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3,708,326

STABILIZATION OF ACRYLIC FIBERS AND FILMS
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18 Claims

ABSTRACT OF THE DISCLOSURE

An improved process for the thermal stabilization of an acrylic fibrous material or film is provided. The fibrous precursor or film is impregnated with a stabilization promoting agent by contact with a solution of the same provided at a moderate temperature, dried to remove the solvent, and heated in an oxygen-containing atmosphere at a more highly elevated temperature until a stabilized fibrous material or film is formed. The stabilization promoting agents employed in the present process are mineral acids, sulfonic acids, and certain carboxylic acids. The resulting stabilized fibrous material or film is non-burning, and may be utilized as a fire resistant fiber, fabric, or film, or optionally carbonized or carbonized and graphitized to form a carbonaceous fibrous material or film.

BACKGROUND OF THE INVENTION

In the past procedures have been proposed for the conversion of fibers formed from acrylic polymers to a modified form possessing enhanced thermal stability. Such modification has generally been accomplished by heating fibrous material in an oxygen-containing atmosphere at a moderate temperature for an extended period of time.

U.S. Pats. Nos. 2,913,802 to Barnett and 3,285,696 to Tsunoda disclose processes for the conversion of fibers of acrylonitrile homopolymers or copolymers to a heat resistant form. The stabilization of fibers of acrylonitrile homopolymers and copolymers in an oxygen-containing atmosphere involves (1) a chain scission and oxidative cross-linking reaction of adjoining molecules as well as (2) a cyclization reaction of pendant nitrile groups. It is generally recognized that the rate at which the stabilization reaction takes place increases with the temperature of the oxygen-containing atmosphere. However, the stabilization reaction must by necessity be conducted at relatively low temperatures (i.e. below about 300° C.), since the cyclization reaction is exothermic in nature and must be controlled if the original fibrous configuration of the material undergoing stabilization is to be preserved. Accordingly the stabilization reaction tends to be time consuming, and economically demanding because of low productivity necessitated by the excessive time requirements. Prior processes proposed to shorten the period required by the stabilization reaction include that disclosed in U.S. Pat. No. 3,416,874. See also the process of commonly assigned U.S. Ser. No. 777,901, filed Nov. 21, 1968 (now U.S. Pat. No. 3,592,595) of Klaus H. Gump and Dagobert E. Stuetz wherein the cyclization of pendant nitrile groups of the acrylic fibrous material is catalytically enhanced while the fibrous material is immersed in a solution of a Lewis acid at a temperature of about 160 to 260° C.

While stabilized acrylic fibrous materials may be used directly in applications where a non-burning fiber is required, demands for the same have been increasingly presented by manufactures of carbonized fibrous materials. Carbonized fibrous materials are commonly formed by heating a stabilized acrylic fibrous material

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in an inert atmosphere, such as nitrogen or argon, at a more highly elevated temperature. During the carbonization reaction elements such as nitrogen, oxygen, and hydrogen are substantially expelled. Accordingly, the term "carbonized" as used in the art commonly designates a material consisting of at least about 90 percent carbon by weight, and generally at least about 95 percent carbon by weight. Depending upon the conditions under which a carbonized fibrous material is processed, it may or may not contain graphitic carbon as determined by the characteristic X-ray diffraction pattern of graphite. See, for instance, commonly assigned U.S. Ser. No. 777,275, filed Nov. 20, 1968, now abandoned, of Charles M. Clarke for a preferred procedure for forming carbonized and graphitized fibrous materials from a stabilized acrylic fibrous material.

It is an object of the invention to provide an improved process for enhancing the thermal stability of a shaped acrylic article.

It is an object of the invention to provide an improved process for the flame-proofing of a fibrous material or film formed from acrylic polymers.

It is an object of the invention to provide a process wherein the thermal stabilization of an acrylic fibrous material or film is accelerated.

It is another object of the invention to provide an improved process for the stabilization of fibrous materials or films formed from acrylic polymers which results in a product which is suitable for carbonization, or carbonization and graphitization.

