

The present invention relates to a process for protecting or finishing keratinous material or keratin-containing material against attack by insects that feed on keratin by treating these materials with specific 3-phenoxybenzyl (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylates.

Synthetic pyrethroids have long been known as insecticidal active compounds. Some of these synthetic pyrethroids, including 3-phenoxybenzyl esters of 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid, have also been described as active compounds against pests that feed on keratin. (See for example J. Text. Inst. 1976, No. 3, Vol. 67, 77; DE-A 2,923,217; US-A 4,219,593; EP-B 11 789; US-A 4,283,444; EP-A 105 030). These pyrethroids are very effective against the larvae of moths, as well as against the larvae of fur beetles and carpet beetles. In the cited publications, the active compounds are used as mixtures of isomers as obtained in the usual synthesis but which are not more clearly defined.

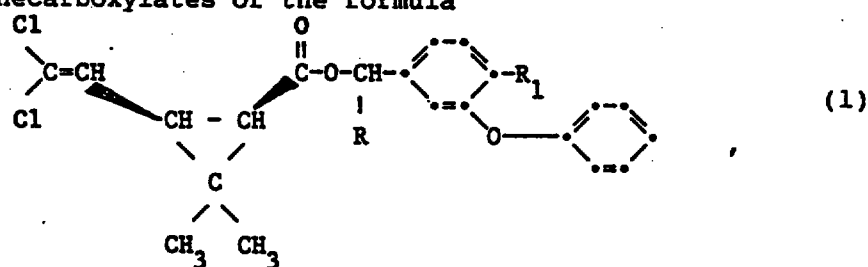
Owing to their stereochemical properties, 3-phenoxybenzyl esters of 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid are obtained as 2 geometrical isomers (cis, trans) and, depending on the substitution at the α -carbon atom of the alcohol component, as 4 or 8 different optical isomers. Various geometrical and optical isomers and mixtures of isomers are described in DE-A 2,439,177 and in Pesticide Science, 1975 (6), 537-542 and 1974 (5), 791-799. Both of these publications also teach that specific optical isomers, namely those having the R-configuration with respect to the cyclopropane ring, have particularly pronounced insecticidal activity especially against houseflies and mustard beetles. Furthermore, the inference is to be drawn from these publications that a specific geometrical isomer is not in all respects more effective than the other. The results show that, on the contrary, in certain cases the cis-isomer is more effective and in other cases the trans-isomer.

Some geometrical and optical isomers of specific 3-phenoxybenzyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylates are also known

from DE-A 2,547,534. Among these isomers, the trans-form is preferred (see formulations 1, 6 to 10, 13, 14 and 16).

Surprisingly, it has now been found that the cis-isomers (or the mixtures of cis-enantiomers) of a small group of 3-phenoxybenzyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylates have exceptionally good action against insects that feed on keratin. These isomers exhibit in all respects a substantially greater activity against pests that feed on keratin than the corresponding trans-isomers or the mixtures of isomers obtained in random distribution which are normally used. Accordingly, said cis-isomers are exceptionally suitable for protecting keratinous material, in particular wool, against attack by insects that feed on keratin.

The process according to the invention for protecting or finishing keratinous material or keratin-containing material against attack by insects that feed on keratin comprises treating the material to be protected with 3-phenoxybenzyl (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropanecarboxylates of the formula



wherein R is hydrogen, $-C\equiv CH$, $-C\equiv C-CH_3$ or CN, and R_1 is hydrogen or fluorine, or with a mixture of isomers containing at least 90% of these cis-isomers.

The invention further relates to material which has been protected or finished with the aid of compounds of the formula (1).

In the process according to the invention, there are used e.g. those compounds of the formula (1) wherein R is hydrogen or CN, and R_1 is hydrogen.

Preferred compounds for the application in the process according to

the invention are those of the formula (1) wherein R is hydrogen or CN, and R₁ is fluorine, or also those wherein R is C≡C-CH₃, and R₁ is hydrogen or fluorine.

The compounds of the formula (1) which can be used in the process according to the invention for protecting keratinous material against insects that feed on keratin are effective in particular for example against Lepidoptera larvae that feed on keratin, e.g. *Tineola spec.* and *Tinea spec.*, and also Coleoptera larvae which feed on keratin, e.g. *Anthrenus spec.* and *Attagenus spec.* They are most suitable for protecting keratinous material or keratin-containing material against feeding damage by insects, especially for washfast and lightfast finishing against insects, in particular for proofing such materials against moths and beetles. The keratinous material or keratin-containing material can be proofed both in the raw and in the processed state, for example raw or processed sheep's wool or products made of other animal hairs, hides, furs and feathers.

