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(54) Title: INSECT-REPELLENT FIBER

(57) **Abstract:** The invention provides an insect-repellent fiber which is pliable and excellent in fabrication quality. The invention relates to an insect-repellent fiber obtained by melt-spinning an insect-repellent resin composition which comprises a pyrethroid type insect-repellent compound whose vapor pressure is 1 X 10^{-6} mmHg or lower at 20 °C, an antioxidant and an ethylene based resin, characterized in that the content of said pyrethroid type insect-repellent compound in 1 kg of said insect-repellent fiber is from 10 to 300 g, and in that the content of said antioxidant in 1 kg of said insect-repellent fiber is from 250 to 500 mg.

DESCRIPTION

Insect-Repellent Fiber

Field of the Invention

The present invention relates to insect-repellent fibers.

Background of the Invention

Shaped articles, such as sheets, obtained by shaping a mixture of an insect-repellent compound and an ethylene based resin are used in various fields such as insect-repellent of clothing, etc., since such sheets can maintain insect-repellent performance over a long period of time. For example, JP-A-11-277686/1999 discloses a laminate material which comprises an intermediate layer formed of a mixture of an insect-repellent compound and an ethylene based resin, and both outermost layers formed of a thermoplastic resin composition having a function to gradually release the insect-repellent compound (cf. JP-A-11-277686/1999).

Disclosure of the Invention

However, insect-repellent fibers obtained by melt-spinning the mixture of the insect-repellent compound and the ethylene based resin lack pliability, and thus, it is hard to fabricate such insect-repellent fibers into net-

like materials or the like.

As a result of the present inventors' intensive efforts to improve the pliability of such insect-repellent fibers, they found that it is important to make insect-repellent fibers contain a specific amount of an antioxidant and they accomplished the present invention based on such a finding.

The present invention provides an insect-repellent fiber obtained by melt-spinning an insect-repellent resin composition which comprises a pyrethroid type insect-repellent compound whose vapor pressure is 1 X 10^{-6} mmHg or lower at 20°C, an antioxidant and an ethylene based resin, and this insect-repellent fiber is characterized in that the content of the pyrethroid type insect-repellent compound in 1 kg of the insect-repellent fiber is from 10 to 300 g, and in that the content of the antioxidant in 1 kg of the insect-repellent fiber is from 250 to 500 mg.

The insect-repellent fiber of the present invention is pliable and excellent in fabrication quality.

Best Modes for Carrying out the Invention

The insect-repellent fiber of the present invention is obtained by melt-spinning an insect-repellent resin composition which comprises a pyrethroid type insect-repellent compound, an antioxidant and an ethylene based resin. The pyrethroid type insect-repellent compound of

the present invention shows a vapor pressure of 1 X 10^{-6} mmHg or lower, preferably a vapor pressure of from 1 X 10^{-8} to 1 X 10^{-6} mmHg, at 20°C. Examples of such a pyrethroid type insect-repellent compound include permethrin, cyphenothrin, d-phenothrin, 4-resmethrin, fenvalerate, fenpropathrin, etofenprox, tralomethrin, etc. The insect-repellent fiber of the present invention, which contains 10 to 300 g of such an insect-repellent compound in 1 kg of the insect-repellent fiber, is able to make the insect-repellent compound bleed to the surface thereof constantly over a long period of time, and thus can sustain the insect-repellent effect over a long period of time. The content of the insect-repellent compound in 1 kg of the insect-repellent fiber is preferably 20 g or more, more preferably 50 g or more. In view of the tenacity of the fiber, the content of the insect-repellent compound in 1 kg of the insect-repellent fiber is preferably 200 g or less, more preferably 100 g or less.

