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(71) Applicant: **Beijing Saioulan Flame Retardant Fiber Co., Ltd.**
Beijing 100011 (CN)

(72) Inventors:
- **BI, Shenping**
  Beijing, 100011 (CN)
- **HU, Jinlong**
  Beijing, 100011 (CN)
- **RAN, Guoqing**
  Beijing, 100011 (CN)

(74) Representative: **Dantz, Jan Henning et al**
Loesenbeck - Specht - Dantz
Patent- und Rechtsanwälte
Am Zwinger 2
33602 Bielefeld (DE)

(54) ORGANIC SILICON-NITROGEN FLAME-RETARDANT REGENERATED CELLULOSE FIBER

(57) Disclosed is an organic silicon-nitrogen flame-retardant regenerated cellulose fiber, including silicon 5-15wt%, nitrogen 0.1-5wt%, oxygen 30-60wt%, carbon 20-40wt%, hydrogen 1-7wt%, titanium 1-7wt% and calcium 1-7wt%. The organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to the present invention exhibits a higher limiting oxygen index, a better flame-retarding performance and a far infrared function, and the normal emission rate testing data reach the normal emission rate standard requirements of the textile article.

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Description

Field of the Invention

[0001] The present invention relates to the technical field of textile articles, and particularly to an organic silicon-nitrogen flame-retardant regenerated cellulose fiber.

Background of the Invention

[0002] At present, more than 60% fire accidents in the globe are caused by textile articles, and more than 80% casualty from fire accidents are caused by inhaling toxic smoke or suffocation. As human civilization develops and countries promulgate anti-fire security laws and regulations, people raise higher and higher requirements for flame-retardant materials. The requirements change from pure consideration of flame-retardant performance of materials to environment-friendliness, health care, appearance and comfort of flame-retardant materials. Although flame-retardant synthetic fibers (flame-retardant polyester fiber, flame-retardant acrylic fiber and the like) and intrinsically flame-retardant fibers (aramid fiber, polyimide and the like) have excellent flame-retardant performance, they have already failed to satisfy people's requirements for comfort and security of clothes and accessories because of undesirable comfort of fiber fabric and drawbacks such as shrinking, melting and drippage when catching on fire.

[0003] Flame-retardant regenerated cellulose fibers (e.g., flame-retardant viscose fiber) currently available in the market may satisfy requirements for flame-retardant clothes and accessories and people's requirements for fundamental comfort (moisture absorption and air permeation) of dresses, they still have drawbacks to different degrees. For example, phosphorous flame-retardant viscose fibers generate a lot of harmful fume upon burning, phosphorous element is contained in fibers and fabric, the harmful fume generated upon burning is prone to suffocate people, and their waste cause adverse effects such as eutrophicating water resource during degradation; silicon-containing flame-retardant viscose fibers have defects such as less strength and failure to ensure alkali washing, can only be used as a non-woven fabric or filler, and cannot be used as a shell fabric.

[0004] As compared with the above flame-retardant regenerated cellulose fibers, silicon-nitrogen-containing flame-retardant regenerated cellulose fibers employ silicon-nitrogen-containing flame retardant agent, overcome drawbacks such as large harmful fume emission of phosphorus-containing flame-retardant viscose fibers and undesirable strength and non-endurance of alkali washing of silicon-containing flame-retardant viscose fibers, can obtain products with high flame-retardant performance and high textile performance, and are flame-retardant regenerated cellulose fibers with promising development prospect. For example, patent applications CN103789858 and CN104032401 publish silicon-nitrogen flame-retardant viscose fibers.

[0005] However, as the market raises increasing demands for performance of flame-retardant regenerated cellulose fiber products, the current silicon-nitrogen containing flame-retardant regenerated cellulose fibers are not be further improved in performance such as flame retarding. Therefore, it is desirable to provide a silicon-nitrogen containing flame-retardant regenerated cellulose fiber with better performance.