Of particular practical importance is the effectiveness of the compounds of formula (1) against the larvae of the webbing clothes moth (*Tineola bisselliella*), of the pelt moth (*Tinea pellionella*) and of the seed moth (*Hofmannophila pseudospretella*), as well as against the larvae of fur beetles and carpet beetles (*Attagenus spec.* and *Anthrenus spec.* respectively), e.g. of the varied carpet beetle (*Anthrenus verbasci*), of the pimperl flower beetle (*Anthrenus pimpinellae*), of the carpet beetle (*Anthrenus scrophulariae*), of the carpet beetle (*Anthrenus fasciatus*), of the fur beetle (*Attagenus pellio*) and, in particular, of the black carpet beetle (*Attagenus piceus*) and of the furniture carpet beetle (*Anthrenus flavipes*).

The process according to the invention is therefore preferably used on the one hand for protecting wool textiles, for example wool blankets, wool carpets, wool underwear, wool clothing, knits and wool-containing textiles such as fabric blends, one component of which is wool, for example fabric blends of wool and other natural fibres, preferably cotton, or of wool and synthetic fibres, and, on the other hand, also for

protecting furs and hides from attack by the abovementioned pests.

The compounds of the formula (1) are applied to the abovementioned substrates, in particular to wool textiles and wool-containing textiles, preferably with the aid of methods known in dyeing, such as the exhaust dyeing process and padding. To this end, an aqueous solution or dispersion (or emulsion or suspension) of the respective active compound is formulated. The active compound can be dissolved beforehand in an organic solvent, such as an aliphatic or alicyclic alcohol, a ketone, a hydrocarbon, such as benzene, a xylene, toluene, a petroleum distillate, and also a chlorinated or fluorinated hydrocarbon, especially in propylene glycol, methoxyethanol, ethoxyethanol or dimethylformamide, and then added to the treatment bath, which can contain additional assistants conventionally used in dyeing, for example dispersants, wetting agents, acids, bases and/or dyes, where the organic stock formulation can already contain such assistants.

The textile materials can be impregnated with the active compounds e.g. by means of hot or cold aqueous dye, bleaching, chroming or aftertreatment baths, various textile finishing processes being possible, for example the pad or exhaust process.

The treatment is advantageously carried out at temperatures from 10 to 100°C, in the dye bath preferably at from about 60 to 100°C and in the aftertreatment or wash bath preferably at from 10 to 70, in particular from 20 to 60°C.

As further assistants there may be added to the treatment liquors e.g. dispersants, emulsifiers or surfactants. The liquor can additionally contain further conventional assistants, such as water-soluble perborates, polyphosphates, carbonates, silicates, fluorescent whitening agents, softeners, salts with acid reaction, such as ammonium or zinc silicate fluoride, or certain organic acids such as oxalic acid, acetic acid or, in particular, formic acid, and also antimicrobial agents and finishing agents, for example those based on synthetic resins or starch. If the mothproof and beetle-resistant finishing is carried out together with the dyeing of the material (e.g. wool), the liquors additionally

contain the corresponding dyes and, if appropriate, the necessary assistants, e.g. levelling agents.

The aqueous treatment liquors may contain, for example, surfactants, for example anionic compounds, such as soaps and other carboxylates (e.g. alkali metal salts of higher fatty acids), derivatives of sulfur oxyacids (e.g. the sodium salt of dodecylbenzenesulfonic acid, water-soluble salts of sulfuric acid monoesters of higher molecular weight alcohols or of their polyglycol ethers, such as soluble salts of dodecyl alcohol sulfate or of dodecyl alcohol polyglycol ether sulfate), derivatives of phosphorus oxyacids (e.g. phosphates), derivatives with acid (electrophilic) nitrogen in the hydrophilic group (e.g. disulfine salts), cationic surfactants, such as amines and their salts (e.g. lauryldiethylenetriamine), onium compounds, amine oxides or nonionic surfactants, such as polyhydroxy compounds, surfactants based on mono- or polysaccharides, higher molecular weight acetylene glycols, polyglycol ethers (e.g. polyglycol ethers of higher fatty alcohols, polyglycol ethers of higher molecular weight alkylated phenols).

In the event of non-aqueous application (solvent application), an appropriate amount of a compound of the formula (1) may also be added to a suitable solvent and the material to be protected may be impregnated with the solution so obtained. Suitable solvents for this application are, inter alia, trichloroethylene, methylene chloride, hydrocarbons, propylene glycol, methoxyethanol, ethoxyethanol, dimethylformamide, to which dispersants (e.g. emulsifiers, such as sulfated castor oil, fatty alcohol sulfates etc.) and/or other assistants can be added. The material to be protected is usually simply impregnated with these solutions.