It is a further object of the invention to provide a process for converting a fibrous acrylic material or film to a stabilized form possessing essentially the identical configuration as the starting material.

These and other objects, as well as the scope, nature, and utilization of the invention will be apparent from the following detailed description and appended claims.

SUMMARY OF THE INVENTION

It has been found that a process for the stabilization of an acrylic fibrous material or film selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers containing at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith comprises (a) impregnating said fibrous material or film with a catalytic quantity of a stabilization promoting agent selected from the group consisting of hydrochloric acid, phosphoric acid, sulfuric acid, nitric acid, methane sulfonic acid, aromatic sulfonic acids, and carboxylic acids having a pK_A value below about 4.5 by contact with a solution of said agent in a solvent incapable of dissolving said acrylic fibrous material or film having a temperature of about 0 to 100° C. while preserving the original configuration of said fibrous material or film essentially intact, (b) drying said fibrous material or film to substantially remove said solvent therefrom, and (c) heating said resulting impregnated and dried fibrous material or film in an oxygen-containing atmosphere at a temperature of about 200 to 320° C. until a stabilized fibrous material or film is formed which retains its original configuration essentially intact and which is non-burning when subjected to an ordinary match flame.

DESCRIPTION OF PREFERRED EMBODIMENTS

The acrylic shaped articles, i.e. fibers or films, undergoing stabilization in the present process may be formed by conventional solution spinning techniques (i.e., may be dry spun or wet spun) or by conventional solvent casting techniques, and are commonly drawn to increase their orientation. As is known in the art, dry spinning is commonly conducted by dissolving the polymer in an appro-

appropriate solvent, such as N,N-dimethylformamide or N,N-dimethylacetamide, and passing the solution through an opening of predetermined shape into an evaporative atmosphere (e.g., nitrogen) in which much of the solvent is evaporated. Wet spinning is commonly conducted by passing a solution of the polymer through an opening of predetermined shape into an aqueous coagulation bath. Casting is commonly conducted by placing a solution containing the polymer upon a support, and evaporating the solvent therefrom.

The acrylic polymer utilized as the starting material is formed primarily of recurring acrylonitrile units. For instance, the acrylic polymer should generally contain not less than about 85 mol percent of acrylonitrile units and not more than about 15 mol percent of units derived from a monovinyl compound which is copolymerizable with acrylonitrile such as styrene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl pyridine, and the like, or a plurality of such monomers.

The preferred acrylic precursor is an acrylonitrile homopolymer. Preferred acrylonitrile copolymers contain at least about 95 mol percent of acrylonitrile units and up to about 5 mol percent of one or more monovinyl units copolymerized therewith.

The acrylic precursor is preferably provided as a continuous length of a fibrous material and may be in a variety of physical configurations. For instance, the acrylic fibrous materials may be present in the form of continuous lengths of multifilament yarns, tows, tapes, strands, cables, or similar fibrous assemblages. Alternatively, acrylic films of relatively thin thickness, e.g. about 1 to 10 mils, may be selected as the precursor.

When the starting material is a continuous multifilament yarn, a twist may be imparted to the same to improve the handling characteristics. For instance, a twist of about 0.1 to 5 t.p.i., (i.e. about 0.1 to 5 turns per inch), and preferably about 0.3 to 1.0 t.p.i. may be utilized. Also a false twist may be used instead of or in addition to a real twist. Alternatively, one may select bundles of fibrous material which possess essentially no twist.

The starting material may be drawn in accordance with conventional techniques in order to improve its orientation. For instance, the starting material may be drawn by stretching while in contact with a hot shoe at a temperature of about 140 to 160° C. Additional representative drawing techniques are disclosed in U.S. Pats. Nos. 2,455,173; 2,948,581; and 3,122,412. It is recommended that the acrylic fibrous materials selected for use in the process be drawn to a single filament tenacity of at least about 3 grams per denier. If desired, however, the starting material may be more highly oriented, e.g. drawn up to a single filament tenacity of about 7.5 to 8 grams per denier, or more. Acrylic films optionally may be either uniaxially or biaxially oriented.

