

PATENT SPECIFICATION (11)

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(54) PET COLLAR

(71) We, A. H. ROBINS COMPANY, INCORPORATED, a Corporation organised and existing under the Laws of the State of Virginia, United States of America, of 1407 Cummings Drive, Richmond, Virginia 23220, 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 the control of fleas on warm blooded animals, such as dogs and cats, by application of an insecticidal gas generator device. More particularly, this invention relates to flea control collars for such animals, the collars being of the type comprising a strip of a synthetic resin such as polyvinyl chloride (PVC) having an insecticide dispersed therein.

Heretofore, collars comprising a strip of a PVC resin having dispersed therein the insecticide dimethyl 2,2-di-chlorovinyl phosphate, commonly known as DDVP or by the trade mark VAPONA, have been widely used for the purpose of controlling fleas on dogs and cats. DDVP has been reported to have an objectionable depressing effect on the plasma and red cell cholinesterase which is particularly acute at the high concentrations which are produced during the first few days after a collar has first been applied to the neck of the animal. In addition, local skin irritation has occasionally occurred at the site of the collar, especially when a new collar is first placed on the animal, notwithstanding the smooth surface of the collar. This is believed due to the fact that liberation of DDVP from presently available DDVP collars and tags is not at a uniform rate, but rather there is a high liberation rate of DDVP gas during the first few days after activation, i.e. removal of the collar from the packing and placing it on the neck of the animal. Moreover, the aforementioned initial high liberation rate represents an unduly rapid loss of insecticide and creates an upper limit on the

period that DDVP is liberated at a rate sufficient to effectively control fleas.

According to one aspect of the present invention a flea control collar for a warm blooded animal comprises a strip of a length sufficient to encircle the neck of the animal and clamping means at or near one end of the strip for engaging a portion of the strip spaced from the clamping means to prevent loss of the collar from the animal, the strip comprising a mixture of a flexible synthetic resin such as PVC and between 5 and 25 percent by weight of the strip of the insecticide dimethyl 1,2-dibromo-2,2-dichloroethyl phosphate, commonly known as hereinafter referred to as naled and the strip having surface openings in communication with pores in the strip whereby, upon use of the strip as a collar, the strip releases naled gas vapour at a rate effective to control fleas on the animal but insufficient to form as droplets on the strip or to be toxic to the animal.

Preferably the strip contains sufficient naled to be released in the form of vapour at a rate effective to control fleas on the animal throughout a period of at least ninety days.

Furthermore, there is provided a method of making such a flea control which comprises forming into a strip having a length suitable for use as the collar a dispersion of the flexible synthetic resin, naled, and a surface porosity control component that is non-reactive in the dispersion and has a boiling point at or below the curing temperature of the resin; the forming step including heating the dispersion to the curing temperature of the resin to produce surface openings in communication with pores in the strip by vaporisation of the porosity control component such that, upon application of the collar to the neck of the animal, the strip releases naled vapour at a rate effective to control fleas on the animal but insufficient to form as droplets on the strip or to be toxic to the animal, and providing at or adjacent one end of the strip a clamping

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means for engaging a collar portion spaced from the clamping means to prevent loss of the collar from the neck of the animal.

5 The invention also relates to a method of treating a warm blooded animal for fleas which comprises placing and maintaining on the animal a flea control collar in accordance with the invention.

10 The flea control collar of the invention may employ naled alone or in combination with a lesser amount of another insecticide such as DDVP.

15 The preparation of naled is described in United States Patent Specification No. 2,971,882 (Osmonson et al). PVC resin-naled combinations have been proposed for use as an insecticide of a general nature in French Patent Specification No. 1,568,198, and in British Patent Specification No. 955,350. Netherlands published Patent Application No. 6,610,279 discloses fly strips composed of PVC-naled as well as PVC-DDVP combinations which are stated to have such high insecticide release rates as to require an outer laminate layer to retard the insecticide release. United States Patent Specification No. 3,334,021 discloses PVC-naled combinations for use as an anthelmintic composition.

30 A number of problems have been encountered in providing a commercially satisfactory PVC resin-naled combination as a pet collar. First, there must be a sufficient amount of naled released to provide effective control of fleas over periods of not less than 90 days. Contrary to statements in the prior art disclosures, we have found that release rates for naled are very much less than the release rates for DDVP. Naled has a low vapour pressures of about 2×10^{-4} mm. Hg. at 20°C . as compared to that for DDVP of 1.2×10^{-2} to be thus only about 1.7% of the vapour pressure of DDVP.

45 The concept of a vapour-emission controlled PCV-naled resin combination in the form of a collar to control fleas on dogs and cats requires significant emission rate to provide effective flea control. We have found it is not possible to increase the concentration of naled materially above about 25% without causing droplets of naled to form on the surface of the collar. Naled is toxic to animals and humans, and therefore concentrations of naled in excess of about 25% in a pet collar are not suitable.

50 A further unexpected problem found with a PVC-naled composition was the tendency of the resin to decompose during the shaping process. For example, unsatisfactory results were obtained in early tests where naled was substituted for DDVP in PVC combinations employed in extrusion apparatus used for making the prior art PVC-DDVP pet collar. Burning and charring

of the extrudate were found to occur during curing of the collars, and the finished collar underwent an unexplainable reduction in the naled concentration as compared with the naled concentration in the original plastisol dispersion.