The proofing of the material to be protected may also be combined with a dry-cleaning process. To this end, an appropriate amount of a compound of the formula (1) is dissolved in the cleaning agent (such as a lower halogenated alkane, e.g. trichloroethylene etc.) and the cleaning process is carried out in the usual manner.

However, an amount of a compound of the formula (1) may also be dissolved in a readily volatile organic solvent and the solution may then be sprayed onto the substrate to be protected (spray application). Textiles which contain wool, furs and feathers are particularly suitable for this form of application. The advantage of spray application is that pollution of the wastewaters is avoided on account of the recovery of the solvent.

In the process according to the invention, the compounds of the formula (1) may also be used in combination with other protectants which act against insects that feed on keratin, for example in combination with urea derivatives, benzimidazoles, aromatic sulfonamides, phosphoric and phosphonic acid esters and 5-phenylcarbamoylbarbituric acid derivatives.

The particular amount of compound of the formula (1) added to the particular treatment bath or non-aqueous solvent depends on the particular substrate and the method of application. However, this amount is ordinarily dimensioned to be such that, after application to the material to be protected, the latter contains about 10 to 2,000 ppm, preferably 100 to 1,000 ppm, of compound of the formula (1) with the upper limit being largely determined by considerations of an economic nature, whereas the lower limit depends on criteria such as the intended breadth and permanency of the protective action. This results, for example, in concentrations of 0.001 to 1 g of active substance per litre of treatment bath using the exhaust process at a liquor to goods ratio of 20:1, depending on the degree of exhaustion attainable. In the pad process concentrations of up to 2 g of active substance per litre are possible.

As can be seen from the definition of the above process, the pure cis-isomers of the formula (1) or mixtures of isomers containing at least 90% of the cis-isomers can be used in the process of the present invention. All statements in the above detailed process description referring to compounds of the formula (1) also apply to mixtures of isomers containing at least 90% of the compound of the formula (1). In the process of the present invention it is preferred to use those mixtures of isomers

containing at least 95% of cis-compound of the formula (1), the practically pure cis-isomers being particularly preferred.

The 3-phenoxybenzyl (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate ("cis-Permethrin") and the 3-phenoxy- α -cyanobenzyl (+)-cis-2,2-dimethyl(2,2-dichlorovinyl)cyclopropanecarboxylate ("cis-Cypermethrin") are already known from Pesticide Science, 1975 (6), 537-542 and 1974 (5), 791-799.

The cis-isomers of the formula (1) and the mixtures of isomers containing at least 90% of these isomers can be obtained according to various processes which are known per se. One process comprises reacting (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid or a functional derivative thereof with a compound of the formula



wherein R_3 is the hydroxyl group or a halogen atom.

Suitable functional derivatives of cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid are, in addition to the salts thereof, preferably acid halides ($-COX$) and esters ($-COOR_4$), wherein X is a halogen atom, in particular chlorine or bromine, and R_4 is preferably alkyl, in particular ethyl or methyl. The process is preferably carried out as follows:

- a) reacting cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid with a compound of the formula (2), wherein R_3 is halogen, in the presence of an acid acceptor;
- b) reacting an acid halide (in particular the chloride or bromide) of cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid with a compound of the formula (2), wherein R_3 is hydroxyl, in the presence of an acid acceptor;

- c) reacting *cis*-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid with a compound of the formula (2), wherein R₃ is hydroxyl, in the presence of a hydrophilic agent; or
- d) reacting an alkyl ester of *cis*-2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropanecarboxylic acid with a compound of the formula (2), wherein R₃ is hydroxyl, with removal of alcohol.

Particularly suitable acid acceptors for process a and b are tertiary amines, such as trialkylamine and pyridine, and also hydroxides, oxides, carbonates and bicarbonates of alkali metals, alkaline earth metals and alkali metal alcoholates, e.g. potassium *tert*-butylate and sodium methylate. For process, c, e.g. dicyclohexylcarbodiimide can be used as hydrophilic agent. Processes a to d are carried out e.g. at a reaction temperature between -10 and 120°C, usually between 20 and 80°C, under normal or increased pressure and preferably in an inert solvent or diluent. Suitable solvents or diluents are e.g. ether and ethereal compounds such as diethyl ether, dipropyl ether, dioxane, dimethoxyethane and tetrahydrofuran; amides such as *N,N*-dialkylated carboxylic acid amides; aliphatic, aromatic and halogenated hydrocarbons, in particular benzene, toluene, xylene, chloroform and chlorobenzene; nitriles such as acetonitrile; dimethylsulfoxide and ketones such as acetone and methyl ethyl ketone.

