

[54] **ACRYLIC SYNTHETIC FIBERS HAVING INCREASED FLAME RETARDANCE AND METHOD OF PRODUCING SAME**

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[22] Filed: **Oct. 11, 1973**

[21] Appl. No.: **405,319**

[30] **Foreign Application Priority Data**

Oct. 18, 1972 Japan..... 47-104666

[52] U.S. Cl. **266/28.5 A**, 260/45.7 R, 260/45.75 B,
260/45.9 NP, 264/182, 264/206

[51] Int. Cl. **C08c 11/70**

[58] Field of Search ... 260/45.7 R, 28.5 A, 45.75 B,
260/45.9 NP; 264/182, 206

[56]

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[57]

ABSTRACT

An acrylic synthetic fiber having increased flame retardance, consisting essentially of 20 to 90 weight percent acrylonitrile, 80 to 10 weight percent vinyl chloride, 0 to 30 weight percent other ethylenically unsaturated compounds copolymerizable with acrylonitrile or vinyl chloride and 0.5 to 30 weight percent flame retardant additive comprising a magnesium compound selected from the group consisting essentially of MgO, Mg(OH)₂, MgCO₃ and mixtures thereof, and method of producing same.

14 Claims, No Drawings

ACRYLIC SYNTHETIC FIBERS HAVING INCREASED FLAME RETARDANCE AND METHOD OF PRODUCING SAME

BACKGROUND OF THE INVENTION

This invention relates to acrylic synthetic fibres having increased flame retardance and method of producing same.

Among the various known acrylic synthetic fibers, the so-called modified acrylic type which contains a comparatively large portion of flame resistant monomer units, such as vinyl chloride or vinylidene chloride, in the fiber forming polymer, is known to have not only the same or similar texture and touch or feel as other types of acrylic fibers, but also markedly increased flame retardance thereover.

Recently, because of increased consumer and governmental concern for loss of human life and human injuries and because of the desirability of preventing large fires, the social need for flame retardance of textile goods has increased substantially. Moreover, increasingly severe legal regulations are necessitating flame retardance of textile goods.

There are a number of known ways for enhancing flame retardance of textile fibers, namely (1) copolymerization of flame retardant monomers, (2) addition of flame retardant additives in a spinning solution, and (3) application of flame retardant additives by post-processing of fibers or textile materials.

Each of these methods has its merits and demerits, but the second (2) method is thought to be advantageous because of its simplicity and production of long term lasting effects.

Heretofore, there were known to exist as flame retardant additives, such compounds as those of antimony, zinc, boron, bromine, chlorine and phosphorus. Among these, only a few are known to be effective with acrylic fibers. Others are known to be effective only when used in considerably large quantities. For example, chlorine compounds such as chlorinated paraffin or tetrabromoethane, chlorine-phosphorus compounds such as tris-(2,3-dibromopropyl) phosphate or tris-(2,3-dichloropropyl) phosphate show no substantial effect unless more than 25% by weight (based on the polymer weight; hereinafter similar notation will be used) is added.

SUMMARY OF THE INVENTION

Through a series of studies and experiments, we have discovered a class of additives which shows specific and surprising flame retarding effect with synthetic fibers made only of copolymers of acrylonitrile and vinyl chloride as discussed more specifically hereinbelow.

This invention contains acrylic fibers having increased flame retardance, obtained from a spinning composition containing from 0.5 to 30 weight percent (based on the weight of the polymer) of at least one compound selected from the group of magnesium compounds consisting of magnesium monoxide (MgO), magnesium hydroxide (Mg(OH)₂), magnesium carbonate (MgCO₃) and mixtures thereof.

Acrylic synthetic fibers which may be used in this invention are those made of copolymers of 20 to 90 weight percent of acrylonitrile, 80 to 10 weight percent of vinyl chloride, preferably of 40 to 70 weight percent acrylonitrile and 60 to 30 weight percent vinyl chloride, and from 0 to 30 weight percent of other ethyleni-

cally unsaturated compounds copolymerizable with acrylonitrile or vinyl chloride.

