is simultaneously obtained by placing a second PVC collar containing O,O,O',O' - tetramethyl O,O' - thiodi - *p* - phenylene phosphorothioate around the neck of the animal.

14. A dry blended polyvinyl chloride composition, according to Claim 1 and substantially as described in any one of Examples 1, 2 and 4 herein.

15. An acaricidal collar for an animal moulded from a composition according to Claim 14.

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