(+)-*Cis*-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid, and the derivatives thereof, employed as starting compounds are known. See *Pesticide Science*, 1974 (5), 791-799.

The compounds of the formula (1) can also be obtained in accordance with the processes described in US-A 4,242,278 and GB-A 1,598,472.

A further possibility of obtaining the *cis*-isomers of the formula (1) comprises separating by methods known per se a mixture of *cis/trans*-isomers obtained in the non-stereospecific synthesis of 3-phenoxybenzyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylates into the two geometrical isomers. This separation can be effected, for example, by

fractional crystallisation in a suitable solvent (for example, in an aliphatic or aromatic hydrocarbon such as hexane, toluene etc.) or preferably by column chromatography using suitable eluants (e.g. the solvents indicated above). In order to keep the loss of cis-isomers as low as possible in these methods, the separation can, for example, be effected only until a mixture of isomers which still contains up to 10% of the trans-isomers is obtained, which mixture of isomers can also be used in the process according to the invention.

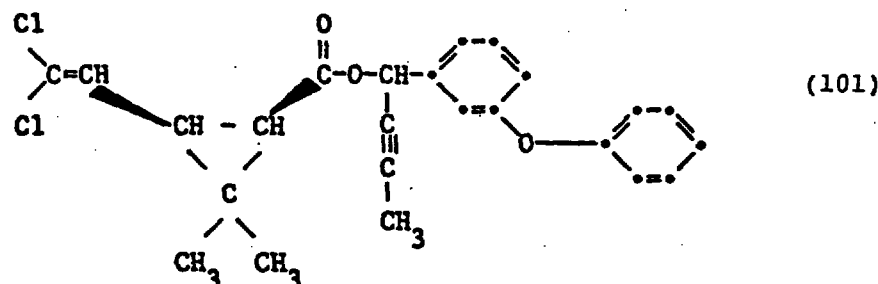
The mixtures of cis/trans-isomers containing the two isomers in approximately equal amounts (e.g. cis:trans 40:60) and the preparation thereof are known from the literature. See, for example, DE-A 2,326,077, DE-A 2,709,264 and EP-A 8 331).

The following Examples illustrate in more detail the process according to the invention and also the preparation of active substances of the formula (1) used therein. It must, however, be emphasised that the invention is not restricted to these Examples.

In the following Examples, as also in the entire description and in the patent claims, parts and percentages are by weight unless otherwise stated.

Example 1: While cooling with ice and with exclusion of air (N₂ flushing), 2.3 g of pyridine followed by a solution of 5.2 g of 3-phenoxy- α -propyn-1-ylbenzyl alcohol in 10 ml of toluene are added dropwise to a solution of 5 g of (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid chloride in 20 ml of toluene. Then a spatula tip of 4-dimethylaminopyridine is added. The reaction mixture is stirred overnight and then diluted with about 200 ml of toluene and about 200 ml of water, extracted in succession with 2N HCl, 10% K₂CO₃-, 10% NaHCO₃- and a saturated solution of sodium chloride, dried over MgSO₄ and concentrated in a rotary evaporator. The concentrated solution is filtered in a 300 g collecting beaker over 200 g of silica gel and eluted with hexane/ether 95:5. The solvent is removed, affording 8.6 g of 3-phenoxy- α -propyn-1-ylbenzyl (+)-cis-2,2-dimethyl-3-(2,2-dichloro-

vinyl)cyclopropanecarboxylate of the formula



in the form of a pale yellow oil with a refractive index of $n_D^{20} = 1.5712$.

For purposes of comparison, using (+)-trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid chloride as starting material, the isomeric 3-phenoxy- α -propyn-1-ylbenzyl (+)-trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate (compound 102) is obtained in analogous manner as a yellow oil with a refractive index of $n_D^{20} = 1.5687$.

The mixture of cis/trans-isomers of 3-phenoxy- α -propyn-1-ylbenzyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate (compound 103) known from EP-A 8 332 has a refractive index of $n_D^{20} = 1.5700$.

Example 2: Using 3-phenoxybenzyl alcohol or 3-phenoxy- α -cyanobenzyl alcohol and (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid chloride as starting materials, the following compounds are obtained in a manner analogous to that of Example 1:

3-phenoxybenzyl (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate (compound 201) with a refractive index of $n_D^{20} = 1.5680$, and

3-phenoxy- α -cyanobenzyl (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate (compound 202) with a refractive index of $n_D^{20} = 1.5610$.

