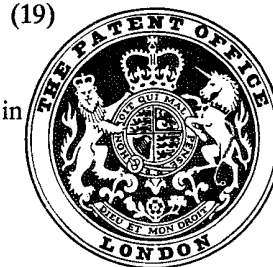


1 568 945

- (21) Application No. 12933/78 (22) Filed 3 Apr. 1978
- (31) Convention Application No's 2715595 (32) Filed 7 Apr. 1977
2715596 7Apr. 1977
2758571 29 Dec. 1977 in
- (33) Fed. Rep. of Germany (DE)
- (44) Complete Specification Published 11 Jun. 1980
- (51) INT. CL.³ A01N 25/34
- (54) Index at Acceptance
ASE 300 326 405 406 411 503 509 C
J
- (72) Inventors: MIKLOS VON BITTERA
HANS ULRICH SIEVEKING
WILHELM STENDEL
HERBERT VOEGE



(54) ANIMAL COLLARS HAVING ECTOPARASITICIDAL ACTIVITY AND PLASTICS COMPOSITION FOR USE THEREIN

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate, organised under the laws of Germany, of Leverkusen, Federal Republic of Germany, 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:

5 The present invention relates to plastics compositions having ectoparasitidal, in particular insecticidal and acaricidal, activity which contain a particular ectoparasiticide and particular polyurethanes, and to animal collars comprising such plastics compositions.

10 Animal collars having ectoparasitidal activity have been known for some years. Using them, it is possible to protect, in particular, small animals (especially dogs and cats) against infestation by *Mallophaga* and *Siphonaptera* and, in some cases, also against *Ixodidae*.

15 In general, the ectoparasitidally active animal collars hitherto commercially available consist of thermoplastic polyvinyl chloride, into which an insecticidal active compound, usually O,O-dimethyldichlorovinyl phosphate (DDVP), has been incorporated by co-extrusion. However, collars based on DDVP lead to the occasional occurrence of skin irritations on the animal; the short life of the collar as a result of the relatively high vapour pressure of DDVP (1.2×10^{-1} mm Hg) is also a disadvantage.

20 Animal collars based on plasticised, thermoplastic polymers (preferably plasticised polyvinyl chloride) and which contain less highly volatile carbamates as insecticidal active compounds are described in U.S. Patent Specification 3,852,416. Whereas highly volatile active compounds such as DDVP rapidly pass directly into the gas phase from the ectoparasitidally active plastic collars hitherto known, insecticides of lower volatility, for example the carbamates just mentioned, diffuse slowly out of the collar and form a white, dusty layer on its surface. Some of the active compound passes into the vapour phase by sublimation and is active there and some is distributed, in the form of a dust, over the animal to be treated.

25 The deposition mentioned of the active compound on the surface of the collar ("efflorescence" or "exudation") is associated with a number of disadvantages:

1. When the collar is stored for a prolonged period before use, a relatively large amount of the active compound diffuses to the surface and becomes concentrated there. When the collar is used, there is then a very high dose of the insecticide on the surface, which indeed ensures good immediate action but may also reach the point of being toxic to the animal.
- 30 2. The active compound present on the surface is rubbed off rapidly. However, the active substance in the deeper layers of the collar subsequently diffuses to the surface only very slowly. Thus the release of the insecticide is not linear over as long as possible a period, as is desired.
- 35 3. The dusty, whitish active compound present on the surface of the animal collar imparts to this an extremely unattractive, dusty or mouldy appearance.

40 Plasticised polymers (*inter alia* vinyl polymers, polyesters, polyurethanes and epoxide resins) are described as carriers for various insecticides in French Patent Specification 1,568,194. The materials are to be employed in the form of a tape or powder, for example, for

combating insects; furthermore, no carbamates are mentioned amongst the suitable insecticides.

5 U.S. Patent Specification 3,576,760 relates to pulverulent, water-soluble vinyl polymers which contain various active compounds (amongst which carbamates are mentioned as insecticides). These polymer powders make it possible to apply an active compound in the dry form, for example to the earth's surface, where it is then released under the action of water. No reference to animal collars is made in the patent specification. 5

10 U.S. Patent Specifications 3,822,238 and 3,975,350 relate to hydrophilic, water-absorbing polyurethanes and polyurethane hydrogels and their use as carriers for the most diverse active substances. Insecticides are also mentioned quite generally as such active compounds (for example also those according to U.S. Patent Specification 3,576,760). However, there is no reference to animal collars; the materials would also be unsuitable for this purpose, because of their swellability in water. 10

15 The present invention now provides a plastics composition having an ectoparasitocidal action, which comprises 75 to 98% by weight of a hydrophobic polyurethane which is not swellable in water and 2 to 25%, preferably 5 to 15%, by weight of 2-isopropoxyphenyl N-methylcarbamate. 15

20 The present invention also provides an animal collar having ectoparasitocidal activity, which comprises such a plastics composition. 20