Summary of the Invention

[0006] The present invention provides an organic silicon-nitrogen flame-retardant regenerated cellulose fiber. It is surprisingly found that introducing a certain proportion of titanium (Ti) and calcium (Ca) simultaneously into the organic silicon-nitrogen flame-retardant regenerated cellulose fiber can effectively improve the fiber flame-retarding performance and substantively improve far infrared performance of the fiber without causing loss of mechanics performance of the fiber.

[0007] The organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to the present invention includes silicon 5-15wt%, nitrogen 0.1-5wt%, oxygen 30-60wt%, carbon 20-40wt%, hydrogen 1-7wt%, titanium 1-7wt% and calcium 1-7wt%.

[0008] Preferably, the organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to the present invention includes silicon 8.5-12.1wt%, nitrogen 1.0-2.3wt%, oxygen 45-49.1wt%, carbon 28-31.5wt%, hydrogen 2.5-4.3wt%, titanium 3.5-4.6wt% and calcium 1.9-3.4wt%.

[0009] The organic silicon-nitrogen flame-retardant regenerated cellulose fiber is formed by allowing cellulose solution and organic silicon-nitrogen flame retardant to undergo grating reaction, and then spinning, coagulating and regenerating. Specifically, the flame retardant is added to the cellulose solution (e.g., viscose original liquid) in a form of a hydrolytic dispersion liquid of silane. In the organic silicon-nitrogen flame-retardant regenerated cellulose fiber, the flame-retarding component exists in the fiber mainly in the form of oxides of silicon and amide, and additionally, in the form of a small amount of oxides of titanium and oxides of calcium, and furthermore, the flame-retarding component forms a crossing network with a linear regenerated cellulose in a "T-shaped" structure. A total content of SiO_2, TiO_2 and CaO in the flame retardant is 12.3-57wt%, and content of amide is 6.5-30wt%, wherein a ratio of silicon, titanium and calcium (mole ratio)

is 1-10:1-5:1-23. The silicon, titanium and calcium in the flame retardant are combined on a regenerated cellulose main chain, form a silicon-titanium-calcium ceramic network, and constitute a far infrared emission group.

[0010] A chemical formula of the organic silane hydrolytic dispersion liquid is:

$$[Me_xO_y \cdot n\ SiO_2] + [\text{--CONH}]$$

Wherein Me represents metal ion; and the metal ion is Ti^{4+} and Ca^{2+}.

[0011] The organic silicon-nitrogen flame-retardant regenerated cellulose fiber may also be formed by injecting other additive such as colorant, antimicrobial agent, antistatic agent before spinning to satisfy different demands of use.

[0012] The present invention further provides a method of preparing the organic silicon-nitrogen flame-retardant regenerated cellulose fiber. The method comprises the following steps: cellulose solution→blending with the organic silicon-nitrogen flame retardant→spinning→water wash→drying. Furthermore, the method comprises the following steps: cellulose solution→blending with the organic silicon-nitrogen flame retardant→spinning→water wash→fixing and cross-linking→water wash→drying. Furthermore, the method comprises the following steps: cellulose solution→blending with the organic silicon-nitrogen flame retardant→spinning→water wash→fixing and cross-linking → water wash → oiling → drying. The process of adding the flame retardant is: in the above blending step, sufficiently blending the flame retardant and pre-formulated cellulose solution, and the amount of addition of the flame retardant is 25-50%(w/w) of cellulose content. The cellulose solution is preferably viscose original liquid.

[0013] Preferably, the process of preparing the organic silicon-nitrogen flame-retardant regenerated cellulose fiber is:

1) Preparing viscose original liquid, sufficiently blending the organic silicon-nitrogen flame retardant and pre-formulated viscose original liquid, the amount of addition of the organic silicon-nitrogen flame retardant is 25-50%(w/w) of cellulose content in the viscose original liquid, fabricating spinning adhesive, and then spinning and water washing;
2) Performing fixing and cross-linking bath treatment for fibers after spinning and water washing.
3) Performing oiling treatment for the fibers having undergone the fixing and cross-linking bath treatment, and drying them.