For purposes of comparison, using (+)-trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid chloride, the following two isomeric trans-compounds are obtained in analogous manner:

3-phenoxybenzyl (+)-trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate (compound 203) with a refractive index of $n_D^{20} = 1.5642$, and

3-phenoxy- α -cyanobenzyl (+)-trans-2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropanecarboxylate (compound 204) with a refractive index of $n_D^{20} = 1.5623$.

Further, for purposes of comparison, the corresponding mixtures of cis/trans-isomers known from DE-A 2,326,077 are referred to:

3-phenoxybenzyl (+)-cis/trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate (compound 205) known under the name of "Permethrin", ratio of cis:trans circa 40:60, and

3-phenoxy- α -cyanobenzyl (+)-cis/trans-2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropanecarboxylate (compound 206) known under the name of "Cypermethrin", ratio of cis:trans circa 40:60.

The (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid chloride required as starting material in Examples 1 and 2 can be obtained as follows:

a) The preparation of both (+)-cis- and (+)-trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid is described in Pesticide Science, 1974 (5), 791-799, sections 2.1 to 2.3.

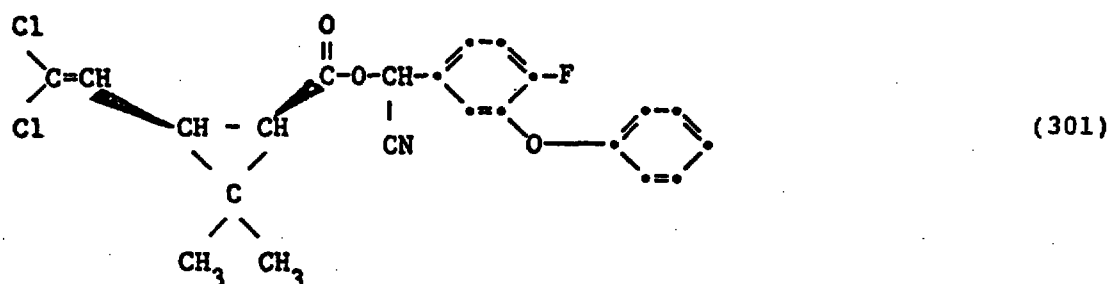
b) 8 g of (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid are heated in 80 ml of hexane to reflux temperature. After the addition of one drop of dimethylformamide, a solution of 6 g of oxalic acid chloride in 10 ml of hexane is slowly added dropwise in the course of 1 hour. After boiling at reflux for a further $3\frac{1}{2}$ hours, the evolution of gas is no longer detectable. The solvent is removed in a rotary evaporator and the residue is distilled in a bulb tube at 80°C and 0.1 torr. The resultant (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid chloride can be used directly for the reaction according to Example 1 or 2.

The corresponding trans-acid chloride is prepared in analogous manner.

Example 3: 11 g of the mixture of isomers 3-phenoxy-4-fluoro- α -cyanobenzyl

(+)-cis/trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate (yellow oil, cis:trans ratio circa 40:60, $n_D^{23} = 1.5548$) obtainable according to Example 2 of DE-A 2,709,264 are chromatographed in a column of silica gel eluted with toluene/hexane 1:1 [net weight of the silica gel (331-246 μm = 40/60 mesh) 1200 g; column diameter 9 cm]. 3 fractions are eluted, the first of which contains the mixture of cis-isomers, the third the mixture of trans-isomers, and the second a mixture of cis/trans-isomers. The solvent is removed, affording from fractions 1 and 3

3.8 g of 3-phenoxy-4-fluoro- α -cyanobenzyl (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate of the formula



as a yellow oil with a refractive index of $n_D^{20} = 1.5567$ and an NMR spectrum as shown in Fig. 1, as well as

4.7 g of 3-phenoxy-4-fluoro- α -cyanobenzyl (+)-trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate (compound 302) as a yellowish wax, the NMR spectrum of which is shown in Fig. 2.

Example 4: Application in the exhaust bath

A stock solution of each of the test compounds 101, 102, 201, 203, 205, 301 and 302 is prepared by dissolving 50 mg of the active substance in 25 ml of ethylene glycol monoethyl ether.

Thoroughly prewetted wool fabric samples of 3 g in weight are put into an aqueous liquor at 30°C containing the following ingredients:

x ppm, based on the weight of the wool, of each test compound (a

corresponding amount of the stock solution described above is added to the liquor),

1%, based on the weight of the wool, of 80% acetic acid,
4%, based on the weight of the wool, of ammonium sulfate,
0.5 g of a wetting agent and dispersant per litre of liquor.