Prior to heating the acrylic fibrous material or film in an oxygen-containing atmosphere to accomplish the desired stabilization (as described hereafter), the precursor is impregnated with a catalytic quantity of a stabilization promoting agent by contact with a solution of the same, and is dried to substantially remove the solvent used in the formation of the solution.

Suitable mineral acid stabilization promoting agents are hydrochloric acid, phosphoric acid, sulfuric acid, and nitric acid. The preferred mineral acid for use in the process is orthophosphoric acid.

Suitable sulfonic acid stabilization promoting agents are methane sulfonic acid and the aromatic sulfonic acids. Representative aromatic sulfonic acids include: o-toluene sulfonic acid, m-toluene sulfonic acid, p-toluene sulfonic acid, 2,4-xylene sulfonic acid, benzene sulfonic acid, m-nitrobenzene sulfonic acid, m-benzene disulfonic acid, toluene-2,4-disulfonic acid, p-chlorobenzene sulfonic acid, 2-naphthalenesulfonic acid, etc. The preferred aro-

matic sulfonic acid for use in the process is p-toluene sulfonic acid.

Suitable carboxylic acid stabilization promoting agents are those carboxylic acids having a pK_A value below about 4.5. Such pK_A values may be conventionally ascertained by determining the negative logarithm of the K_A for a given carboxylic acid in a 0.1 M aqueous solution at 25° C. Those carboxylic acids possessing a pK_A above about 4.5 (e.g. acetic acid) have been found to possess insufficient strength to promote the stabilization reaction to any significant degree. The carboxylic acids may be monobasic or dibasic. Representative carboxylic acids for use in the process include: formic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, fluoroacetic acid, trifluoroacetic acid, alpha-chlorobutyric acid, beta-chlorobutyric acid, methoxyacetic acid, vinylacetic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, benzoic acid, o-nitrobenzoic acid, phenylacetic acid, etc. The preferred carboxylic acid for use in the process is formic acid.

The nature of the solvent utilized to form the solution of the stabilization promoting agent which is contacted with the acrylic precursor during the impregnation step of the process may be varied widely. It is essential that the solvent have the ability to dissolve the stabilization promoting agent while being incapable of dissolving or otherwise adversely influencing the acrylic material undergoing treatment. It is not essential that the stabilization promoting agent be capable of undergoing ionization in the particular solvent selected. The solvent preferably also has the ability to cause the swelling of the acrylic precursor and to thereby more readily facilitate impregnation. Representative solvents for the stabilization promoting agent include water, acetonitrile, pyridine, tetrahydrofuran, etc., and mixed solvents such as mixtures of water with N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, and N-methyl-2-pyrrolidone, etc. The preferred solvent for use with many of the stabilization promoting agents is water.

The concentration of a mineral acid stabilization promoting agent in the solution used during the impregnation step is commonly from about 5 to 85 percent by weight. For instance, a 37 percent by weight aqueous hydrochloric acid solution may be conveniently selected, or a 30 to 85 percent by weight aqueous solution of orthophosphoric acid. The concentration of sulfonic acid and carboxylic acid stabilization promoting agents in the solution used during the impregnation step is commonly about 1 to 20 percent by weight, and preferably about 1 to 10 percent by weight, e.g. about 5 percent by weight. The concentration of the stabilization promoting agent in the solution is adjusted to a level wherein the configuration of the acrylic precursor is not adversely influenced during the impregnation step, such as by dissolution, decomposition, or degradation. When an extremely strong acid serves as the stabilization promoting agent, then it is advantageously provided in a relatively lower concentration than an acid of moderate strength.