Ethylenically unsaturated compounds which may be used in this invention can be any compound which is ethylenically unsaturated and copolymerizable with acrylonitrile or vinyl chloride. For example, such compounds may be, although not limited thereto, acrylic acid, methacrylic acid or esters thereof; acrylamide, methacrylamide or N-mono- or dialkyl substitutes thereof; halogenated olefinic compounds such as vinylidene chloride, vinyl bromide, or vinylidene bromide; vinyl carboxylates such as vinyl acetate or vinyl chloroacetate; vinyl pyridines such as 2-vinyl pyridine or 2-methyl-5-vinyl pyridine; styrene, α -, substitutes of styrene; allyl- or methallylsulfonic acid or salts thereof. Appropriate mixtures of the foregoing may be employed.

The copolymerization process can be selected from any of emulsion polymerization, solution polymerization and suspension polymerization.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The magnesium compounds which may be used in this invention are magnesium monoxide (MgO), magnesium hydroxide (Mg(OH)₂), magnesium carbonate (MgCO₃) and mixtures thereof.

From a result of the studies, the inventors have discovered and made the following novel observations, such as

1. Magnesium monoxide, magnesium hydroxide and magnesium carbonate show specific, surprising and outstanding flame retarding effect only for the above-mentioned acrylonitrile-vinyl chloride copolymers and copolymers of acrylonitrile and vinyl chloride and ethylenically unsaturated compounds, while no such effect was produced when the mentioned magnesium compounds were used with polyacrylonitrile or polyvinyl chloride themselves, or for polyacrylonitrile-polyvinyl chloride blends having the same composition percentages as the corresponding acrylonitrile-vinyl chloride copolymers.

2. Magnesium compounds other than magnesium monoxide, magnesium hydroxide and magnesium carbonate, for example magnesium phosphate, magnesium silicate, show only poor flame retarding effect.

3. The burning behavior of acrylic synthetic fibers containing magnesium monoxide, magnesium hydroxide or magnesium carbonate, is apparently different from that of acrylic synthetic fibers which do not contain such magnesium compounds in some respect. First, fibers containing the above-mentioned magnesium compounds leave markedly increased amounts of carbonaceous residue (ca.) after burning. When the carbonaceous residue after burning was measured using twisted and doubled specimen of filaments resulting from different spinning compositions and percentage recovery was calculated from the weights of specimen before and after burning, the results were ca. 17% for the control specimen (without addition of the above-mentioned magnesium compounds), while the percentage recovery reached up to ca. 40% for the instant invention when for example 10% by weight of magnesium monoxide was added. This observation was confirmed by experiments using a thermobalance. Second, fibers containing the above-mentioned magnesium compounds swell considerably at the moment of

ignition. This is probably due, it is thought, to surface enclosure of blow-out gas emerging from inside of the specimen, which may also, to a certain degree, lead to flame retardance effect. Such a phenomena was never observed at the moment of ignition of the control specimen.

Hence, the inventive additives magnesium monoxide, magnesium hydroxide and magnesium carbonate impart flame-retardance specifically to acrylic synthetic fibers of certain polymer compositions as herein discussed and the flame retardant effect is surprising, marked and substantial.

When compared with antimony trioxide (which is reputed to exert comparatively marked flame retardant effect on acrylic synthetic fibers) in measurement of limiting oxygen indices, using specimen forms described later, this invention showed surprising and outstanding results. For example, the limiting oxygen index for specimen using 10 weight % addition of magnesium monoxide, for example, was 42.0, while those for control specimen using 10 weight percent addition of antimony trioxide was 34.5 and for a second control specimen not employing any additive was 27.0. These results showed clearly the marked and surprising effect of use of the inventive magnesium compounds.