The temperature of the liquor is raised to 98°C in the course of 20 minutes and treatment is carried out for 60 minutes at this temperature. After cooling, the samples are rinsed individually with water and dried at room temperature.

The dry wool samples which have been proofed with the test compounds are then subjected to the mothproofing test (protection against feeding damage caused by the webbing clothes moth *Tineola bisselliella* Hum.) and to the resistance test against larvae of the black carpet beetle (*Attagenus piceus* Oliv.) and of the furniture carpet beetle (*Anthrenus flavipes* var. *seminiveus*) in accordance with the method of Swiss Standard specification SNV 195901.

In these tests, larvae of *Tineola*, larvae of *Anthrenus* and 6- to 7-week-old larvae of *Attagenus* are used.

Pieces of the same size are cut out of the treated wool flannel samples and subjected for 14 days at constant temperature (28°C) and constant relative humidity (65%) to attack (feeding) by 15 larvae of each of the pests. Evaluation for all 3 pests is made according to the loss in weight of the wool sample.

The following Table 1 shows the concentration (in ppm, based on the weight of the wool) of each of the test compounds and the loss in weight (in mg) of the test samples caused by pest feeding:

Table 1

Compound	Tineola		Attagenus		Anthrenus	
	Concentration (ppm)	Loss in weight (mg)	Concentration (ppm)	Loss in weight (mg)	Concentration (ppm)	Loss in weight (mg)
101 (cis)	30	1.2	30	9.0	300	9.2
102 (trans)	30	2.6	30	43.4	300	51.7
201 (cis)	7.5	1.7	30	4.3	125	18.9
203 (trans)	7.5	26.9	30	54.2	125	68.3
205 (cis/ trans)	7.5	5.8	30	14.9	125	29.2
301 (cis)	7.5	0	7.5	11.4	125	14.9
302 (trans)	7.5	0.4	7.5	51.4	125	48.0

The results show that each cis-isomer has a very substantially better activity than both the trans-isomer and the tested mixture of isomers.

Example 5: Application by padding

12.5 ml of a stock solution of each of the test compounds 101, 102, 201, 203, 205, 301 and 302 according to Example 4 are diluted with ethylene glycol monoethyl ether containing 1 g/l of a wetting agent and dispersant. the dilution is carried out such that the concentration of each test compound in the padding liquor obtained is so adjusted that after padding, x ppm of the respective active compound is present on the wool fabric (see Table 2). 3 ml of each solution obtained are poured into crystallisation dishes. With the aid of pincers, a baited disc of wool fabric is wetted for circa 3 seconds therein. The moist discs are pad-mangled between 2 aluminium sheets in such a way that after they have been squeezed the discs have each taken up 100%, based on their weight, of liquor. The moist discs are then dried in the air and subjected to the same biological tests as described in Example 4. The results are summarized in the following Table 2:

Table 2

Compound	Tineola		Attagenus		Anthrenus	
	Concentration (ppm)	Loss in weight (mg)	Concentration (ppm)	Loss in weight (mg)	Concentration (ppm)	Loss in weight (mg)
101 (cis)	30	1.0	30	2.0	250	1.1
102 (trans)	30	4.4	30	15.3	250	27.1
201 (cis)	7.5	1.9	15	3.7	125	1.2
203 (trans)	7.5	17.4	15	39.3	125	28.1
205 (cis/ trans)	7.5	5.5	15	32.5	125	11.0
301 (cis)	---	---	7.5	0.8	125	0.1
302 (trans)	---	---	7.5	9.3	125	16.3

The results show that each cis-isomer has a very substantially better activity than both the trans-isomer and the tested mixture of isomers.

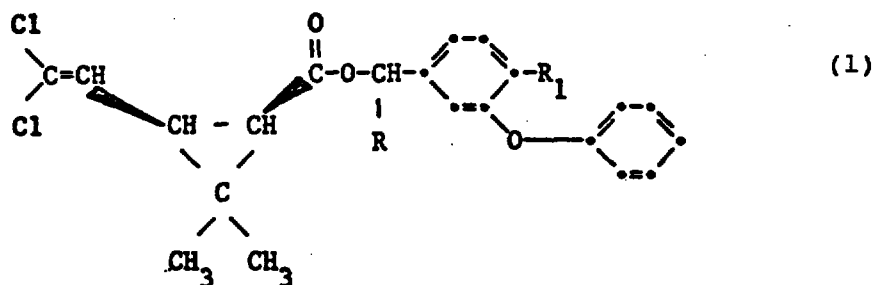
Example 6: A 10% solution of each of the compounds 101, 201, 202 and 301 in ethylene glycol monomethyl ether is prepared. One part by volume of this solution is diluted with 200 parts by volume of a solvent suitable for dry cleaning, e.g. a suitable petroleum fraction or perchloroethylene. If desired, cleaning promoters can be added. Wool articles are then treated in the conventional manner in this cleaning fluid and subsequently centrifuged to a solvent content of circa 100% of the weight of the wool. After drying, the articles are excellently protected against the pests that feed on keratin indicated in Example 4.