In the accompanying drawings:—

Figure 1 is a plan view of a representative pet collar embodying the present invention;

Figure 2 is a view of the collar in cross section taken along lines 2—2 of Figure 1;

Figure 3 is a graph showing the comparative rate of naled release in collars employing naled with a surface porosity control component or additive in accordance with the present invention and naled without the additive;

Figure 4A is a photomicrograph enlarged by 100 times showing a section of the upper surface of a collar prepared in accordance with the invention;

Figure 4B is a similar view of the lower side of the collar that has been in contact with the casting mould;

Figure 4C is a similar view showing a side cut of the same collar;

Figure 4D is a similar view showing a longitudinal cross section of the same collar;

Figure 5A is a view similar to view Figure 4A of a collar containing naled but which was made without employing the surface porosity control component or additive of the present invention;

Figures 5B, 5C and 5D are views of the collar of Figure 5A that correspond to the views shown in Figures 4B, 4C and 4D.

Referring now to the drawings, Figures 1 and 2 show a typical collar adapted for pets such as dogs or cats. The components making up a satisfactory naled containing pet collar include a synthetic resin that is sufficiently pliable or flexible to encircle the animal's neck and has a strength sufficient to remain on the animal throughout a period of at least $4\frac{1}{2}$ months or the period during which naled is released in amounts effective to control fleas.

The collar constitutes a band or strip of a PVC-naled combination with the concentration of PVC sufficiently large to give the collar physical properties such as strength, flexibility, and freedom from tackiness to make it suitable for use as a collar for the animal. Normally, the cross-sectional dimensions of the collar vary from about $\frac{1}{4}$ " to $\frac{3}{8}$ " in width, and from about $\frac{3}{32}$ " to $\frac{3}{16}$ " in thickness. For collars of the present invention employing the PVC-naled combination, the preferred dimensions are $\frac{3}{8}$ " in width and $\frac{1}{4}$ " in thickness, and the cross section is as illustrated in Figure 2.

The collars are made of sufficient length to encircle the neck of the largest dog or cat to be encountered, and for smaller animals, the end of the collar may be cut

off to reduce the size of the collar to correspond with the size of the animal. With the PVC-naled combination and dimensions as given above, the perimeter of the collar is about one inch and the mass of the collar is about one gram per lineal inch. By use of a clasp having a friction grip, the collar can be adjustably placed on the animal without the need for holes.

From the standpoint of toxicity, collars for dogs should be constructed so as to release no more than about two milligrams of naled per square inch of surface area per day. Because of increased toxicity and their generally smaller size, the release rate from collars for cats should be approximately one-half of that for dogs. It has been ascertained that when the release rate falls off to about 0.1 to about 0.2 milligrams of naled per square inch of surface area per day, that the effectiveness of the collar for flea control has been reduced to the point where it should be replaced. Because cats are smaller and have a tendency to sleep in a curled-up position, a lower naled release rate is effective for cat collars thereby allowing naled concentrations to be as low as 8% or as low as 5% when used in combination with another insecticide.

Naled exists within the matrix of the resin of the collar as a separate entity to be gradually released upon migration to the surface where it is dispersed to the immediate environment of the collar. Most of the naled escapes as vapour. In order for the naled to escape, it moves outward through the interstices or pores of the resin to the porous surface openings. The internal porosity, texture and surface porosity of the resin must be sufficiently coordinated to allow a sufficient release of naled from the resin to effectively control fleas for a period of at least 90 days, but insufficient to form as droplets on the collar or to be toxic to the host animal.

The rate of expulsion of liquid naled can be further controlled as will be discussed below. It is, however, imperative that for animal collars, the amount of naled be kept below the level where the naled is expelled so rapidly as to form as liquid droplets, otherwise known in the art as "spew" on the collar surface in view of its toxicity to animals and humans. While prior art descriptions of naled containing compositions suggest that up to 75 wt. % of a synthetic resin-naled combination may be produced and used as an insecticidal strip, we have found that no more than about 25 wt. % can be used without encountering "spew".

The various known synthetic resins which can be used for a naled containing pet collar include materials such as polyethylene, polypropylene, copolymers of ethylene and

propylene, nylon, regenerated cellulose, polyacrylates, such as polymers and copolymers of methyl acrylate, ethyl acrylate, methyl methacrylate and ethyl methacrylate; polymers of vinyl compounds, such as polystyrene, polymerized divinylbenzene; polyvinyl halogenides, such as polyvinylchloride; polyvinylacetals, such as polyvinylbutyral; polyvinylidene compounds, such as polyvinylidenechloride; polyvinylacetate; ethylvinylacetate-vinylacetate copolymers; copolymers of vinylchloride and vinylacetate; polyurethanes, polyaldehydes; and thermoplastics.

Polyvinylchloride (PVC) homopolymers and copolymers with other polymers such as polyvinyl acetate (PVA) are preferred synthetic resin materials. Suitable PVC resins are commercially available and include, for example, PVC homopolymer dispersion resin Diamond PVC-7502 and PVC homopolymer extender resin Diamond PVC-7-466 (DIAMOND is a trade mark), both available from The Diamond Shamrock Co., U.S.A., and mixtures thereof. Other suitable, commercially available PVC resins are known in the art. Suitable PVC-PVA copolymers are also commercially available and include, for example, Geon 135 (Goodrich Corp., U.S.A. — GEON is a trade mark), PVC-74 (Diamond Alkali Co., U.S.A.) and XR-6338 (Exxon-Firestone, U.S.A.). Other PVC-PVA copolymers are also known in the art.

The preparation of synthetic resin-naled combinations is achieved by conventional methods. Because of the great compatibility of naled in the resin dispersions, the compositions may be prepared merely by mechanical mixing of the pesticides with powdered resin. Fluid pastes, or plastisol dispersions, can be made which, as is known, can be molded, extruded, cast, or otherwise formed into the shape of a band or strip. Where the prepolymerized resin exists in liquid form, as in the case of such monomers as styrene or methyl methacrylate, the naled may be incorporated in the liquid before it is polymerized or cured. The term "dispersion" as used herein is intended to include mixtures of a solid with a liquid, a liquid with a liquid and a solid with a solid.