The amount of magnesium compounds to be added to this invention is from 0.5 to 30 weight percent, preferably from 1 to 10 weight percent, based on the weight of the acrylic fiber forming polymer. No substantial effect can be expected when the magnesium compound is added in less than 0.5%, while addition of more than 30% impairs mechanical properties, for example tensile strength and elongation of the obtained fibers and also leads to economical disadvantages.

The amounts of acrylonitrile, vinyl chloride, and other ethylenically unsaturated compounds, to be used in this invention have been set forth above. Amounts outside of those ranges produce various disadvantages, and hence should not be used.

Furthermore, these above mentioned magnesium compounds can be used in combination with compounds which are known to have flame retardance effect. For example, such compounds may include inorganic compounds such as antimony trioxide; aromatic halogen compounds such as hexabromobenzene; aliphatic halogen compounds such as chlorinated paraffin; halogen and phosphorus containing compounds such as tris (2,3-dibromopropyl) phosphate; organic phosphorus compounds such as dibutylamine phosphate; inorganic phosphorus compounds such as polyphosphoric acid, ammonium polyphosphate and combinations thereof. Among the foregoing, a marked synergistic effect was observed when the inventive magnesium compounds were used in combination with antimony trioxide.

The addition of magnesium monoxide, magnesium hydroxide, magnesium carbonate or their mixtures to acrylic fiber forming polymers can be carried out either in the polymerization stage or in the spinning stage.

The spinning process used to spin the spinning solution containing the above-mentioned magnesium compound can be either a dry spinning process or a wet spinning process.

A solvent can be used in the spinning solution in both cases; such solvent can be any compound which dissolves acrylonitrile copolymers in use, for example ace-

tone, acetonitrile, dimethylformamide, dimethylacetamide, and mixtures thereof.

The method used for evaluating flame retardance of fibers obtained by this invention was as follows.

Evaluation was made by limiting oxygen indices test (see "Modern Plastics," Vo. 44., No. 3, Page 141 (Nov. 1966)). This test determines minimal volume fraction of oxygen in a slowly rising gaseous atmosphere that will sustain a candle like burning of a stick-formed specimen. Therefore, the higher the value of the index, the greater is the flame retardance of the specimen. The method was originally developed for molded plastic materials, and cannot directly be applied to textile goods, where the evaluation of flame retardance is generally carried out for specimen in the form of textile fabric. There are a number of factors which exert effects on the test results, which do not appear in the case of molded plastic materials, for example, density and uniformity of structure, twisting density and count of component yarns. Thus, to evaluate the flame retardance of the fiber itself as accurately as possible, a standardized specimen form was established by using double twisting filaments and measurements were carried out for specimen in that form. To illustrate, 12 bundles of twisted fibers each comprising 300 of 3 denier acrylic fiber was doubled and heat-set, and was erected on a specimen holder of a limiting oxygen indices tester. Then, the minimal volume fraction of oxygen was determined, that will sustain the burning of the specimen for 5 cm of its length.

The invention is further illustrated by, but not limited to, the following example.

EXAMPLE 1

A fiber forming copolymer composed of 50.0 weight percent acrylonitrile, 46.0 weight percent vinyl chloride, 3.0 weight % methyl methacrylate, and 1.0 weight percent sodium p-styrenesulfonate was dissolved into acetone to a polymer concentration of 20.0%, and a variety of additives were added to give spinning compositions. The spinning compositions were spun into acetone-water coagulation bath through nozzles of 0.1 mm diameter, followed by drying at 120°C, hot stretching to 300% and heat treatment at 140°C for 5 minutes. The thusly obtained samples were subjected to measurement of the flame retardance properties by the above discussed testing method.

As is evident from Table 1, specimen containing magnesium monoxide, magnesium hydroxide or magnesium carbonate showed marked and surprisingly superior flame retardance.

Table 1.