25 In addition to an industrially uncomplicated preparation process, the collars, according to the invention, based on polyurethane have, above all, the advantage that the active compound is continuously released from them over a period of some months in an essentially linear manner. In fact, surprisingly, the active compound diffuses out of the polyurethane onto the surface in such a controlled manner that from there it is uniformly released into the surroundings by sublimation or by mechanical means. No noticeable efflorescence forms on the surface, so that a pleasant appearance of the collar is preserved, even on prolonged storage, and no toxicity problems occur. Compared with conventional PVC collars, the period of activity is extended. 25

30 The invention also provides a method of protecting or freeing an animal from ectoparasites which comprises fitting the animal with a collar of this invention. 30

By "hydrophobic" and "not swellable" there are understood, according to the invention, polyurethane plastics which, when immersed in water at 20°C, take up less than 2% by weight, preferably less than 0.5% by weight, of water by swelling in the course of 24 hours.

35 As stated above, 2-isopropoxyphenyl N-methylcarbamate ("Propoxur"), which has a vapour pressure of 6.5×10^{-6} mm Hg, is employed as the ectoparasitocidal component (see U.S. Patent Specifications Nos. 3,852,416; 2,903,478 and 3,203,853). 35

40 The polyurethane used as the carrier may be prepared in a manner which is in itself known by reacting polyisocyanates with higher-molecular compounds containing at least two groups which are reactive towards isocyanates, and optionally low-molecular chain lengthening agents and/or monofunctional chain stoppers. 40

45 Possible starting components for the preparation of the polyurethanes are aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates, such as are described, for example, by W. Siefken in Justus Liebigs Annalen der Chemie, 562, pages 75 to 136, for example ethylene-diisocyanate, tetramethylene-1,4-diisocyanate, hexamethylene-1,6-diisocyanate, dodecane-1,12-diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate as well as any desired mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-4-isocyanatomethylcyclohexane (DAS (German Published Specification) 1,202,785 and U.S. Patent Specification 3,401,190), hexahydrotoluylene-2,4- and -2,6-diisocyanate as well as any desired mixtures of these isomers, 50 hexahydrophenylene-1,3- and/or -1,4-diisocyanate, perhydrodiphenylmethane-2,4'- and/or -4,4'-diisocyanate, phenylene-1,3- and -1,4-diisocyanate, toluylene-2,4- and -2,6-diisocyanate as well as any desired mixtures of these isomers, diphenylmethane-2,4'- and/or -4,4'-diisocyanate, naphthylene-1,5-diisocyanate, triphenyl-methane-4,4',5'-triisocyanate, polyphenyl-polymethylene-polyisocyanates, such as are obtained by aniline/formaldehyde condensation and subsequent phosgenation of the product and are described, for example, in British Patent Specifications 874,430 and 848,671, *m*- and *p*-isocyanatophenylsulphonyl-isocyanates according to U.S. Patent Specification 3,454,606, perchlorinated aryl-polyisocyanates, such as are described, for example, in German Auslegeschrift (German Published Specification) 1,157,601 (U.S. Patent Specification 3,277,138), polyisocyanates containing carbodiimide groups, such as are described in German Patent Specification 1,092,007 (U.S. Patent Specification 3,152,162), diisocyanates, such as are described in U.S. Patent Specification 3,492,330, polyisocyanates containing allophanate groups, such as are described, for example, in British Patent Specification 994,890, Belgian Patent Specification 761,626 and Dutch Published Patent Application 65 7.102.524, polyisocyanates containing isocyanurate groups, such as are described, for exam-

ple, in U.S. Patent Specification 3,001,973, in German Patent Specifications 1,022,789, 1,222,067 and 1,027,394 and in German Offenlegungsschriften (German Published Specifications) 1,929,034 and 2,004,048, polyisocyanates containing urethane groups, such as are described, for example, in Belgian Patent Specification 752,261 or in U.S. Patent Specification 3,394,164, polyisocyanates containing acylated urea groups, according to German Patent Specification 1,230,778, polyisocyanates containing biuret groups, such as are described, for example, in German Patent Specification 1,101,394 (U.S. Patent Specifications 3,124,605 and 3,201,372) and in British Patent Specification 889,050, polyisocyanates which are prepared by telomerisation reactions, such as are described, for example, in U.S. Patent Specification 3,654,106, polyisocyanates containing ester groups, such as are mentioned, for example, in British Patent Specifications 965,474 and 1,072,956, in U.S. Patent Specification 3,567,763 and in German Patent Specification 1,231,688, reaction products of the above-mentioned isocyanates with acetals, according to German Patent Specification 1,072,385, and polyisocyanates containing polymeric fatty acid radicals, according to U.S. Patent Specification 3,455,883.

It is also possible to employ the distillation residues, containing isocyanate groups, obtained in the industrial preparation of isocyanates, optionally dissolved in one or more of the above-mentioned polyisocyanates. Furthermore, it is possible to use any desired mixtures of the above-mentioned polyisocyanates.

In general, the toluylene-diisocyanates and the di-phenylmethane-diisocyanates are preferred polyisocyanates.