In the embodiments where polyvinyl resins are used, plasticizers and other additives commonly used for providing the flexibility, strength and surface characteristics desired for a pet collar are well known to those skilled in this art, and no further discussion is deemed necessary here. In addition colouring and odour control agents may be employed in the collars of the present invention to enhance consumer acceptance.

Naled is added to the plastisol dispersion in an amount sufficient when the synthetic resin is cured to release naled at a rate

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capable of controlling fleas on an animal wearing the collar. Minimum effective release rates for a pet collar are, as stated above, at least 0.1 to 0.2 mg. per square inch per day. To give the collar a useful life of at least 90 days, initial concentrations of naled in the formulations of the present invention should be above 8 wt. % of the collar weight, or about 5 wt. % naled where another insecticide, such as 5 wt. % of DDVP, is used. For dogs, initial concentrations should be above 14 wt. % of the collar. The upper limit of naled in a pet collar should be below that which is toxic to the host animal, and less than 25 wt. % of the collar weight to avoid spewing.

Because of the low vapour pressure of naled, which is believed responsible for a relatively low release rate, the naled release rate from PVC-naled collars is comparatively low and inadequate for a commercially acceptable pet collar. However, we have found that use of an additive in the dispersion can be very helpful in increasing the naled release rate. This makes possible effective flea control at lower initial naled concentrations and a collar having an increased effective life.

The additive, also referred to as a surface porosity control component, is present in the final plastisol dispersion or mix used in forming the collar, and hence must be non-reactive with the other components of the dispersion or mix. The main function of the additive is to provide a surface porosity which preferably includes pores extending part way into the body of the collar. The desired surface characteristics are obtained by the vaporization of the additive during the curing period. Hence the additive should comprise one or more compounds having a boiling point at or below the curing temperature of the resin.

Compounds which are suitable as the surface porosity control component in PVC resins which are cured at a temperature in the range of from 300° to 375°F include aldehydes and their lower alkyl acetals containing bromine or chlorine. The porosity control component may thus include one or more of the following which have approximate boiling point temperatures as set forth:

Name	B.P. °F.
chloroacetaldehyde	185
dichloroacetaldehyde	192
chloral	218
bromoacetaldehyde	176—221
dibromoacetaldehyde	288
bromal	346
bromodichloroacetaldehyde	258
chlorodibromoacetaldehyde	299
bromochloroacetaldehyde	233
2-bromopropanol	229

The surface porosity control component is included in the synthetic resin-naled combination in an amount sufficient to produce surface porosity by its vaporization during curing of the dispersion whereby said cured strip releases naled vapour at a rate effective to control fleas throughout a period of at least about 90 days without forming droplets on the strip. While the amount of the porosity control component to be used depends on the density of surface openings desired and somewhat on the particular procedure used for curing the resin, it is generally from 0.8 to 4, preferably from 1 to 3, wt. % of the dispersion.

It has been observed in analyses of the emitted vapour from the collar that some of the additive remains in the cured collar and is emitted when the package is initially opened. In some instances, the rate of naled release during the first few days after the collar package is opened has been measured to be somewhat lower than the naled release during the second and succeeding weeks. The rate of weight loss of the collar due to vapour emission is the greatest during the first days, thus confirming the emission of components from the collar other than naled. These observations are somewhat at variance with the prior art statements that indicate a faster insecticide release rate in the beginning. Chemical analyses indicate that with a PVC-naled combination formed according to the present invention, the average naled release rate per day increases over a period up to about three to ten days, and thereafter begins to decrease. The overall release rate during a period of 4½ months decreases by perhaps 50% from its maximum depending upon ambient conditions surrounding the collar.

The extent to which the naled release is increased by use of the volatile additive in accordance with the present invention is demonstrated graphically by Figure 3. At the end of 20 weeks, a dog collar made according to the Comparative Example below without the additive for controlling surface porosity released only 27.65% of the available naled in the collar, while a collar made according to the invention and having the surface porosity control additive released 38.73% which constitutes about a 40% increase in naled release. The residual amount of naled that will be retained in the collar is greater where the porosity control component or additive is not used. With the use of the porosity control additive, the naled concentration in the collar as manufactured can be sufficiently less than the amount which causes spewing to assure the proper physical condition of the collar when delivered to the consumer, and a greater proportion of the naled in the collar will be delivered during the useful life of the collar.

The treatment of warm blooded animals for fleas in accordance with the present invention involves placing on the neck of an animal a collar formed of a synthetic resin, and naled in an amount sufficient to kill fleas but insufficient to be toxic to the host animal.

The invention is additionally illustrated in connection with the following Examples which are to be considered as illustrative of the present invention. It should be understood, however, that the invention is not limited to the specific details of the Examples.

EXAMPLE 1

A mixture in percentages by weight of

- 37.7 PVC homopolymer dispersion resin ("Diamond PVC-7502")
- 16.2 PVC homopolymer extender resin ("Diamond PVC-7-44L")
- 17.8 di-2-ethylhexylphthalate (DOP)
- 2.4 epoxidized octyl tallate (EPO)
- 0.9 calcium and zinc stearate powders (50—50 by wt.)
- 22.7 naled (dimethyl 1,2-dibromo-2,2-dichloroethyl phosphate)
- 2.3 surface porosity control component (bromodichloroacetaldehyde)

100.0 Total

was thoroughly trituated to form a plastisol dispersion having a viscosity at 25°C. of 16,000 cps. as measured on a Brookfield viscometer at 20 rpm., 12,000 at 2 rpm. A portion of the plastisol was metered to a machined aluminium open-faced cast mould having a cavity $\frac{3}{8}$ " in width $\times$ 21" in length $\times$ $\frac{1}{8}$ " in depth. Temperature of the mould at filling time, as indicated by a thermocouple immediately beneath the cavity surface was 290°F. The mould was placed in an oven and the temperature of the mould was raised by means of hot air and radiant heat in two minutes' time to 360°F. Temperature was maintained at 360°F for 15 seconds to maintain the dispersion at or above the curing temperature, after which cooling was started, the temperature being lowered rapidly to 315°F in 15 seconds. The buckle for the strip was placed in the mould while the dispersion was uncured. The cured strip with its buckle was immediately thereafter removed from the mould and cooled rapidly to room temperature. The colour of the collar was brownish bronze. A strong medicinal odour emanating from the finished resin was detected. The top side of the collar was rounded due to the meniscus formed on filling the mould, the shape being retained during curing.