[0014] Preferably, raw materials of the fixing and cross-linking agent employed by the fixing and cross-linking bath comprise components such as polyhydroxy carboxylic acid, polyhroxy alcohol, sugar and metal. The polyhdroxy carboxylic acid is one of or a mixture of more of lactic acid, tartaric acid, citric acid or β -hydroxybutyric acid; the poyhdroxy alcohol is one of or a mixture of more of propylene glycol, glycerol, glycol or polyhydroxy sterol, and preferably uses C_6 polyhdroxy alcohol. The sugar is one of or a mixture of more of sucrose, fructose or glucose. The metal component is one or a mixture of more of titanium tetrachloride, calcium chloride, aluminum sulfate or four isopropyl titanate. The content of the fixing and cross-linking agent is 3-6wt%.

[0015] The organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to the present invention may include other added components such as colorant, antimicrobial agent, antistatic agent. During production, the above different components are added to produce the organic silicon-nitrogen flame-retardant colored regenerated cellulose fiber, organic silicon-nitrogen flame-retardant antimicrobial regenerated cellulose fiber, and organic silicon-nitrogen flame-retardant antistatic regenerated cellulose fiber.

[0016] The organic silicon-nitrogen flame-retardant regenerated cellulose fiber may be purely spun into a yarn, fabric and shell fabric, and may also be spun with other fibers or raw materials into blended fibers, for example, spun with multiple fibers such as phosphorous-containing flame retardant regenerated cellulose fiber, silicon-containing flame-retardant regenerated cellulose fiber, pure cotton, flame-retardant cotton, various regenerated cellulose fibers (e.g., ordinary viscose fiber, modal fiber and Tencel), wool, cashmere, aramid fiber, psa, polyimide, alginate fiber, various synthetic fibers, various flame-retardant synthetic fibers, pre-oxidized fiber and glass fiber in proportions, to produce yarns, fabrics and shell fabrics with different functions.

[0017] The organic silicon-nitrogen flame-retardant regenerated cellulose fiber or blended fiber according to the present invention may also exist in the form of cellophane, and then may be used as a high-rate decoration material or packaging material.

[0018] The organic silicon-nitrogen flame-retardant regenerated cellulose fiber or blended fiber according to the present invention may also exist in the form of foam and may be used as various flame-retardant filters such as flame-retardant mattress, flame-retardant cushion or the like.

[0019] The organic silicon-nitrogen flame-retardant regenerated cellulose fiber or blended fiber according to the present invention may also be used for protective clothing, the wounded and patients' garments, the elderly's garment, infant and kid's garment, interior decoration of marine, land and air transport vehicles, seat covers of public places, sofa, mattress and curtain, close-fitting underwear, socks, joint protective sheath (kneecap, elbow pad and wrist pad), bedding articles, garments and the like.

[0020] The oxygen index of the fabric made of organic silicon-nitrogen flame-retardant regenerated cellulose fiber

according to the present invention reaches 33-40%, and the fabric is resistant to high temperature and washing with dilute soda-containing water, and satisfies requirements of burning performance test of GB/5455-85 *Textile Fabric Flame-retarding Performance Testing, and Perpendicular Method.*

[0021] In addition, the organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to the present invention not only maintains the comfort (moisture absorption and air permeation) of natural cellulose fibers, but also exhibits a far infrared normal emission rate up to about 87%, may promotes human body blood circulation and metabolism, and has a health care function of relieving fatigue, restoring strength, and easing pain symptoms.

Detailed Description of Preferred Embodiments

Example 1

[0022] Pouring organic silicon-nitrogen flame retardant which accounts for 30wt% of the amount of cellulose fibers into duly-formulated viscose original liquid, allowing viscose to react with the flame retardant for 30 minutes, blending viscosity 70 seconds, with a degree of ripeness (10% ammonium chloride) 10ml. using a spinning nozzle to spin to regenerate in a coagulating bath, the coagulating bath including components: sulphuric acid 75g/l, sodium sulphate 160g/l and zinc sulphate 20g/l, and the temperature being 40°C. The regenerated fiber bundles are drawn, cut, washed, fixed and cross-linked, bleached, oiled, dried, and packaged. The conditions for fixing and cross-linking are: fixing and cross-linking agent:pure water:sodium bisulfite (weight ratio)=33:66:1, the treatment duration is 15-40 minutes and the treatment temperature is 75°C.