The insect-repellent fiber of the present invention contains 250 to 500 mg of an antioxidant in 1 kg of the insect-repellent fiber. The content of the antioxidant in the insect-repellent fiber is preferably from 280 mg inclusive to 450 mg inclusive, more preferably from 300 mg inclusive to 450 mg inclusive. The insect-repellent fiber of the present invention, which contains the antioxidant

within the above specified range, is excellent in pliability, and thus can be easily knitted or woven, in other words, the insect-repellent fiber of the present invention is excellent in fabrication quality.

Examples of the antioxidant for use in the present invention include phenolic antioxidants such as 2,6-di-tert-butyl-4-methylphenol (hereinafter referred to as BHT), stearyl β(3,5-tert-butyl-4-hydroxyphenyl)propionate, and tetrakis[methylene-3(3',5'-di-tert-butyl-4-hydroxyphenyl)propionate]methane; phosphorus antioxidants such as tris(2,4-di-tert-butylphenyl)phosphite, tetrakis(2,4-di-tert-butylphenyl)4',4'-biphenylene diphosphonite, and 6-[3-(3-tert-butyl-4-hydroxy-5-methyl)propoxy]-2,4,8,10-tetra-tert-butyldibenz[d,f][1,3,2]-dioxaphosphepin. Each of such antioxidants may be used singly, or two or more species selected therefrom may be used as a mixture. Insect-repellent fibers containing BHT are excellent in pliability.

Examples of the ethylene based resin for use in the present invention include a low density polyethylene having a density of 0.85 to 0.93 g/cm^3, a linear low density polyethylene, a high density polyethylene having a density of 0.94 g/cm^3 or more, and copolymers of ethylene and at least one monomer selected from the group consisting of vinyl carboxylates and unsaturated carboxylates. Such

copolymers include an ethylene-vinyl acetate copolymer and an ethylene-unsaturated carboxylate copolymer. The ethylene-vinyl carboxylate copolymer may be an ethylene-vinyl acetate copolymer. The ethylene-unsaturated carboxylate copolymer may be an ethylene-methyl methacrylate copolymer, an ethylene-methyl acrylate copolymer, an ethylene-ethyl acrylate copolymer, etc. In view of balance between processability for melt-spinning and pliability of the resultant insect-repellent fiber, the ethylene based resin in the present invention is preferably a mixture of a linear low density polyethylene and a high density polyethylene. When the ethylene based resin is a mixture of a linear low density polyethylene and a high density polyethylene, the weight ratio of the linear low density polyethylene to the high density polyethylene is preferably 5 to 30 : 70 to 95.

In the process for manufacturing the insect-repellent fiber of the present invention, for example, a master batch of a pyrethroid type insect-repellent compound is prepared, and then melt-spinning is conducted using this master batch and an ethylene based resin. The master batch herein referred to is a composition of an ethylene based resin and a high concentration of an insect-repellent compound.

To prepare a master batch of an insect-repellent compound, preferably, the insect-repellent compound is

mixed with porous particles to support the insect-repellent compound on the porous particles; and then the porous particles supporting the insect-repellent compound thereon are mixed with an ethylene based resin and an antioxidant. The porous particles may be silica or the like. When porous particles having too small an average particle size are used, an agglomerate of the porous particles tends to occur in the compounding of the components and it becomes hard to homogenously disperse the porous particles. When porous particles having too large an average particle size are used, a filter is likely to be clogged during the spinning, or the resultant fiber is likely to cut, or the tenacity of the resultant fiber tends to lower. Therefore, the use of porous particles having an average particle size of 0.01 to 40 μm is preferred. The ethylene based resin for use in the preparation of the master batch is preferably a linear low density polyethylene, because the use of the linear low density polyethylene is effective to process the composition at a low temperature, and to suppress the loss of the insect-repellent compound during the processing, and further to provide a pliable insect-repellent fiber after the melt-spinning of the composition. The porous particles supporting the insect-repellent compound thereon, the antioxidant and the ethylene based resin are kneaded in an extruder or the like, and the

kneaded mixture is extruded and then pelletized. Thus, the master batch of the insect-repellent compound is obtained.