Further starting components for the preparation of the polyurethanes are compounds which have at least two hydrogen atoms which are reactive towards isocyanates and which generally have a molecular weight of 400 - 10,000. In addition to compounds containing amino groups, thiol groups or carboxyl groups, there are preferably used polyhydroxy compounds, in particular compounds containing two to eight hydroxyl groups, especially those of molecular weight 800 to 10,000, preferably 1,000 to 6,000, for example polyesters, polyethers, polythioethers, polyacetals, polycarbonates and polyesteramides containing at least two, in general 2 to 8, but preferably 2 to 4, hydroxyl groups, such as those which are known per se for the preparation of homogeneous and cellular polyurethanes.

Examples of possible polyesters containing hydroxyl groups are reaction products of polyhydric, preferably dihydric and optionally also trihydric, alcohols with polybasic, preferably dibasic, carboxylic acids. Instead of the free polycarboxylic acids it is also possible to use the corresponding polycarboxylic acid anhydrides or corresponding polycarboxylic acid esters of lower alcohols or their mixtures for the preparation of the polyesters. The polycarboxylic acids can be of an aliphatic, cycloaliphatic, aromatic and/or heterocyclic nature and can be optionally substituted, for example by halogen atoms, and/or unsaturated.

Examples of these which may be mentioned are succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, trimellitic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylenetetrahydrophthalic anhydride, glutaric anhydride, maleic acid, maleic anhydride, fumaric acid, dimeric and trimeric fatty acids, such as oleic acid, optionally mixed with monomeric fatty acids, terephthalic acid dimethyl ester and terephthalic acid bis-glycol ester. Examples of possible polyhydric alcohols are ethylene glycol, propylene 1,2-glycol and 1,3-glycol, butylene 1,4-glycol and 2,3-glycol, hexane-1,6-diol, octane-1,8-diol, neopentylglycol, cyclohexanedimethanol (1,4-bis-hydroxymethylcyclohexane), 2-methyl-propane-1,3-diol, glycerol, trimethylolpropane, hexane-1,2,6-triol, butane-1,2,4-triol, trimethylolethane, pentaerythritol, quinitol, mannitol, sorbitol, methyl glycoside, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycols, dipropylene glycol, polypropylene glycols, dibutylene glycol and polybutylene glycols. The polyesters may contain a proportion of terminal carboxyl groups. Polyesters of lactones, for example ϵ -caprolactone, or from hydroxycarboxylic acid, for example ω -hydroxycaproic acid, can also be employed.

Suitable polyethers containing at least two, in general two to eight, preferably two to three, hydroxyl groups are also those of the type which is in itself known and are prepared, for example, by the self-polymerisation of epoxides, such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorohydrin, for example in the presence of BF_3 , or by addition of these epoxides, optionally mixed or successively, onto starting components containing reactive hydrogen atoms, such as water alcohols, ammonia or amines, for example ethylene glycol, propylene 1,3-glycol or 1,2-glycol, trimethylolpropane, 4,4'-dihydroxy-diphenylpropane, aniline, ethanolamine or ethylenediamine. Sucrose polyethers, such as are described, for example, in German Auslegeschriften (German Published Specifications) 1,176,358 and 1,064,938, can also be used. Those polyethers which predominantly contain (up to 90% by weight, relative to all the OH groups present in the polyether) primary OH groups are preferred in many cases. Polyethers modified by vinyl polymers, such as are

formed, for example, by polymerisation of styrene and acrylonitrile in the presence of polyethers (U.S. Patent Specifications 3,383,351 3,304,273, 3,523,093 and 3,110,695 and German Patent Specification 1,152,536), are also suitable, as are polybutadienes containing OH groups.

5 Polythioethers which may be mentioned are, in particular, the self-condensation products of thiodiglycol and/or the condensation products of thiodiglycol and other glycols, dicarboxylic acids, formaldehyde, aminocarboxylic acids or aminoalcohols. Depending on the co-components, the products are mixed polythioethers, polythioether-esters or polythioether-ester-amides. 5

10 Examples of possible polyacetals are the compounds which can be prepared from glycols, such as diethylene glycol, triethylene glycol, 4,4'-dihydroxyethoxy-diphenyldimethylmethane or hexanediol, and formaldehyde. Polyacetals which are suitable according to the invention can also be prepared by the polymerisation of cyclic acetals. 10

15 Possible polycarbonates containing hydroxyl groups are those of the type which is in itself known, such as can be prepared, for example, by reacting diols, such as propane-1,3-diol, butane-1,4-diol and/or hexane-1,6-diol, diethylene glycol, triethylene glycol or tetraethylene glycol with diaryl carbonates, for example diphenyl carbonate, or phosgene. 15

20 The polyester-amides and polyamides include, for example, the predominantly linear condensation products obtained from polybasic saturated and unsaturated carboxylic acids or their anhydrides and polyhydric saturated and unsaturated aminoalcohols, diamines, polyamines and their mixtures. 20