Compounds	Percent Added (Based on Wt. of polymer)	Limiting Oxygen Index
Magnesium oxide (MgO)	10	41.0
Magnesium hydroxide (Mg(OH) ₂)	10	42.0
Magnesium carbonate (MgCO ₃)	10	41.0
Tetrabromobutane	10	30.0
Tris (2,3-dibromopropyl)phosphate	10	29.5
Antimony trioxide	10	34.5
Chlorinated paraffin	10	30.0
Control	none	27.5

EXAMPLE 2

A fiber forming copolymer composed of 47.5 weight

percent acrylonitrile, 42.5 weight percent vinyl chloride and 10% by weight vinylidene chloride, was dissolved in dimethylformamide to a polymer concentration of 24.0%, and a variety of amounts of magnesium monoxide, magnesium hydroxide and magnesium carbonates were respectively added in the range of 0.2 to 30 weight percent, based on the weight of the polymer. Fibers spun from these compositions were measured for their flame retardance, which results are shown in Table 2. The measurement tests were as in Example 1.

Table 2.

% added (Based on wt. of polymer)	Magnesium oxide (MgO)	Magnesium hydroxide (Mg(OH) ₂)	Magnesium Carbonate (MgCO ₃)
Control	28.8	28.8	28.8
0.2	29.0	29.0	29.0
0.5	31.5	32.0	32.0
1	33.5	34.5	34.0
5	39.0	40.0	40.0
10	43.5	44.5	43.5
20	48.5	49.0	47.0
30	Over 50	over 50	Over 50

EXAMPLE 3

A fiber forming copolymer composed of 65 weight % acrylonitrile, 34.0 weight % vinyl chloride and 1.0% by weight sodium p-styrenesulfonate, was dissolved into acetonitrile to a polymer concentration of 20%, and a variety of magnesium compounds were added respectively in amounts of 10% by weight. The compositions were spun into acetonitrile-water coagulation bath and then flame retardance of which was measured as in Example 1. The results are shown in Table 3.

Table 3

Compound	% added (Based on wt. of polymer)	Limiting oxygen index
control	none	26.0
Magnesium oxide (MgO)	10	40.0
Magnesium hydroxide (Mg(OH) ₂)	10	41.0
Magnesium carbonate (MgCO ₃)	10	40.0
Magnesium phosphate (Octahydrate)	10	27.2
Magnesium pyrophosphate	10	27.3
Magnesium aluminate	10	31.3
Magnesium trisilicate	10	31.2
Magnesium fluoride	10	29.0

EXAMPLE 4

A fiber forming copolymer composed of 39.0 wt% acrylonitrile, and 61.0 wt.% vinyl chloride, was dissolved into acetone to a polymer concentration of 23%. To the solution, a variety of flame retardant additives were added in combination with magnesium monoxide, and spun in the manner of Example 1 to evaluate flame retardance. The results are shown in Table 4.

Table 4

Compound	Percent added (Based on wt. of polymer)	Limiting Oxygen index
Control	None	30.0
Magnesium oxide (MgO)	5	45.0
Antimony Trioxide	5	
Magnesium oxide (MgO)	5	44.0
Zirconium oxide	5	
Magnesium oxide (MgO)	5	43.5
Hexabromobenzene	5	

Table 4 - Continued

Magnesium oxide (MgO)	5	41.0
1,2,3,4-tetrabromobutane	5	
Magnesium oxide (MgO)	5	42.0
Tris-(2,3-dibromopropyl)Phosphate	5	
Magnesium oxide (MgO)	5	44.0
Ammonium polyphosphate	5	
Magnesium oxide (MgO)	5	42.0
Chlorinated paraffin	5	

EXAMPLE 5

A fiber forming copolymer composed of 90 wt.% acrylonitrile, and 10 Wt.% vinyl chloride, was dissolved into dimethylformamide to a polymer concentration of 16%, and after addition of 10% by weight magnesium carbonate, spun into filaments to measure flame retardance as in Example 1. The results are shown in Table 5.