Analysis of the collar after curing and cooling showed the naled content of the collar to be 21% by weight. Other com-

ponents calculated on a weight percentage basis in the product were 56.8 PVC, 18.8 DOP, 2.5 EPO, and 0.9 Ca, Zn stearate.

"Diamond PVC 7502" is commercially available from The Diamond Shamrock Company, U.S.A. and is a high molecular weight homopolymer dispersion resin having particle size less than two microns; specific viscosity is 1.62 to 1.68 as measured in a 1% solution of the resin in cyclohexane at 30°C. according to ASTM procedure.

"Diamond PVC-7-44L" is commercially available from Diamond Shamrock Chemical Company, U.S.A. and is an intermediate molecular weight homopolymer extender resin having particle size such that 95% passes through 140 mesh with specific viscosity of 1.15 as measured in a 1% solution of the resin in cyclohexane at 30°C. according to ASTM procedure.

DOP is a plasticizer for PVC and EPO is a stabilizer. The calcium and zinc stearate powders are stabilizers.

The above dispersion and extender resins are as easy to work with in producing a satisfactory pet collar as any that have been used. However, as those skilled in this art well know, a large number of other materials, as discussed above, can be used. Naled is not known to react chemically with any synthetic resin, and considerable variations in both ingredients and proportions can be used successfully in forming a collar.

EXAMPLE 2

Following the procedures and utilizing the quantities of materials in Example 1, except that the heating time was reduced from two minutes to one minute and thirty seconds in the same oven during which time the mould temperature reached about 355°F, the collar produced was almost colourless. By chemical analysis, the naled content was 21.2 wt. %. The same medicinal odour was present.

EXAMPLE 3

Following the procedure of Example 1 and using a plastisol dispersion consisting in parts by weight of:

- 40.8 PVC homopolymer dispersion resin ("Diamond PVC-7502")
- 17.6 PVC homopolymer extender resin ("Diamond PVC-7-44L")
- 19.1 di-2-ethylhexylphthalate (DOP)
- 2.5 epoxidized octyl tallate
- 1.0 calcium and zinc stearate powders (50—50 by weight)
- 17.3 naled (dimethyl 1,2-dibromo-2,2-dichloroethyl phosphate)
- 1.7 surface porosity control component (bromodichloroacetaldehyde)

100.0 Total

a bronze coloured resin suitable as a dog collar was obtained which analyzed 16.0% by weight of naled after curing and cooling. A medicinal odour was present.

EXAMPLE 4

Following the procedure of Example 1 and using a plastisol dispersion consisting in parts by weight of

43.8	PVC homopolymer dispersion resin ("Diamond PVC-7502")
18.2	PVC homopolymer extender resin ("Diamond PVC-7-44L")
20.6	di-2-ethylhexylphthalate (DOP)
2.8	epoxidized octyl tallate
1.0	calcium and zinc stearate powders (50—50 by weight)
11.8	naled (dimethyl 1,2-dibromo-2,2-dichloroethyl phosphate)
1.2	surface porosity control component (bromodichloroacetaldehyde)
100.0	Total

a bronze coloured resin suitable for a cat collar was obtained after curing and cooling which analyzed 11.05 weight percent naled after curing and cooling. A medicinal odour was present. Width of the collar was 0.3125 inch and the thickness was 0.125 to 0.128 inch as taken from cast mould. Average tensile strength as measured by the procedure of ASTM D-638 was 1690/240; 1690 psi. being required for breakage and 240% elongation occurring before breakage occurred. Hardness as measured by the Shore Durometer was A-2 = 82.5; D = 36.5. Specific gravity was 1.38.

EXAMPLE 5

Following the procedure of Example 1 and using a PVC plastisol dispersion containing 17.4 naled and a composition otherwise the same but proportionate, a synthetic resin analyzing 16.8 naled suitable as a dog collar was prepared. Width of the collar was 0.3750 inch and thickness was 0.132—0.148 inches as taken from the cast. The collar was bronze coloured and had a medicinal odour. Average tensile strength as measured by the procedure of ASTM D-638 was 1243/200; 1243 psi. being required for breakage and 200% elongation occurring before breakage occurred. Hardness as measured by the Short A-2 Durometer was A-2 = 77; D = 32. Specific gravity of the resin was 1.39.

Comparative Example

Following the procedure of Example 1 and using a plastisol dispersion consisting in parts by weight of

41.0	PVC homopolymer dispersion resin ("Diamond PVC-7502")
17.6	PVC homopolymer extender resin ("Diamond PVC-7-44L")
19.4	di-2-ethylhexylphthalate
2.6	epoxidized octyl tallate
1.0	calcium and zinc stearate powders (50—50 by wt.)
18.4	naled (dimethyl 1,2-dibromo-2,2-dichloroethyl phosphate)

100.0 Total 75

a finished collar was produced whose analysis showed that the resin contained 16.2% weight naled, indicating that 12% of the naled initially present in the dispersion was lost during the curing process. This is greater than the naled lost in the other Examples. The resin was slightly yellow and no odour could be detected. Width of the collar was 0.3750 inch and thickness was 0.108—0.113 inch. Average tensile strength as measured by the procedure of ASTM D-638 was 577/130; 577 psi. being required for breakage and 130% elongation occurring before breakage occurred. Hardness as measured by the Shore Durometer was A-2 = 73; D = 30. Specific gravity of the resin was 1.43.