25 Polyhydroxy compounds which already contain urethane groups or urea groups and optionally modified natural polyols, such as castor oil, carbohydrates or starch can also be used. It is also possible to employ addition products of alkylene oxides with phenol/formaldehyde resins or also with urea/formaldehyde resins. 25

30 Representatives of these compounds to be used according to the invention are described, for example, in High Polymers, volume XVI, "Polyurethanes, Chemistry and Technology", edited by Saunders-Frisch, Interscience Publishers, New York, London, volume I, 1962, pages 32-42 and pages 44-54 and volume II, 1964, pages 5-6 and 198-199, and in Kunststoff-Handbuch (Plastics Handbook), volume VII, Vieweg-Höchtlen, Carl-Hanser-Verlag, Munich, 1966, for example on pages 45-71. 30

It is also possible, of course, to employ mixtures of the above-mentioned compounds which contain at least two hydrogen atoms which are reactive towards isocyanates and which have a molecular weight of 400 - 10,000, for example mixtures of polyethers and polyesters.

35 Possible starting components which are to be optionally employed are also compounds which contain at least two hydrogen atoms which are reactive towards isocyanates and have a molecular weight of 32-400. In this case also, these are understood as compounds containing hydroxyl groups and/or amino groups and/or thiol groups and/or carboxyl groups, preferably compounds containing hydroxyl groups and/or amino groups, which serve as chain lengthening agents or crosslinking agents. As a rule, these compounds contain 2 to 8 40 hydrogen atoms which are reactive towards isocyanates, preferably 2 or 3 reactive hydrogen atoms. 40

45 Examples which may be mentioned of compounds of this type are: ethylene glycol, propylene 1,2-glycol and 1,3-glycol, butylene 1,4-glycol and 2,3-glycol, pentane-1,5-diol, hexane-1,6-diol, octane-1,8-diol, neopentylglycol, 1,4-bis-hydroxymethyl-cyclohexane, 2-methyl-1,3-propanediol, glycerol, trimethylolpropane, hexane-1,2,6-triol, trimethylolethane, pentaerythritol, quinitol, mannitol, sorbitol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycols with a molecular weight of up to 400, dipropylene glycol, polypropylene glycols with a molecular weight of up to 400, 50 dibutylene glycol, polybutylene glycols with a molecular weight of up to 400, 4,4'-dihydroxy-diphenylpropane, dihydroxymethyl-hydroquinone, ethanolamine, diethanolamine, triethanolamine, 3-aminopropanol, ethylenediamine, 1,3-diaminopropane, 1-mercapto-3-aminopropane, 4-hydroxy- or -aminophthalic acid, succinic acid, adipic acid, hydrazine, N,N'-dimethylhydrazine, 4,4'-diaminodiphenylmethane, toluenediamine, 55 methylene-bis-chloroaniline, methylene-bis-anthranilic acid esters, diaminobenzoic acid esters and the isomeric chlorophenylenediamines. 55

In this case also, it is possible to use mixtures of various compounds which contain at least two hydrogen atoms which are reactive towards isocyanates and have a molecular weight of 32-400.

60 However, it is also possible to employ polyhydroxy compounds in which high-molecular polyadducts or polycondensates are contained in a finely dispersed or dissolved form. Modified polyhydroxy compounds of this type are obtained when polyaddition reactions (for example reactions between polyisocyanates and compounds containing amino functional groups) or polycondensation reactions (for example between formaldehyde and phenols 65 and/or amines) are allowed to proceed directly *in situ* in the above-mentioned compounds 65

containing hydroxyl groups. Processes of this type are described, for example in German Auslegeschriften (German Published Specifications) 1,168,075 and 1,260,142, and German Offenlegungsschriften (German Published Specifications) 2,324,134, 2,423,984, 2,512,385, 2,513,815, 2,550,796, 2,550,797, 2,550,833 and 2,550,862. However, it is also possible, according to U.S. Patent 3,869,413 or German Offenlegungsschrift (German Published Specification) 2,550,860, to mix a ready-made aqueous polymer dispersion with a polyhydroxy compound and then to remove the water from the mixture.

When modified polyhydroxy compounds of the above-mentioned type are used as the starting component in the polyisocyanate polyaddition process, polyurethane plastics with substantially improved mechanical properties are formed in many cases.

When choosing the higher-molecular polyol component used for the preparation of the polyurethane, it must be taken into consideration that the finished polyurethane should not be swellable in water. The use of relatively large amounts of polyhydroxy compounds containing ethylene oxide units (polyethylene glycol polyethers or polyesters with diethylene glycol or triethylene glycol as the diol component) is thus to be avoided. Hydrophobic polyesters, in particular those based on adipic acid and ethylene glycol and/or butanediol and/or neopentylglycol and/or hexanediol, polycarbonate-diols and polyether-polyols based on propylene oxide or tetrahydrofuran are preferably employed. In some cases it is also appropriate (especially if relatively large amounts of mineral fillers are incorporated into the polyurethane) to co-use castor oil as the polyol component in order to render the polyurethane hydrophobic.