Example 7: A 0.5% solution of each of the compounds 101, 201, 202 and 301 in methylene chloride, trichloroethylene or a low boiling petroleum fraction is prepared. Wool articles are sprayed with these solutions with the aid of a conventional spray device, so that $2 \times 15 \text{ g/m}^2$ of active compound solution is applied. About 400 ppm of the respective active compound are then present on the material assuming a 30% utilisation of the aerosol. The wool fabrics thus finished are protected against the pests that feed on keratin indicated in Example 4.



Patent claims

1. A process for protecting or finishing keratinous material or keratin-containing material against attack by insects that feed on keratin, which process comprises treating the material to be protected with a 3-phenoxybenzyl (+)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropane-carboxylate of the formula



wherein R is hydrogen, $-C\equiv CH$, $-C\equiv CH_3$ or CN, and R_1 is hydrogen or fluorine, or with a mixture of isomers containing at least 90% of these cis-isomers.

2. A process according to claim 1, which comprises the use of a compound of the formula (1), wherein R is hydrogen or CN, and R_1 is hydrogen.

3. A process according to claim 1, which comprises the use of a compound of the formula (1), wherein R is $-C\equiv C-CH_3$, and R_1 is hydrogen or fluorine.

4. A process according to claim 1, which comprises the use of a compound of the formula (1), wherein R is hydrogen or CN, and R_1 is fluorine.

5. A process according to claim 1, which comprises treating the material to be protected, by the exhaust or pad process, with an aqueous liquor containing one or more of the compounds as defined in claim 1, where the aqueous liquor may also contain conventional textile assistants such as dispersants, wetting agents, acids, bases and/or dyes.



6. A process according to claim 1, which comprises treating the material to be protected with an organic cleaning liquid containing one or more of the compounds defined in claim 1.

7. A process according to claim 1, which comprises spraying the material to be protected with an organic solvent containing one or more of the compounds defined in claim 1.

8. A process according to claim 1, which comprises applying to the material to be protected the compounds of the formula (1) in an amount of 10 to 2,000 ppm, based on the material to be protected.

9. A process according to claim 5, which comprises treating wool textiles in a dye bath by the exhaust process.

10. A process according to claim 5, which comprises treating wool textiles in an aftertreatment bath by the exhaust process.

11. The keratinous material or keratin-containing material finished according to claim 1.

12. Material according to claim 11 which contains 10 to 2,000 ppm of compounds of the formula (1).

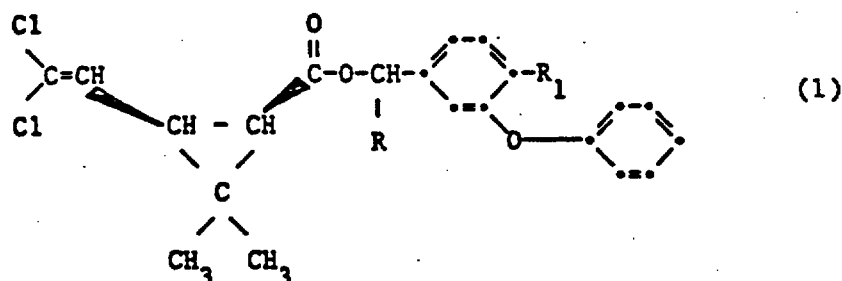
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As printed

Claims

1. A process for protecting or finishing keratinous material or keratin-containing material against attack by insects that feed on keratin, which process comprises treating the material to be protected with a 3-phenoxybenzyl ($\pm$)-cis-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropane-carboxylate of the formula



wherein R is hydrogen, $-C\equiv CH$, $-C\equiv CH_3$ or CN, and R_1 is hydrogen or fluorine, or with a mixture of isomers containing at least 90 % of these cis-isomers.

2. A process according to claim 1, which comprises the use of a compound of the formula (1), wherein R is hydrogen or CN, and R_1 is hydrogen.

3. A process according to claim 1, which comprises the use of a compound of the formula (1), wherein R is $-C\equiv CH_3$, and R_1 is hydrogen or fluorine.

4. A process according to claim 1, which comprises the use of a compound of the formula (1), wherein R is hydrogen or CN, and R_1 is fluorine.