EXAMPLE 6

A mixture in percentages by weight of

37.0	PVC - polyvinylacetate copolymer ("Geon 135")
18.5	PVC homopolymer extender resin ("Diamond PVC-7-44L")
20.0	di-2-ethylhexylphthalate (DOP)
3.5	epoxidized octyl tallate (EPO)
1.6	calcium and zinc stearate powders (50—50 by wt.)
0.6	iron oxide
17.6	naled
1.2	surface porosity control component (bromodichloroacetaldehyde)

100.0 Total 110

is illustrative of a collar prepared by use of a copolymer rather than a homopolymer.

The procedures are essentially identical to the procedure described in connection with Example 1. The external appearance and physical properties are similar to those of Example 1 thereby providing a band which, when provided with a buckle such as illustrated in Figure 1, is suitable for a pet collar.

EXAMPLE 7

The mixture of Example 1 is repeated except that 18 weight percent of a technical

grade of naled commercially available from the Chevron Chemical Company, U.S.A. is used. This product is known to contain certain impurities such as bromodichloroacetaldehyde, chloral, carbon tetrachloride and various forms of phosphates. These impurities constitute about 9 weight percent of the product and in large part are sufficiently volatile as to be released during the curing of the collar or shortly thereafter and hence not to interfere with the functioning of the collar.

The collar formed and cured in the manner indicated in Example 1 is brownish bronze and contains about 16.8 weight percent naled.

EXAMPLE 8

A dog collar is formed using a mixture (parts by weight) of

- 81.2 methyl methacrylate monomer
- 0.5 benzoyl peroxide catalyst
- 15.8 naled
- 2.5 dibromoacetaldehyde (surface porosity control component)

100.0 Total

The benzoyl peroxide, naled and dibromoacetaldehyde are mechanically mixed into the liquid methyl methacrylate monomer and the mixture is poured into the mould of Example 1 and cured at about 300°F. The buckle for the collar was placed in the mould while the dispersion was uncured. The cured strip was removed from the mould and cooled to room temperature. The collar had a clear colour and contained (upon analysis) about 14 weight percent naled.

EXAMPLE 9

Example 8 is repeated using however liquid styrene monomer as the synthetic resin precursor. Benzoyl peroxide (0.5 weight percent) is used as a polymerization initiator and curing is performed at about 250°F to yield a clear, transparent pet collar containing about 14 weight percent naled.

EXAMPLE 10

Example 8 is repeated using however polyurethane as the synthetic resin. A hydroxyl terminated liquid polybutadiene resin prepolymer (100 parts by weight) is blended with 8 parts by weight toluene diisocyanate, 18.5 parts by weight naled, 0.02 parts by weight dibutyl tin laurate (curing catalyst) and 2 parts by weight 2-bromopropanol (surface porosity control component). The blended mixture is cured at a temperature of about 275°F. The resulting cured pet collar contains about 17 weight percent naled.

EXAMPLE 11

19.6 parts by weight naled and 2 parts by weight of chloral are mixed into a melt of parts by weight of high density polyethylene maintained at 250°F. The melt is poured into the mould of Example 1 and rapidly cooled to form a transparent pet collar containing about 18 weight percent naled.

EXAMPLE 12

Example 11 is repeated using polypropylene as the synthetic resin and dichloroacetaldehyde as the surface porosity control component. A collar similar to that of Example 12 is produced. Similar results are obtained if nylon is used in place of polypropylene.

Naled Release Rates

The release rate of naled from compositions utilizable in this invention for a given surface area of a collar of given thickness and surface area per unit length varies depending upon not only the initial naled concentration in the collar, but more importantly on whether or not the volatile additive which serves as a porosity control component has been used as discussed above and shown in Figure 3. A collar formed according to the present invention containing an initial concentration of 15 to 25% naled will release naled in sufficient amount for several months to control fleas on animals of large size such as dogs, and a similar collar containing initially 8 to 15% naled will release naled at a sufficient rate to control fleas on animals of small size such as cats for a similar period.

One significant advantage of the naled collar of the present invention over the prior art DDVP collar in current commercial use is found in the pattern of release of insecticide as a gas during the first few days of activation which starts at the moment of removal from a sealed container. The initial release rate of naled during the first few days is only a fraction of the initial release rate of DDVP from comparable collars due mainly to the difference in vapour pressure. For naled with porosity control additive, the release rate does not decrease noticeably for a period of about 10 weeks; thereafter, the release rate gradually decreases to about 50% of the maximum at the end of about 20 weeks. The pattern of the release rate curve for naled from a PCV collar without the porosity control component is generally parallel.

Illustration of weight loss of dog collars (16.8% naled initial) over 20 weeks' time atmosphere exposure to laboratory air at room temperature of the collar prepared in Example 5 is given as follows:

	Exposure Time, cum days	% Weight Loss, cum.	Average Approx. Weight Loss mg. per day per inch ² surface area (a)
5	1	—	Est. 2.0
	4	0.42	—
	7	0.59	0.5
	14	1.03	—
	21	1.25	—
10	28	1.53	0.4
	35	1.77	—
	42	1.99	—
	49	2.21	—
	56	2.40	—
15	63	2.57	—
	70	2.83	—
	77	2.95	0.2
	84	3.11	0.2
	91	3.27	—
20	98	3.36	—
	105	3.51	0.2
	112	3.69	—
	119	3.80	—
	126	3.78	—
25	133	3.94	0.2

(a) Area = 1 inch² per lineal inch; weight 1 g/lineal inch.