[0023] A total content of SiO_2, TiO_2 and CaO in the flame retardant is 18.7wt%, content of amide is 12.5wt%; a ratio of silicon, titanium and calcium (mole ratio) is 5.4:2.7:7.0.

Example 2

[0024] Pouring organic silicon-nitrogen flame retardant which accounts for 33wt% of the amount of cellulose fibers into duly-formulated viscose original liquid, allowing viscose to react with the flame retardant for 50 minutes, blending viscosity 80 seconds, with a degree of ripeness (10% ammonium chloride) 14ml. using a spinning nozzle to spin to regenerate in a coagulating bath, the coagulating bath including components: sulphuric acid 100g/l, sodium sulphate 180g/l and zinc sulphate 30g/l, and the temperature being 40°C. The regenerated fiber bundles are drawn, cut, washed, fixed and cross-linked, bleached, oiled, dried, and packaged. The conditions for fixing and cross-linking are: fixing and cross-linking agent:pure water:sodium bisulfite (weight ratio)=33:66:1, the treatment duration is 15-40 minutes and the treatment temperature is 75°C.

[0025] A total content of SiO_2, TiO_2 and CaO in the flame retardant is 23wt%, content of amide is 18.7wt%; a ratio of silicon, titanium and calcium (mole ratio) is 6.7:3.5:9.2.

Example 3

[0026] Pouring organic silicon-nitrogen flame retardant which accounts for 35wt% of the amount of cellulose fibers into duly-formulated viscose original liquid, allowing viscose to react with the flame retardant for 60 minutes, blending viscosity 70 seconds, with a degree of ripeness (10% ammonium chloride) 16ml. using a spinning nozzle to spin to regenerate in a coagulating bath, the coagulating bath including components: sulphuric acid 125g/l, sodium sulphate 280g/l and zinc sulphate 50g/l, and the temperature being 45°C. The regenerated fiber bundles are drawn, cut, washed, fixed and cross-linked, bleached, oiled, dried, and packaged. The conditions for fixing and cross-linking are: fixing and cross-linking agent:pure water:sodium bisulfite (weight ratio)=33:66:1, the treatment duration is 15-40 minutes and the treatment temperature is 75°C.

[0027] A total content of SiO_2, TiO_2 and CaO in the flame retardant is 33wt%, content of amide is 28wt%; a ratio of silicon, titanium and calcium (mole ratio) is 7.2:3.8:12.3.

Comparative example:

[0028] The flame-retardant viscose fiber is prepared according to the technical solution of Example 2 of patent application CN104032401B.

Performance test

[0029]

A. Dry breaking strength: tested by employing GB/T 14337 chemical fibers and by a short fiber extension performance testing method;
B: Limiting oxygen index: tested by using FZ/T 50016 chemical fibers and using a viscose short fiber flame-retarding performance testing method oxygen index method;
C: Burning performance: tested according to requirements of the GB/5455-85 standard;
D: Far infrared normal emission rate: tested by an experiment method of FZ/T 64010-2000.

[0030] Table 1 shows main quality data resulting from detecting the resultant organic silicon-nitrogen flame-retardant regenerated cellulose fibers according to a detection method or relevant standards. The dried fibers are spun into 32S yarns, and then the yarns are knitted into 220g/m^2 shell fabric. Table 2 shows burning test data resulting from a burning performance test according to the requirement of GB/T 5455-85 standard. Table 3 shows data of detection of far infrared normal emission rate by a testing method of FZ/T 64010-2000.