Table 5

Compound	Limiting Oxygen Index
Control	19.5
10% by wt. magnesium carbonate(MgCO ₃)	24.0

EXAMPLE 6

A fiber forming copolymer composed of 20 wt.% acrylonitrile and 80% by wt. vinyl chloride, was dissolved into dimethylformamide to a polymer concentration of 18%, and after addition of 10 wt.% magnesium hydroxide, spun into filaments which were then subjected to measurement for flame retardance by measurement of limiting oxygen indices as in Example 1. The results are shown in Table 6.

Table 6

Compound	Limiting Oxygen Index
Control	45
10% by wt. magnesium hydroxide (Mg(OH) ₂)	Over 50

EXAMPLE 7

In order to test the flame retarding effects of magnesium monoxide, magnesium hydroxide and magnesium carbonate on fibers based on polymers other than acrylonitrile-vinyl chloride copolymer, tests were carried out on the following polymer substrates. Because some of the substrates were unspinnable into fiber form, limiting oxygen indices were measured for specimen in the form of pressed strips in this example. Thus, strips of 1 mm thickness, 10 mm width and 80 mm length were cut out from pressed sheets which had been prepared under pressure of 150 kg/cm² at a temperature of 140° to 165°C, from mixtures of finely granulated polymer substrates and additives, on which

flame retardance was evaluated. As a comparative example, there are also shown data for specimen containing antimony trioxide, which was previously stated to be reputed to exert comparatively marked flame retardance effect on acrylic fibers.

From the results shown in below Table 7, it is evident that the three above-mentioned magnesium compounds show a specific, surprising and marked flame retardant effect only to acrylic copolymers, as above discussed, while no such effect was observed in the cases or other polymer compositions.

Table 7

Substitute Polymer (% by weight)	Control	10% Magnesium oxide(MgO)	10% Magnesium hydroxide(Mg(OH) ₂)	10% Magnesium carbonate(MgCO ₃)	10% Antimony Trioxide
Copolymer of Acrylonitrile-40.2% Vinyl Chloride-60.8%	30.8	49.2	49.0	49.2	35.0
Blend of Polyacrylonitrile-40% Poly(vinyl chloride)-60%	30.3	32.0	—*	—	38.0
Polyacrylonitrile 100%	20.7	21.3	21.4	21.6	22.5
Poly(vinyl chloride)-100%	43.2	44.8	—	—	51.8
Blend of Poly(vinyl chloride)-50% Poly(vinyl alcohol)-50%	29.2	29.0	—	—	36.8
Blend of Poly(vinylidene chloride)-10% Poly(vinyl alcohol)-90%	28.0	26.2	—	—	37.2
Blend of Poly(vinyl chloride)-50% Poly(methyl methacrylate)-50%	22.8	25.2	25.2	—	29.8
Blend of Poly(vinyl chloride)-50% MBS** -50%	21.4	25.8	—	25.2	—

* no experiment

** graft polymer of methyl methacrylate, butadiene, and styrene

EXAMPLE 8

Fiber strength properties were measured on magnesium oxide containing specimen prepared in Example 1. As can be clearly seen in Table 8, no substantial degradation of fiber strength properties took place by addition of magnesium oxide. The results of light exposure resistance by Fade-o-meter, also gave no substantial difference with control specimen wherein no additive were added.

Table 8

		10% MgO added	Control
Tensile Strength	g/denier	2.88	2.89
Elongation	%	31.6	32.2
Young's modulus	kg/mm	428.9	440.8
Knot Strength	g/denier	2.42	2.33

The foregoing description is for purposes of illustration of the invention. Numerous other variations and modifications thereof would be apparent to the worker skilled in the art. All such variations and modifications are to be considered to be within the spirit and scope of the invention.

What is claimed is:

1. An acrylic synthetic fiber having an increased flame retardance consisting essentially of

A. fiber forming copolymer consisting essentially of 20 to 90 weight percent acrylonitrile, 80 to 10 weight percent vinyl chloride and 0 to 30 weight percent ethylenically unsaturated compound copolymerizable with acrylonitrile or vinyl chloride, and

B. 0.5 to 30 weight percent, based on the weight of said fiber forming copolymer, of a flame retarding

additive comprising a magnesium compound selected from the group consisting of magnesium monoxide, magnesium hydroxide, magnesium carbonate and mixtures thereof.