Further illustration of weight loss of cat collars over 20 week's time atmosphere exposure to laboratory air of the collar prepared in Example 4 (11.0 percent naled initial) is given as follows:

	Exposure Time, cum days	% Weight Loss, cum.	Av. Approx. Weight Loss mg per day per Inch ² Surface Area (a)
35	1	—	Est. 1.5
	4	0.22	—
40	7	0.30	0.3
	14	0.53	0.3
	21	0.66	—
	28	0.81	—
	35	0.94	0.2
45	42	1.04	—
	49	1.16	—
	56	1.26	—
	63	1.33	0.1
	70	1.48	—
50	77	1.56	—
	84	1.63	0.1
	91	1.72	—
	98	1.75	—
	105	1.84	0.1
55	112	1.94	0.1
	119	2.00	0.1
	126	1.96	0.005
	133	2.03	0.1

(a) Area = 1 inch² per lineal inch; weight 1 g/lineal inch.

With reference to Figure 3, the lower curve approximates the naled release rate for a collar prepared using the formulation of the Comparative Example, and the upper curve approximates the same release rates for a collar prepared using a formulation similar to Example 1. Comparison of release rates of naled from resins prepared without a volatile additive that serves to provide the desired surface porosity with

those prepared having such an additive shows that the naled release rate is substantially less with the former. This has been demonstrated by making the following comparison of naled loss as measured by analysis over a five month period of four collars taken at random from groups of collars, and

is illustrated by Figure 3. The end analysis shows that the percentage of naled liberated was 42% greater for collars made following the formulation using the porosity control component as compared with collars made following the formulation of the comparative Example.

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	Collars From Example 1	Collars From Comparative Example
	(Naled With Porosity Control Component)	(Naled Without Porosity Control Component)
Initial naled content in collar wt. % (a)	16.8	16.2
Naled content in collar 5 mo. after activation (a)	10.3	11.8
Naled released as a % of initial naled content	38.6	27.1
Increased naled release as a % of initial naled content due to surface porosity control component	11.5	

(a) By analysis

Insecticidal Efficacy of Naled Plastic Compositions

Insecticidal efficacy of naled plastic compositions in the form of animal pet collars was determined in either of two ways. In the first method, fleas were counted by inspecting the body regions of the animal and recorded on an animal profile chart over a period of four months. With this method it is sometimes difficult to obtain accurate counts due to movement of fleas and presence of dead fleas in the case of stick-tight fleas killed by insecticide. In the second method, flea egg counts are made by examining trays placed in the area beneath the animals. The following Table I demonstrates insecticidal efficacy of the 15% PVC-naled collars made in accordance with Example 1 on dogs in the practice of the method of this invention as measured by flea count over a period of 112 days. Table II demonstrates insecticidal efficacy of 10% naled compositions on cats by the flea egg shed count method over a period of 120

days. Similar results are obtained using the collars of Examples 2 to 12.

Test I

Effectiveness of naled plastic collars for controlling fleas on dogs was conducted in Northwest Mississippi from the end of September to mid-January. A pack of 29 Walker hounds were each individually collared with naled plastic collars of Example 1 and the dogs were kenneled in six pens each with its individual dog house. Flea counts were made before collaring and at 1, 2, 3 and 7 days, and 2, 3, 4, 5, 7, 10, 13, 14 and 16 weeks. At the start of the test, flea populations in the dog houses were enormous. Results are in Table I. Some of the dogs lost their collars during the test, the dogs counted being the number of dogs still having collars and remaining in the test. There was no evidence of deleterious effects in appearance and behaviour of the dogs so treated.

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TABLE 1

Effect of Naled Plastic Collars on Dogs
(Walker Hounds in Mississippi)

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Time		Total Flea Counts Per Total Dogs Retaining Collars	Average Fleas Per Dog
10	Day 0	2543/39	65.2
	1	741/39	19.0
	2	390/39	10.0
	3	256/39	6.6
	7	335/38	8.8
15	Week 2	314/36	8.7
	3	335/33	13.5
	4	234/32	7.3
	5	143/33	4.3
	7	273/31	8.8
20	10	63/28	2.3
	12	99/25	4.0
	13	114/25	4.6
	14	55/25	2.2
	16	92/20	4.6

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Test 2

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One group of twelve cats was arbitrarily selected and isolated from a total of twenty-two cats for treatment with PVC collars containing 10% naled and the remaining ten were used as control. All cats were observed for two weeks prior to the test in regard to flea egg shed, the group selected for treatment having a mean daily egg shed of 224 and the control group having a mean

daily egg shed of 207. Both groups were infested with 100 fleas at weekly intervals during the entire test period one day prior to the test. PVC collars (10% naled) prepared as in Example 4 were taken from sealed packages, placed about the necks of the test cats and the following observations made on flea eggs shed as indicated in Table II.

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TABLE II

Flea Egg Counts From Cats Wearing
10% Naled Collars and Control Subjects

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Mean Flea Egg Counts			
Interval In Days	Naled Collars	Control	Percent ¹ Reduction
Pretreatment	224	207	—
0	—	—	—
1	172	223	31
2—8	2	109	98
9—15	5	324	99
16—22	6	301	98
23—29	7	329	97
30—36	6	156	97
37—43	16	258	94
44—50	10	310	97
51—57	11	215	95
58—64	20	225	92
65—71	12	208	95
72—85	8	129	94
86—92	13	160	92
93—99	7	205	97
100—106	17	127	89
107—113	12	176	93
114—120	19	246	92
121	—	Collars Removed	—
131	86	110	30

¹Adjusted for control group variations by means of Abbott's formula. Abbott, W.S.J. *Econ. Entom.* 18, pp. 265—7. See also *Statistical Methods in Biol. Assay*, Finney, p. 564 (1925).