Table 1: Comparison of main quality data

Nome of items	Example 1	Example 2	Example 3	Comparative example
Dry braking strength (CN/dtex)	2.3	2.2	2.3	1.9
Limiting oxygen index (%)	35.7	37.5	39.6	30.2

Table 2 : GB/ 5455-85 burning performance test data

Items	Testing levels			Example 1	Example 2	Example 3	Comparative example
	Level 1	Level 2	Level 3				
Damage length/mm ≤	50	100	150	46	45	37	76
Afterflame duration/s ≤	0	4	8	0	0	0	2
Smolder duration/s ≤	0	4	8	0	0	0	4
Melting and dripping	Not ignite absorbent cotton	Not ignite absorbent cotton	Not ignite absorbent cotton	none	none	none	none

Table 3: FZ/T64010-2000 normal emission rate testing data

Normal emission rate standard of far infrared textile products	Example 1	Example 2	Example 3	Comparative example
≥83%	87%	88%	89%	80%
Notes: 1. Ordinary cotton normal emission rate is 75%; 2. An improvement value of a normal emission rate of far infrared textile products should be ≥8%.				

[0031] It can be seen from the above that the flame-retardant regenerated cellulose fiber according to the present invention exhibits a higher limiting oxygen index, a better flame-retarding performance and a far infrared function, and the normal emission rate testing data reach the normal emission rate standard requirements of the textile article.

Claims

1. An organic silicon-nitrogen flame-retardant regenerated cellulose fiber, wherein the organic silicon-nitrogen flame-

retardant regenerated cellulose fiber includes silicon 5-15wt%, nitrogen 0.1-5wt%, oxygen 30-60wt%, carbon 20-40wt%, hydrogen 1-7wt%, titanium 1-7wt% and calcium 1-7wt%.

2. The organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to claim 1, wherein the flame-retardant components in the fiber exist in the form of silicon oxides, titanium oxides, calcium oxides and amide structure.

3. The organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to claim 2, wherein the flame-retardant components exist in the form of SiO_2, TiO_2, CaO and amide structure, and a total content of SiO_2, TiO_2 and CaO in the flame retardant components is 12.3-57wt%, and content of amide is 6.5-30wt%,

4. The organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to claim 3, wherein a mole ratio of silicon, titanium and calcium is 1-10:1-5:1-23.

5. The organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to claim 2, wherein the flame-retardant components form a crossing network with a linear regenerated cellulose in a "T-shaped" structure.

6. The organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to claim 2, wherein the flame-retardant components are added to a cellulose solution in a form of an organic silane hydrolytic dispersion liquid as a flame retardant; a chemical formula of the organic silane hydrolytic dispersion liquid is:

$$[Me_xO_y \cdot n\ SiO_2] + [\text{--CONH}]$$

wherein Me represents metal ion; and the metal ion is Ti^{4+} and Ca^{2+}.

7. The organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to claim 1, wherein the fiber further includes one or more additives selected from a group consisting of colorant, antimicrobial agent and antistatic agent.

8. A method of preparing the organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to any one of claims 1-7, wherein the method comprises the following steps: cellulose solution→blending with the organic silicon-nitrogen flame retardant→spinning→water wash→drying; an amount of addition of the organic silicon-nitrogen flame retardant is 25-50%(w/w) of cellulose content.

9. The method according to claim 8, wherein one or more additives selected from a group consisting of colorant, antimicrobial agent and antistatic agent are added before spinning.

10. A blended fiber comprising the organic silicon-nitrogen flame-retardant regenerated cellulose fiber according to any one of claims 1-7, , and one or more of the following fibers: phosphorous-containing flame retardant regenerated cellulose fiber, silicon-containing flame-retardant regenerated cellulose fiber, pure cotton, flame-retardant cotton, non-flame-retardant viscose fiber, modal fiber, Tencel, wool, cashmere, aramid fiber, psa, polyimide, alginate fiber, synthetic fibers, flame-retardant synthetic fibers, pre-oxidized fiber and glass fiber.

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EUROPEAN SEARCH REPORT

Application Number
EP 17 17 6821

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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TECHNICAL FIELDS SEARCHED (IPC)

D01F
D01D
C08L
C08K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	28 November 2017	Verschuren, Jo

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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