A mixture of the master batch of the insect-repellent compound obtained as above and an ethylene based resin, and if needed, an antioxidant, is kneaded with an extruder, and is extruded as a strand. This strand is cooled and is taken off at a take-off rate of 20 to 150 m/min. in a hot bath to thereby provide an insect-repellent fiber. The ethylene based resin to be used in combination with the master batch of the insect-repellent compound is preferably a high density polyethylene in view of processability.

In the present invention, it is needed to adjust the amount of the antioxidant in accordance with the manufacturing conditions (e.g. temperature, etc.) so that the content of the antioxidant in 1 kg of the resultant insect-repellent fiber can be from 250 to 500 mg. Specifically, the master batch of the insect-repellent compound is prepared by kneading 0.5 to 30 wt.% of the pyrethroid type insect-repellent compound, 50 wt.% or less of the porous particles, 30 to 90 wt.% of the ethylene based resin and 0.1 to 2 wt.% of BHT at a temperature of 150 to 250°C with an extruder. Further, 5 to 30 wt.% of the master batch and 70 to 95 wt.% of the ethylene based resin are kneaded at a temperature of 150 to 250°C with an extruder, and the kneaded mixture is extruded as a strand.

This strand is cooled and is taken off at a take-off rate of 20 to 150 m/min. in a hot bath to obtain the insect-repellent fiber of the present invention. When the concentration of the antioxidant in the master batch is lower than 0.1 wt.%, 0.3 wt. parts or less of the antioxidant may be optionally added to 100 wt. parts of the master batch.

The insect-repellent fiber of the present invention may contain a UV absorber, antistatic agent, lubricant, anti-blocking agent, pigment, nucleator, metal soap, etc. Also, the insect-repellent fiber of the present invention may contain other active compounds, for example, an insecticidal component such as a pyrethroid type compound other than the pyrethroid type compounds specified in the present invention, an insecticidal or pesticidal active component, an antibacterial and fungicidal component, etc.

The insect-repellent fiber of the present invention is knitted or woven by any of the known methods to provide a net-like material. The knitted or woven material of the insect-repellent fiber is sewn to provide a mosquito net or the like.

Examples

Hereinafter, the present invention will be described in more detail by way of Examples thereof, which should not be construed as limiting the scope of the present invention

in any way.

Evaluation was made as follows.

(1) Analysis of Amount of BHT

A sample (1 g) was precisely weighed and was put in a 30 ml conical flask with a cap. Tetrahydrofuran (10 ml) was added thereto, and the sample was extracted by ultrasonic wave for 60 minutes. After that, the extract was passed through a 0.45 μ filter, and the filtrate was used as a sample for analysis.

Separately, a solution containing BHT at a known concentration was prepared to obtain an analytical curve.

Gas chromatography was conducted under the following analytical conditions:

Instrument: Gas chromatography mass spectrometer

Column: ULTRA ALLOY +5

Temperature: 100°C maintained for 1 minute and then raised to 300°C at a rate of 10°C/min.

Carrier gas: helium

(2) Analysis of Insect-Repellent Compound

A sample (about 2 g) was put in a flat bottom flask and was precisely weighed. After that, an internal standard solution (6,000 ppm of n-octyl phthalate/xylene) (5 ml) was added thereto, followed by the addition of xylene (45 ml). The flask was set on a refluxing apparatus to extract the sample at 75°C for 2 hours. The extract was

cooled and analyzed by gas chromatography.

Analytical conditions for gas chromatography

Detector: flame ionization detector

Column: DB-17 capillary column

Column temperature: 225°C

Gasification chamber temperature: 270°C

Detector temperature: 280°C

(3) Measurement of Elongation Elastic Modulus of Insect-Repellent Fiber

Measurement was made according to the testing method for man-made filament yarns in JIS L 1013. The detailed measuring conditions were as follows:

Testing conditions: 23°C and 50%RH

Measuring method: Method A

Clamping interval: 200 mm

Pulling rate: 20 mm/min.