Catalysts are frequently also used in the preparation of the polyurethanes. Catalysts which may be used are those of the type which is in itself known, for example tertiary amines, such as triethylamine, tri-butylamine, N-methyl-morpholine, N-ethyl-morpholine, N-coconut alkyl-morpholine, N,N,N',N'-tetramethyl-ethylene-diamine, 1,4-diazabicyclo-(2,2,2)-octane, N-methyl-N'-dimethylaminoethyl-piperazine, N,N-dimethylbenzylamine, bis-(N,N-diethylaminoethyl) adipate, N,N-diethylbenzyl-amine, pentamethyldiethylenetriamine, N,N-dimethylcyclohexylamine, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N-dimethyl- β -phenylethylamine, 1,2-dimethylimidazole and 2-methylimidazole. Mannich bases, which are in themselves known, obtained from secondary amines, such as dimethylamine, and aldehydes, preferably formaldehyde, or ketones, such as acetone, methyl ethyl ketone or cyclohexanone, and phenols, such as phenol, nonylphenol or bisphenol, can also be used as catalysts.

Examples of tertiary amines which contain hydrogen atoms which are active towards isocyanate groups and may be used as catalysts are triethanolamine, triisopropanolamine, N-methyldiethanolamine, N-ethyl-diethanolamine and N,N-dimethylethanolamine, and their reaction products with alkylene oxides, such as propylene oxide and/or ethylene oxide.

Further possible catalysts are sila-amines with carbon-silicon bonds, such as are described, for example, in German Patent Specification 1,229,290 (U.S. Patent Specification 3,620,980), for example 2,2,4-trimethyl-2-silamorpholine and 1,3-diethylaminomethyl-tetramethyl-disiloxane.

Other possible catalysts are nitrogen-containing bases, such as tetraalkylammonium hydroxides, and furthermore alkali metal hydroxides, such as sodium hydroxide, alkali metal phenolates, such as sodium phenolate, or alkali metal alcoholates, such as sodium methylate. Hexahydrotriazines can also be employed as catalysts.

Organic metal compounds, in particular organic tin compounds, can also be used as catalysts.

Preferred organic tin compounds are tin(II) salts of carboxylic acids, such as tin(II) acetate, tin(II) octoate, tin(II) ethylhexoate and tin(II) laurate, and tin(IV) compounds, for example dibutyl-tin oxide, dibutyl-tin dichloride, dibutyl-tin diacetate, dibutyl-tin dilaurate, dibutyl-tin maleate or dioctyl-tin diacetate. All the above-mentioned catalysts can, of course, also be employed as mixtures.

Yet further representatives of catalysts that can be used and details of the mode of action of the catalysts are described in *Kunststoff-Handbuch* (Plastics Handbook), volume VII, edited by Vieweg and Höchtlen, Carl-Hanser-Verlag, Munich 1966, for example on pages 96 to 102.

As a rule, the catalysts are employed in an amount between 0.001 and 10% by weight, relative to the amount of compounds which contain at least two hydrogen atoms which are reactive towards isocyanates and have a molecular weight of 400 to 10,000.

The plasticisers, fillers, water-binding agents and dyestuffs customary in polyurethane chemistry can, of course also be co-used in the preparation of the polyurethane. Examples of suitable plasticisers are phthalates, such as benzyl butyl phthalate and dioctyl phthalate, and esters of sebacic acid or adipic acid. Phthalates, in particular benzyl butyl phthalate, are preferred. Examples of fillers which may be mentioned are carbon black, chalk, baryte, kaolin and aluminium silicates. Zeolites are the preferred water-absorbing agents. Any

desired dyestuffs for the polyurethane which are in themselves known, for example organic or, preferably, inorganic coloured pigments, in particular iron oxide pigments, can be employed in order to impart the desired colouration to the collars according to the invention.

5 The polyurethanes which are used, according to the invention, as the carrier can be prepared in a manner which is in itself known, either by a single stage process or by a prepolymer or semi-prepolymer process. 5

10 Thermoplastic polyurethanes such as are formed by reacting diisocyanates with higher-molecular dihydroxy compounds and low-molecular glycols, as chain lengthening agents, in a NCO/OH ratio between 0.97 and 1.05, are a class of carriers which is preferred according to the invention. Thermoplastic polyurethanes of this type are described, for example, in British Patent Specifications 1,210,737, 1,270,836, 1,075,274, 1,110,118, 1,025,970, 1,057,018, 1,087,743 and 849,136, German Patent Specifications 1,189,268, 1,103,024, 1,106,958, and 1,106,959 and German Offenlegungsschriften (German Published Specifications) 2,323,393 and 2,418,075. 10