2. The fiber of claim 1, wherein said magnesium compound is in an amount of from 1.0 to 10 weight percent, based on the weight of said fiber forming copolymer.

3. The fiber of claim 1, wherein said flame retarding additive further comprises in combination with said magnesium compound at least one compound selected from the group consisting of antimony trioxide, hexabromobenzene, chlorinated paraffin, tris (2,3-dibromopropyl)phosphate, dibutylamine phosphate and ammonium polyphosphate and mixtures thereof.

4. The fiber of claim 1, wherein said fiber forming copolymer comprises 40 to 70 weight percent acrylonitrile, 60 to 30 weight percent vinyl chloride and 0 to 30 weight percent of ethylenically unsaturated compound copolymerizable with acrylonitrile or vinyl chloride.

5. The fiber of claim 1, wherein said ethylenically unsaturated compound is selected from the group consisting of acrylic acid, methacrylic acid or esters thereof; acrylamide, methacrylamide or N-mono- or dialkyl substitutes thereof; vinyl and vinylidene halides; vinyl carboxylates; vinyl pyridines; styrene or α -substitutes of styrene, β -substitutes of styrene or aromatic nucleous -substitutes of styrene; allyl- or methallylsulfonic acid or salts thereof and mixtures thereof.

6. A method of producing an acrylic synthetic fiber having an increased flame retardance, comprising the steps of preparing and spinning a spinning solution comprising an organic solvent and the following components

A. a fiber forming copolymer consisting essentially of 20 to 90 weight % acrylonitrile, 80 to 10 weight % vinyl chloride and 0 to 30 weight % ethylenically unsaturated compound copolymerizable with acrylonitrile or vinyl chloride, and

B. 0.5 to 30% based on the weight of said fiber forming copolymer, of a flame retardant additive comprising a magnesium compound selected from the group consisting of magnesium monoxide, magnesium hydroxide, magnesium carbonate and mixtures thereof.

7. The method of claim 6, wherein said magnesium is 1.0 to 10.0 weight % based on the weight of said fiber forming copolymer.

8. The method of claim 6, wherein said flame retardant additive further comprises in combination with said magnesium compound at least one compound selected from the group consisting of antimony trioxide, hexabromobenzene, chlorinated paraffin, tris (2,3-dibromopropyl) phosphate, dibutylamine phosphate, ammonium polyphosphate and mixtures thereof.

9. The method of claim 6, wherein addition of said magnesium compound to said fiber forming copolymer

is carried out either in the polymerization stage or in the spinning stage.

10. The method of claim 6, wherein said fiber forming copolymer consists essentially of 40 to 70 wt.% acrylonitrile, 60 to 30 wt.% vinyl chloride and 0 to 30 wt.% ethylenically unsaturated compound copolymerizable with acrylonitrile or vinyl chloride.

11. The method of claim 6, wherein said ethylenically unsaturated compound is selected from the group consisting of acrylic acid, methacrylic acid or esters thereof; acrylamide, methacrylamide or N-mono- or dialkyl substitutes thereof; vinyl or vinylidene halides; vinyl carboxylates; vinyl pyridines; styrene or α -substitutes of styrene, β -substitutes of styrene or aromatic nucleus substitutes of styrene; allyl- or methallyl sulfonic acid or salts thereof, and mixtures thereof.

12. The method of claim 6, wherein said copolymer is produced by emulsion polymerization, solution polymerization or suspension polymerization.

13. The method of claim 6, wherein said spinning is carried out by dry spinning process or wet spinning process.

14. The method of claim 6, wherein said organic solvent is selected from the group consisting of acetone, acetonitrile, dimethylformamide, dimethylacetamide, and mixtures thereof.

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