Elongation percentage: 3%

Example 1

(1) Preparation of Master Batch

Porous particles (porous silica with an average particle size of 12 μm) (35.5 wt. parts) and permethrin (showing a vapor pressure of 5 X 10^{-7} mmHg at 20°C) (38.1 wt. parts) as a pyrethroid type insect-repellent compound were mixed with a mixer. BHT (1.1 wt. parts), zinc stearate (21.7 wt. parts) and a blue pigment (ultramarine violet)

(3.6 wt. parts) were further added and mixed to obtain an insect-repellent compound-containing mixture.

The insect-repellent compound-containing mixture (41.5 wt. parts) and a linear low density polyethylene (LLDPE) (Sumikathene L GA807 manufactured by Sumitomo Chemical Company, Limited; density = 0.913 g/cm^3) (58.5 wt. parts) were mixed, and the mixture was extruded with a twin-screw extruder at a melt-kneading zone temperature of 200°C and a die temperature of 200°C. The extruded strand was allowed to pass through a cooling water tank to be cooled, and was then cut with a pelletizer to obtain mater batch pellets which contained 0.38 wt.% of BHT and 15.8 wt.% of permethrin.

(2) Preparation of Insect-Repellent Resin Composition

The above mater batch pellets (14 wt.%) and a high density polyethylene (HDPE) (HI-ZEX 5000S manufactured by MITSUI CHEMICALS, INC.; density = 0.950 g/cm^3) (86 wt.%) were mixed, and the mixture was extruded with a twin-screw extruder at a melt-kneading zone temperature of 210°C and a die temperature of 210°C. The extruded strand was allowed to pass through a cooling water tank to be cooled, and was then cut with a pelletizer to obtain pellets of the insect-repellent resin composition. This pellet contained 0.044 wt.% of BHT and 2.0 wt.% of permethrin.

(3) Manufacturing of Insect-Repellent Fiber

The above insect-repellent resin composition was melt-spun. A strand of this resin composition, extruded with an extruder at a cylinder temperature of 130 to 210°C and a die temperature of 230°C, was taken off at a first take-off speed of 13 m/min. while being cooled with water, and was then introduced into a drawing water tank and was taken off in the drawing water tank in a boiling state (95°C or higher) at a second take-off speed of 105 m/min. Thus, an insect-repellent fiber with a fineness of 182 denier, drawn longer at a drawing multiplying factor of 8, was obtained. The contents of BHT and permethrin in 1 kg of this fiber were 400 mg and 20 g, respectively. The elongation elastic modulus of the resultant insect-repellent fiber was 7%, and the fiber was pliable.

Comparative Example 1

Example 1 was repeated, except that the melt-kneading zone temperature of the twin-screw extruder was changed to 260°C, and the die temperature, to 210°C, in the (1) Preparation of Master Batch, and that 0.43 wt. parts of BHT was added per 100 wt. parts of the master batch in the (2) Preparation of Insect-Repellent Resin Composition, since the concentration of BHT in this master batch was 0.08 wt.%. Thus, an insect-repellent fiber having a fineness of 180 denier was obtained. The contents of BHT and permethrin in 1 kg of this fiber were 550 mg and 19 g, respectively.

The elongation elastic modulus of the resultant insect-repellent fiber was 5%, and this fiber lacked pliability.

Comparative Example 2

(1) Preparation of Master Batch

A master batch was prepared in the same manner as in Example 1, except that HDPE (HI-ZEX 5000S manufactured by MITSUI CHEMICALS, INC.) was used instead of LLDPE used in Example 1. In this operation, the melt-kneading zone temperature was set at 210°C, and the die temperature, at 210°C. However, the heat generation was vigorous, and the melt-kneading zone temperature was raised to 300°C. The contents of BHT and permethrin in this master batch were 0.14 wt.% and 15.4 wt.%, respectively.