Cholinesterase Pharmacology Effects on Dogs

In order to assess the safety of naled-plastic compositions worn as collars by dogs, a study was conducted by Woodard Research Corporation (Chantilly, Virginia) using compositions containing 15 weight percent naled (See Example 1). Four groups of six dogs in each group of various breeds were observed for 16 weeks. One group wore one flea collar, a second group wore two collars, a third group wore four collars, and a fourth group wore placebo collars (PVC with no naled). Dogs were evaluated in terms of weekly body weight, general physical condition, toxic signs, skin irritation of the neck region and appearance and behaviour, all of which were normal. Haemograms consisting of haemoglobin and haematocrit determinations and total and differential leucocyte counts at 2, 4, 6, 8, 12 and 16 weeks were normal compared to initial values. Plasma cholinesterase and red blood cell (RBC) cholinesterase values showed no meaningful changes over the course of the study. No gross pathological signs were seen in any of the dogs at necropsy.

The absence of inhibition of plasma and

RBC cholinesterase activity is considered significant compared to similar tests with collars containing about 10% DDVP wherein 43% inhibition of plasma cholinesterase was reported after installation of one anti-flea collar. Elsea, J.R. et al, *The Journal of The American Veterinary Medical Association*, No. 12 pages 2068—2074 (1970).

Physical Properties

Referring now to Figures 4 and 5, the photographs of Figure 4 are of a naled-containing collar according to the invention and enlarged by 100 times. Figure 4A is a view of the upper surface that does not contact a casting mould wall, whereas Figure 4B is of the opposite side. Both Figures show extensive porous surface openings with the upper surface shown in Figure 4A having a roughened texture with a high density of depressions that are connected to pores which facilitate transport of the naled from the interior of the collar to its surface.

Figures 5A and 5B are similar views of a naled-containing collar which does not have in its dispersion the surface porosity control component as used for forming the collar shown in Figure 4. In Figure 5, the density of porous surface openings and the

roughness of the upper surface shown in Figure 5A are much less than for the collar shown in Figure 4. It is the increase in the number and size of porous openings in the collar shown in Figure 4 which clearly is responsible for the incremental increase in the naled release rate which is graphically represented by Figure 3.

Figures 4C and 4D, when compared with Figure 5C and 5D, are evidence that further support the fact that the collar of Figure 4 made from a dispersion containing the volatile surface porosity control component has a greater concentration of pores to facilitate the escape of the naled from the interior of the collar to the collar surface.

Our results show that it is possible to make pet collars within the present invention which not only have reduced toxicity as compared with the prior art DDVP collar, for the host animal, but which also have an effective life which is about 60% or more longer than the life of the prior art DDVP collars.

Even though naled has been known and commercially available for a number of years prior to the present invention, and considerable research has been done with the use of naled as an insecticide, its substitution for DDVP as a pet collar has not been considered feasible. Efforts to shape a collar containing naled as the insecticide were unsuccessful in the initial research, so that actual testing of the effectiveness of naled for controlling fleas was made quite difficult. In addition, naled was not considered to be a likely candidate as a substitute for DDVP since its vapour pressure is known to be less than 2% of the vapour pressure of DDVP. Moreover, the problem of spewing with naled concentrations above about 25% set upper limits on the amount of naled that can be used in an article such as a collar which contacts the skin of a pet and comes into contact with children and others who may have physical contacts with the pet.

Our results also show that it is possible to make collars within the present invention which do not adversely inhibit the plasma and RBC cholinesterase activity of the animal as does DDVP. By including volatile additives in the plastisol dispersion used in forming the strip, it has been possible to increase the naled release rate to a level which allows for the mass production of a suitable flea collar for pets.

Such collars are produced to have a porous outer surface not only to release naled at a rate higher than otherwise possible and in greater gross amount, but also to release naled at a rate effective to control fleas for a substantially longer period than otherwise possible.

WHAT WE CLAIM IS:—

1. A flea control collar for a warm blooded animal which comprises a strip of a length sufficient to encircle the neck of the animal and clamping means at or near one end of the strip for engaging a portion of the strip spaced from the clamping means to prevent loss of the collar from the animal, strip comprising a mixture of a flexible synthetic resin and between 5 and 25 percent by weight of the strip of naled and the strip having surface openings in communication with pores in the strip whereby, upon use of the strip as a collar, the strip releases naled vapour at a rate effective to control fleas on the animal but insufficient to form as droplets on the strip or to be toxic to the animal.

2. A flea control collar according to claim 1 in which the strip contains sufficient naled to be released in the form of vapour at a rate effective to control fleas on the animal throughout a period of at least ninety days.

3. A flea control collar according to claim 1 or claim 2, in which the synthetic resin is a polyvinyl chloride resin.

4. A flea control collar according to claim 3 in which the polyvinyl chloride resin has been formed into the strip from a liquid plastisol dispersion by filling an open faced casting mould preheated to a temperature of about 290°F, increasing the mould temperature to about 360°F in a hot air radiant heated oven for about two minutes, and thereafter cooling and removing the strip of the mould.

5. A flea control collar according to claim 1 or claim 2 in which the synthetic resin is polymethylmethacrylate, a polystyrene, a polyurethane, a polyethylene, a polypropylene or a nylon.

6. A flea control collar according to any of the preceding claims in which the strip further comprises a minor amount of dimethyl 2, 2-dichlorovinyl phosphate.

7. A flea control collar for a warm blooded animal substantially as described with reference to any of Examples 1 to 12.

8. A method of making a flea control collar as claimed in claim 1 or claim 2 which comprises forming into a strip having a length suitable for use as the collar a dispersion of the flexible synthetic resin, naled, and a surface porosity control component that is non-reactive in the dispersion and has a boiling point at or below the curing temperature of the resin, the forming step including heating the dispersion to the curing temperature of the resin to produce surface openings in communication with pores in the strip by vaporisation of the porosity control component such that, upon application of the collar to the neck of the animal, the strip releases naled vapour at a rate

roughness of the upper surface shown in Figure 5A are much less than for the collar shown in Figure 4. It is the increase in the number and size of porous openings in the collar shown in Figure 4 which clearly is responsible for the incremental increase in the naled release rate which is graphically represented by Figure 3.