15 The ectoparasiticide active compound can be added to the thermoplastic polyurethanes, which are present, for example, in the form of granules, optionally together with plasticisers, fillers and dyestuffs, in suitable mixing devices, for example in drums or in an extruder; however, it is also possible to add the active compound directly during the preparation of the polyurethane, optionally mixed with one of the starting components, for example in a process according to DOS (German Published Specification) 2,302,564 (U.S. Patent 3,963,679), in which polyisocyanates and polyhydroxy compounds are reacted with one another continuously in a twin-shaft screw machine. However, in this procedure it must be ensured that the reaction temperature does not exceed the decomposition point of the carbamate used as the ectoparasiticide. 15

20 Another possibility consists in adding the active compound to a cold-curing two-component polyurethane system comprising a prepolymer containing isocyanate groups, a polyhydroxy compound and a catalyst, such as is in itself known for the preparation of coatings, trowelling compositions and joint-filling compositions. In this case it is appropriate to first mix the ectoparasiticide with the polyol component, which in general already contains the catalyst and, optionally, plasticisers, fillers and dyestuffs, of the two component system and only then to stir this component with the isocyanate component. 20

25 It is also possible to add the ectoparasiticide active compounds to solvent-free reactive systems which contain plasticisers and consist of a higher-molecular polyisocyanate component and a polyamine component, such as are described, for example, in DOS (German Published Specification) 2,448,133. 25

30 It is also possible, of course, to introduce the active compound into a solution of a polyurethane or polyurethane-urea and then to evaporate off the solvent. In this case also, relatively high temperatures must be avoided so that no decomposition of the carbamate occurs. Solutions of polyisocyanate polyaddition products in weakly polar, highly volatile solvents or solvent mixtures are therefore appropriately used. So-called "soft solvent" systems of this type are described, for example, in U.S. Patent 2,957,852, British Patent Specification 1,040,055, Belgian Patent Specification 643,811, DOS (German Published Specification) 1,694,277 (U.S. Patent Specification 3,734,894), U.S. Patents 3,609,112, 3,752,786 and 3,936,409 and German Offenlegungsschriften (German Published Specifications) 2,221,750 (U.S. Patent 3,912,680), 2,221,751 (U.S. Patent Specification 3,867,350) and 2,221,798 (U.S. Patent Specification 3,857,809). Polar solvent systems (for example containing dimethylformamide or N-methyl-pyrrolidone) can also be used if the temperature in the drying step is kept sufficiently low. 30

35 It is possible to prepare animal collars based purely on polyurethane, for example by injection moulding or reactive injection moulding one of the thermoplastics mentioned, or allowing a reactive two-component system to react completely in a suitable mould. However, in many cases it is desirable to impregnate and/or coat a suitable carrier (for example a fabric made of natural (such as cotton) and/or synthetic fibres, leather, imitation leather or a porous or homogeneous plastic sheet) with one of the above-mentioned thermoplastic polyurethanes, two-component reactive systems or single component polyurethanes, dissolved in solvents which can be easily evaporated, containing active compounds. In general, this carrier is worn on the outside of the collar and the coating comprising the polyurethane containing the ectoparasiticide is on the inside. In this manner it is possible to give the animal collar virtually any desired appearance. 35

40 The animal collars according to the invention are preferably used for livestock and/or pets, especially for cattle, dogs and cats. The collars according to the invention can be successfully employed against a number of harmful animal parasites (ectoparasites) from the class of *Arachnidae* and the class of insects. 40

Examples which may be mentioned of ectoparasites of the class of *Arachnidae*, which figure prominently in tropical, sub-tropical and temperate latitudes, are, from the family of *Ixodidae*, the Australian and South American one-host cattle tick (*Boophilus microplus*), the African one-host cattle tick (*Boophilus decoloratus*) and multi-host ticks which are parasitic on livestock and pets in all continents, such as *Rhipicephalus appendiculatus*, *Rhipicephalus evertsi*, *Amblyomma variegatum*, *Amblyomma hebraeum*, *Amblyomma cayennense*, *Hyalomma truncatum*, *Dermacentor variabilis* and *Ixodes ricinus*, as well as, from the family of *Gamasidae*, the red poultry mite (*Dermanyssus gallinae*).

Examples which can be mentioned of ectoparasites from the class of insects are: *Mallophaga*, for example the dog biting louse (*Trichodectes canis*), the cattle biting louse (*Damalinea bovis*), the sheep biting louse (*Damalinea ovis*) and the poultry biting louse (*Eomenacanthus stramineus*); *Anoplura*, for example the cattle louse (*Haematopinus eurysternus*) and the pig louse (*Haematopinus suis*); *Diptera*, for example the sheep ked (*Melophagus ovinus*); and *Aphaniptera*, for example the dog flea (*Ctenocephalides canis*).

The active compound is not deposited on the surface of the polyurethane in the form of visible crystals, so that the collars according to the invention do not have a dusty appearance either on the upper side or on the underside. Nevertheless, the collars are active over a period of more than 4 months, as is illustrated in more detail in the Examples which follow. The *in vitro* release experiments show that the active compound is released continuously from the collars according to the invention over relatively long periods (even after prolonged storage of the collar), whilst most of the active compound has already diffused out of a comparable collar based on polyvinyl chloride after a short time, after which only a very small amount of the insecticide is still released per unit time.