(2) Preparation of Insect-Repellent Resin Composition

The above master batch (14 wt.%), HDPE (HI-ZEX 5000S manufactured by MITSUI CHEMICALS, INC.) (82 wt.%) and LLDPE (Sumikathene L GA807 manufactured by Sumitomo Chemical Company, Limited) (4 wt.%) were mixed, and the mixture was extruded with a twin-screw extruder with the melt-kneading zone temperature set at 210°C and the die temperature at 210°C. However, the melt-kneading zone temperature was raised to 290°C. The extruded strand was allowed to pass through a cooling water tank and cooled. Then, the strand was cut with a pelletizer to obtain pellets of the insect-

repellent resin composition. The contents of BHT and permethrin in this pellet were 0.018 wt.% and 1.9 wt.%, respectively.

(3) Manufacturing of Insect-Repellent Fiber

An insect-repellent fiber having a fineness of 179 denier was obtained, using the above insect-repellent resin composition, in the same manner as in Example 1. The contents of BHT and permethrin in 1 kg of the fiber were 160 mg and 19 g, respectively. The elongation elastic modulus of the insect-repellent fiber was 4%, and the fiber lacked pliability.

Table 1

	Kind	Ex. 1	C. Ex. 1	C. Ex. 2
Composition of insect-repellent resin composition (wt.%)	LLDPE	8.2	8.19	4
	HDPE	86	85.95	90.2
	Insect-repellent compound	2.21	2.21	2.21
	Silica	2.06	2.06	2.06
	BHT	0.06	0.12	0.06
	StZn	1.26	1.26	1.26
	Pigment	0.21	0.21	0.21
Content of BHT (mg) in 1 kg of insect-repellent fiber		400	550	160
Content of insect-repellent compound (g) in 1 kg of insect-repellent fiber		20	19	19
Elongation elastic modulus (%)		7	5	4

The major embodiments and the preferred embodiments of

the present invention are listed below.

[1] An insect-repellent fiber obtained by melt-spinning an insect-repellent resin composition which comprises a pyrethroid type insect-repellent compound whose vapor pressure is 1 X 10^{-6} mmHg or lower at 20°C, an antioxidant and an ethylene based resin, characterized in that the content of said pyrethroid type insect-repellent compound in 1 kg of said insect-repellent fiber is from 10 to 300 g, and in that the content of said antioxidant in 1 kg of said insect-repellent fiber is from 250 to 500 mg.

[2] The insect-repellent fiber according to [1], wherein said antioxidant is 2,6-di-tert-butyl-4-methylphenol.

[3] The insect-repellent fiber according to [1] or [2], wherein said ethylene based resin is a mixture of a linear low density polyethylene and a high density polyethylene.

[4] The insect-repellent fiber according to any one of [1] to [3], wherein said insect-repellent resin composition further comprises porous particles.

This application claims Paris Convention priority of Japanese Patent Application No. 2006-245253, the entire contents of which are herein incorporated by reference.

CLAIMS

1. An insect-repellent fiber obtained by melt-spinning an insect-repellent resin composition which comprises a pyrethroid type insect-repellent compound whose vapor pressure is 1 X 10^{-6} mmHg or lower at 20°C, an antioxidant and an ethylene based resin, characterized in that the content of said pyrethroid type insect-repellent compound in 1 kg of said insect-repellent fiber is from 10 to 300 g, and in that the content of said antioxidant in 1 kg of said insect-repellent fiber is from 250 to 500 mg.

2. The insect-repellent fiber according to claim 1, wherein said antioxidant is 2,6-di-tert-butyl-4-methylphenol.

3. The insect-repellent fiber according to claim 1 or 2, wherein said ethylene based resin is a mixture of a linear low density polyethylene and a high density polyethylene.

4. The insect-repellent fiber according to claim 1 or 2, wherein said insect-repellent resin composition further comprises porous particles.