Figures 4C and 4D, when compared with Figure 5C and 5D, are evidence that further support the fact that the collar of Figure 4 made from a dispersion containing the volatile surface porosity control component has a greater concentration of pores to facilitate the escape of the naled from the interior of the collar to the collar surface.

Our results show that it is possible to make pet collars within the present invention which not only have reduced toxicity as compared with the prior art DDVP collar, for the host animal, but which also have an effective life which is about 60% or more longer than the life of the prior art DDVP collars.

Even though naled has been known and commercially available for a number of years prior to the present invention, and considerable research has been done with the use of naled as an insecticide, its substitution for DDVP as a pet collar has not been considered feasible. Efforts to shape a collar containing naled as the insecticide were unsuccessful in the initial research, so that actual testing of the effectiveness of naled for controlling fleas was made quite difficult. In addition, naled was not considered to be a likely candidate as a substitute for DDVP since its vapour pressure is known to be less than 2% of the vapour pressure of DDVP. Moreover, the problem of spewing with naled concentrations above about 25% set upper limits on the amount of naled that can be used in an article such as a collar which contacts the skin of a pet and comes into contact with children and others who may have physical contacts with the pet.

Our results also show that it is possible to make collars within the present invention which do not adversely inhibit the plasma and RBC cholinesterase activity of the animal as does DDVP. By including volatile additives in the plastisol dispersion used in forming the strip, it has been possible to increase the naled release rate to a level which allows for the mass production of a suitable flea collar for pets.

Such collars are produced to have a porous outer surface not only to release naled at a rate higher than otherwise possible and in greater gross amount, but also to release naled at a rate effective to control fleas for a substantially longer period than otherwise possible.

WHAT WE CLAIM IS:—

1. A flea control collar for a warm blooded animal which comprises a strip of a length sufficient to encircle the neck of the animal and clamping means at or near one end of the strip for engaging a portion of the strip spaced from the clamping means to prevent loss of the collar from the animal, strip comprising a mixture of a flexible synthetic resin and between 5 and 25 percent by weight of the strip of naled and the strip having surface openings in communication with pores in the strip whereby, upon use of the strip as a collar, the strip releases naled vapour at a rate effective to control fleas on the animal but insufficient to form as droplets on the strip or to be toxic to the animal.

2. A flea control collar according to claim 1 in which the strip contains sufficient naled to be released in the form of vapour at a rate effective to control fleas on the animal throughout a period of at least ninety days.

3. A flea control collar according to claim 1 or claim 2, in which the synthetic resin is a polyvinyl chloride resin.

4. A flea control collar according to claim 3 in which the polyvinyl chloride resin has been formed into the strip from a liquid plastisol dispersion by filling an open faced casting mould preheated to a temperature of about 290°F, increasing the mould temperature to about 360°F in a hot air radiant heated oven for about two minutes, and thereafter cooling and removing the strip of the mould.

5. A flea control collar according to claim 1 or claim 2 in which the synthetic resin is polymethylmethacrylate, a polystyrene, a polyurethane, a polyethylene, a polypropylene or a nylon.

6. A flea control collar according to any of the preceding claims in which the strip further comprises a minor amount of dimethyl 2, 2-dichlorovinyl phosphate.

7. A flea control collar for a warm blooded animal substantially as described with reference to any of Examples 1 to 12.

8. A method of making a flea control collar as claimed in claim 1 or claim 2 which comprises forming into a strip having a length suitable for use as the collar a dispersion of the flexible synthetic resin, naled, and a surface porosity control component that is non-reactive in the dispersion and has a boiling point at or below the curing temperature of the resin, the forming step including heating the dispersion to the curing temperature of the resin to produce surface openings in communication with pores in the strip by vaporisation of the porosity control component such that, upon application of the collar to the neck of the animal, the strip releases naled vapour at a rate



- effective to control fleas on the animal but insufficient to form as droplets on the strip or to be toxic to the animal, and providing at or adjacent one end of the strip a clamping means for engaging a collar portion spaced from the clamping means to prevent loss of the collar from the neck of the animal.
9. A method according to claim 8 in which the synthetic resin comprises a polyvinyl chloride resin.
10. A method according to claim 9 in which the synthetic resin comprises a polyvinyl chloride resin which is present in an amount of at least 37 percent by weight and a plasticizer in an amount sufficient to produce a strip having flexibility and strength suitable for an animal collar.
11. A method according to claim 9 or claim 10 in which the polyvinyl chloride resin is formed into the strip from a liquid plastisol dispersion by filling an open faced casting mould pre-heated to a temperature of about 290°F, increasing the mould temperature to about 360°F in a hot air radiant heated oven for about two minutes, and thereafter cooling and removing the strip from the mould.
12. A method according to any of claims 8 to 11 in which the naled concentration in the dispersion is such as to produce in the strip a naled concentration of from between 8 and 25 percent by weight of the strip.
13. A method according to any of claims 8 to 12 in which the control agent has a boiling point below 375°F.
14. A method according to any of claims 8 to 13 in which the control agent is present in an amount between 0.8 to 4 percent by weight of the dispersion.
15. A method of making a flea control collar for a warm blooded animal substantially as described in any of Examples 1 to 12.
16. A flea control collar for a warm blooded animal made by a method according to any of claims 8 to 14.
17. A method of treating a warm blooded animal for fleas which comprises placing and maintaining on the animal a collar according to any of claims 1 to 7 or 16.

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