The Examples which follow illustrate the present invention. Unless otherwise indicated, the amounts given are to be understood as parts by weight or % by weight.

The polyurethane used in each of the Examples was hydrophobic and took up less than 2% by weight of water by swelling, when immersed in water at 20°C.

I. systems containing plasticiser

Example 1

Component A: Ethanediol/butanediol/adipic acid polyester (molecular weight 2,000) 30.0 parts

Benzyl butyl phthalate 22.2 parts

Benzyl dimethylamine 0.2 part

Zeolite paste (formulation of a sodium aluminium silicate in castor oil) 7.5 parts

Filler of the Al silicate type 37.0 parts

Organic dyestuff 3.1 parts

Component B: Crude diphenylmethane-diisocyanate 5.0 parts

(Industrial mixture, prepared by reaction of aniline with formaldehyde and subsequent phosgenation of the reaction product)
Benzyl butyl phthalate 5.0 parts

81.8 kg of component A were homogeneously mixed with 10.0 kg of the active compound Propoxur. Thereafter, 8.2 kg of component B were mixed in homogeneously.

The reaction mixture had a processing time of about 2 - 3 hours. During this period, it was applied to a woven fabric or non-woven fabric with a coating thickness of 2.2 to 2.5 mm.

The mass reacted completely in the course of 12 - 14 hours to give a tack-free product which could then be cut into collars having an ectoparasitocidal action.

Example 2

5	<i>Component A:</i>	Butanediol/adipic acid polyester (molecular weight 2,000)	30.0 parts	5
		Benzyl butyl phthalate	22.2 parts	
		Triethylenediamine	0.2 part	
10		Zeolite paste	7.5 parts	10
		Chalk	37.0 parts	
15	<i>Component B:</i>	Crude diphenylmethane-diisocyanate	5.0 parts	15
		Benzyl butyl phthalate	5.0 parts	

20 As a result of using triethylenediamine as the catalyst, the processing time was only about 30 minutes.

The preparation of the coating composition and the application onto the carrier was effected analogously to Example 1.

25 This formulation was particularly suitable for the continuous preparation of collars 25

Example 3

30	<i>Component A:</i>	Polyester from Example 1	30.0 parts	30
		Benzyl dimethylamine	0.2 part	
		Zeolite paste	7.5 parts	
35		Benzyl butyl phthalate	22.2 parts	35
		Filler (baryte)	37.0 parts	
40	<i>Component B:</i>	Industrial diphenylmethane-diisocyanate	5.0 parts	40
		Benzyl butyl phthalate	5.0 parts	

45 The preparation of the coating composition and the coating of the carrier were carried out analogously to Example 1.

II. Plasticiser-free systems

Example 4

5	<i>Component A:</i>	Mixture consisting of 47% of a linear polypropylene glycol terminally modified with ethylene oxide (OH number 28), 47% of a polypropylene oxide obtained using trimethylolpropane as the starter and terminally modified with ethylene oxide, and 6% of diethylene glycol.	55.0 parts	5
10		Filler (chalk)	22.1 parts	10
		Zeolite paste	5.5 parts	
15		Nickel acetylacetonate	0.6 part	15
		Dyestuff (inorganic pigment)	0.3 part	
20	<i>Component B:</i>	Reaction product of 5 mols of diphenylmethane-4, 4'-diisocyanate and 1 mol of tripropylene glycol	16.5 parts	20
25	This formulation was suitable for continuous coating. The mass reacted completely in about 15 minutes. The preparation of the coating composition and its application to the carrier was effected analogously to Example 1.			25

30 *Example 5* 30

35	<i>Component A:</i>	Polyether/glycol mixture from Example 4	55.0 parts	35
		Filler (chalk)	22.55 parts	
		Zeolite paste	5.5 parts	
40		Triethylenediamine	0.15 part	40
		Dyestuff (inorganic pigment)	0.3 part	
45	<i>Component B:</i>	Reaction product of 5 mols of diphenylmethane-4, 4'-diisocyanate and 1 mol of tripropylene	16.5 parts	45

50 The formulation was particularly suitable for use in a discontinuous preparation, analogously to Example 1. 50

55 In Examples 6 to 17 which follow, the components listed in the Table which follows were in each case premixed in a drum mixer (the polyurethane elastomer was in the form of granules here) and then homogeneously mixed in an extruder in a manner which is in itself known. A Reifenhäuser S 45 make of extruder was employed for this purpose, the screw pressure being 50 kp/cm² and the screw speed being adjusted to 22 revolutions per minute and the temperature being adjusted to 130°C in the intake zone and at the nozzle and to 160°C in the middle of the screw. 55

Table

<i>Example</i>	6	7	8	9	10	11	12	13	14	15	16	17
Polyurethane I	88	90	86	88	88							
Polyurethane II						90	86	88				
Polyurethane III									88	90	86	88
Plasticizer	2		2		2		2		2		2	
Propoxur	10	10	10	10	10	10	10	10	10	10	10	10
Dyestuff			2	2			2	2			2	2