5. A process according to claim 1, which comprises treating the material to be protected, by the exhaust or pad process, with an aqueous liquor containing one or more of the compounds as defined in claim 1, where the aqueous liquor may also contain conventional textile assistants such as dispersants, wetting agents, acids, bases and/or dyes.

6. A process according to claim 1, which comprises treating the material to be protected with an organic cleaning liquid containing one or more of the compounds defined in claim 1.

7. A process according to claim 1, which comprises spraying the material to be protected with an organic solvent containing one or more of the compounds defined in claim 1.

8. A process according to claim 1, which comprises applying to the material to be protected the compounds of the formula (1) in an amount of 10 to 2,000 ppm, based on the material to be protected.

9. A process according to claim 5, which comprises treating woollen textiles in a dye bath by the exhaust process.

10. A process according to claim 5, which comprises treating woollen textiles in an aftertreatment bath by the exhaust process.

11. The keratinous material or keratin-containing material finished according to claim 1.

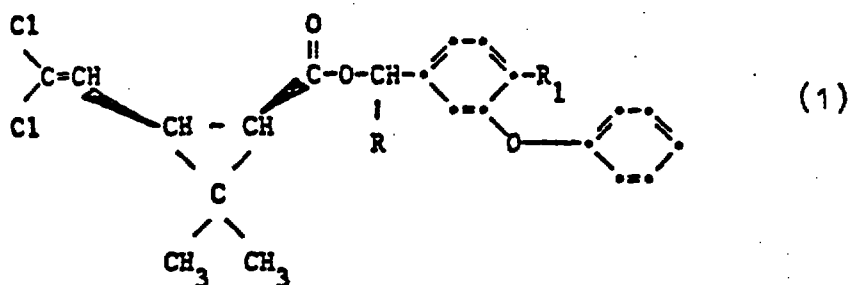
12. Material according to claim 11 which contains 10 to 2,000 ppm of compounds of the formula (1).



As printed

Revendications

1. Procédé pour la protection et l'apprêtage de matière kératinique ou de matière contenant de la kératine avant ou contre l'infection par des insectes dévorant la kératine, caractérisé par le fait que l'on traite la matière à protéger avec des (±)-cis-2,2-diméthyl-3-(2,2-dichlorovinyl)-cyclopropanecarboxylates de 3-phénoxybenzyle de formule:



dans laquelle R représente un hydrogène, -C≡CH, -C≡C-CH₃, ou CN, et R₁ représente un hydrogène ou un fluor, ou biso avec un mélange d'isomères contenant au moins 90 % de ces isomères-cis.

2. Procédé selon la revendication 1, caractérisé par le fait que l'on utilise un composé de formule (1), où R représente un hydrogène ou CN et R₁ représente un hydrogène.

3. Procédé selon la revendication 1, caractérisé par le fait que l'on utilise un composé de formule (1), où R représente -C≡C-CH₃ et R₁ représente un hydrogène ou un fluor.

4. Procédé selon la revendication 1, caractérisé par le fait que l'on utilise un composé de formule (1), où R représente un hydrogène ou CN et R₁ représente un fluor.

5. Procédé selon la revendication 1, caractérisé par le fait que l'on traite la matière à protéger avec un bain aqueux qui contient un ou plusieurs des composés définis dans la revendication 1, selon le procédé par épuisement ou le procédé par foulardage, le bain aqueux pouvant encore contenir d'autres adjuvants pour textiles, comme des dispersants, des agents de mouillage, des acides, des bases et/ou des colorants.

6. Procédé selon la revendication 1, caractérisé par le fait que l'on traite la matière à protéger avec un liquide organique de nettoyage qui contient un ou plusieurs des composés définis dans la revendication 1.

7. Procédé selon la revendication 1, caractérisé par le fait que l'on pulvérise sur la matière à protéger un solvant organique qui contient un ou plusieurs des composés définis dans la revendication 1.

8. Procédé selon la revendication 1, caractérisé par le fait que l'on introduit sur la matière à protéger les composés de formule (1) en une quantité comprise entre 10 et 2.000 ppm, par rapport à la matière à protéger.

9. Procédé selon la revendication 5, caractérisé par le fait que l'on traite les textiles en laine dans le bain de teinture selon le procédé par épuisement.

10. Procédé selon la revendication 5, caractérisé par le fait que l'on traite les textiles en laine dans le bain de post-traitement selon le procédé par épuisement.

11. La matière kératinique ou contenant de la kératine apprêtée selon la revendication 1,

12. Matière selon la revendication 11, contenant entre 10 et 2.000 ppm des composés de formule (1).