The three polyurethane thermoplastics used were prepared in a reaction screw according to DOS (German Published Specification) 2,302,564 (U.S. Patent Specification 3,963,679) from the following components:

Polyurethane I:

- 5 100 parts of a polyester of butanediol and adipic acid (molecular weight 2,000), 11 parts of 1,4-bis-(β -hydroxyethoxy)-benzene and an amount of diphenylmethane-4,4'-diisocyanate corresponding to an NCO/OH ratio of 1.03 5

Polyurethane II:

- 10 100 parts of a polyester of ethylene glycol, butanediol and adipic acid (molecular weight 2,000), 13 parts of butane-1,4-diol and an amount of diphenylmethane-4,4'-diisocyanate corresponding to an NCO/OH ratio of 1.03 10

Polyurethane III:

- 15 50 parts of a polypropylene glycol ether (molecular weight 2,000), 50 parts of a polyester of butane-1,4-diol and adipic acid (molecular weight 2,000), 9 parts of butane-1,4-diol and an amount of diphenylmethane-4,4'-diisocyanate corresponding to an NCO/OH ratio of 1.03. 15

Benzyl butyl phthalate was used as the plasticiser and an iron oxide pigment was used as the dyestuff.

- 20 All the animal collars prepared according to Example 6 to 17 exhibited no efflorescence of the Propoxur on the surface and uniformly released the active compound to the surroundings over several months. 20

Evaluation Experiment

The release of Propoxur from a collar, according to the invention, prepared by the method in Example 1 was compared with that from a conventional PVC collar containing Propoxur (according to Example 5 of U.S. Patent Specification 3,852,416) in the following manner:

- 25 The release of Propoxur in water was followed in a rotary flask apparatus over 24 hours. The content of active compound in the release medium was determined colorimetrically, after hydrolysis to isopropoxyphenol. 25

- 30 2 g of the collar to be investigated (in one piece) and 200 ml of distilled water were put into each vessel of a Souder and Ellenbogen rotary flask apparatus. The release was effected at 37°C and 25 revolutions/minute. Samples of 2 ml each were taken at the start and after 1, 6 and 24 hours. 30

- 35 2 ml of 2N sodium hydroxide solution were added to each of the samples and the mixtures were left to stand for 30 minutes. After acidifying with 2.5 ml of 2N hydrochloric acid, 4-nitrobenzenediazonium tetrafluoroborate was added. The maximum extinction at 508 nm was measured. 35

In the accompanying Figure, the ordinate gives the release of active compound in per cent, whilst the abscissa gives the number of hours (measuring time).

The individual curves in the Figure relate to the following collars:

- 40 Curve A: Propoxur/PVC collar, shortly after preparation, 40
Curve B: Propoxur/PVC collar, stored at 20°C for 8 months,
Curve C: Propoxur collar according to Example 1, shortly after preparation,
Curve D: Propoxur collar according to Example 1, stored at 20°C for 8 months.

It can be seen that in contrast to the PVC collars, the collars according to the invention have a virtually linear release of active compound.

- 45 WHAT WE CLAIM IS: 45

1. A plastics composition having an ectoparasiticial action, which comprises 75 to 98% by weight of a hydrophobic polyurethane which is not swellable in water and 2 to 25% by weight of 2-isopropoxyphenyl N-methylcarbamate.

- 50 2. A plastics composition according to claim 1, in which the polyurethane absorbs less than 0.5% by weight of water by swelling when it is stored in water at 20°C for 24 hours. 50

3. A plastics composition according to claim 1 or 2, in which the polyurethane can be shaped as a thermoplastic.

4. A plastics composition according to claim 1 or 2, in which the polyurethane is a cold-curing two-component system.

- 55 5. An animal collar having ectoparasiticial activity, which comprises a plastics composition according to any of claims 1 to 4. 55

6. An animal collar according to claim 5 which is shaped from a plastics composition according to claim 3.

- 60 7. An animal collar according to claim 5, which is formed from a textile material, leather, imitation leather or a flexible plastics material, and is impregnated and/or coated with the ectoparasiticial plastics composition. 60

8. An animal collar according to claim 7, which is formed from a synthetic textile fabric, cotton, leather or imitation leather and is coated with a plastics composition according to claim 4.

- 65 9. An animal collar according to claim 6, substantially as disclosed in any one of Exam- 65

ples 6 to 17.

10. An animal collar according to claim 8, substantially as disclosed in any one of Examples 1 to 3.

5 11. An animal collar according to claim 5, substantially as disclosed in any one of Examples 4 or 5.

12. A method of protecting or freeing an animal from ectoparasites which comprises fitting the animal with a collar according to any of claims 5 to 11.

10

For the Applicants
CARPMAELS & RANSFORD
Chartered Patent Agents
43 Bloomsbury Square
London WC1A 2RA.

10