The impregnation step of the process may be conducted on either a batch or a continuous basis. For instance, a continuous length of the acrylic precursor may be wound upon a mandrel or other support and immersed in the solution containing the stabilization promoting agent, or continuously passed through the same, e.g. in the direction of its length while guided by rollers or other guide means. Contact between the acrylic material and the solution may alternatively be made by spraying or other padding technique as will be apparent to those skilled in the art. During impregnation the solution is provided at a moderate temperature of about 0 to 100° C., and preferably at a temperature of about 10 to 40° C. Higher temperatures are to be avoided in order to diminish the possibility of the premature chemical modification of the acrylic fibrous material at this point in the process. Accordingly a catalytic quantity of the stabilization promoting agent is able

to substantially impregnate the interior of the precursor fiber or film without the retardation of diffusion resulting from the cyclization of pendant nitrile groups at the surface. Also, more highly elevated temperatures tend to promote excessive shrinkage. Contact times commonly range from 20 minutes to 24 hours, or more, depending primarily upon the concentration of the stabilization promoting agent in the solution, and relative freedom of access of the solution throughout the acrylic material undergoing impregnation. For instance, if a fibrous material is provided as a relatively compact assemblage, longer contact times are required.

Following impregnation the acrylic fibrous material or film is next dried so that the solvent is substantially removed, and a catalytic quantity of the stabilization promoting agent provided in intimate association therewith. The drying step may be conducted in any convenient manner. The impregnated acrylic precursor may be simply exposed to ambient conditions until solvent adhering thereto is substantially evaporated. For instance, drying may be conducted by exposure to a gaseous atmosphere at a temperature of about 10 to 40° C. The drying step can, of course, be expedited by exposure to a circulating gaseous atmosphere at a more highly elevated temperature, or even in the same zone where the stabilization reaction is carried out (as described hereafter). It is recommended, however, that drying be conducted at a moderate temperature below about 100° C. because of the possibility of adversely influencing the tensile properties of the acrylic material during the vigorous evolution of solvent at a more highly elevated temperature. The resulting impregnated and dried acrylic material commonly contains about 0.1 to 5 percent by weight of the stabilization promoting agent.

In a preferred embodiment of the process the acrylic material immediately after contact with the solution of the stabilization promoting agent and prior to drying is rinsed with additional solvent in order to remove any excess stabilization promoting agent adhering to its surface while continuing to maintain the desired degree of impregnation. Such rinsing is particularly recommended when the stabilization promoting agent is phosphoric acid or sulfuric acid. In the absence of such rinse step with an acrylic fibrous material there may be a tendency during the stabilization step for adjoining fibers to fuse in areas where excess agent adheres to the fiber surface.

The resulting impregnated and dried acrylic material is heated in an oxygen-containing atmosphere at a temperature of about 200 to about 320° C. until a stabilized fibrous product or film is formed which retains its original configuration essentially intact and which is non-burning when subjected to an ordinary match flame. In a preferred embodiment of the process, the oxygen-containing atmosphere is air. Preferred temperatures for the oxygen-containing atmosphere range from about 250 to 320° C., and most preferably about 270 to 290° C. If desired, the fibrous material or film may be exposed to a temperature gradient wherein the temperature is progressively increased.

For best results, uniform contact during the stabilization reaction with molecular oxygen throughout all portions of the impregnated acrylic material is encouraged. Such uniform reaction conditions can best be accomplished by limiting the mass of fibrous material or film at any one location so that heat dissipation from within the interior of the same is not unduly impaired, and free access to molecular oxygen is provided. For instance, the acrylic fibrous material or film may be placed in the oxygen-containing atmosphere while wound upon a support to a limited thickness. In a preferred embodiment of the invention, the impregnated acrylic fibrous material or film is continuously passed in the direction of its length through the heated oxygen-containing atmosphere. For instance, a continuous length of the acrylic fibrous material or film may be passed through a circulating oven

or the tube of a muffle furnace. The speed of passage through the heated oxygen-containing atmosphere will be determined by the size of the heating zone and the desired residence time. A particularly preferred continuous heat treatment is disclosed in U.S. Ser. No. 749,957, filed Aug. 5, 1968, which is herein incorporated by reference.

The period of time required to complete the stabilization reaction within the oxygen-containing atmosphere is generally inversely related to the temperature of the atmosphere, and is also influenced by the denier of the acrylic fibrous material or the thickness of the film undergoing treatment, and the concentration of molecular oxygen in the atmosphere. Treatment times in the oxygen-containing atmosphere accordingly commonly range from about 15 minutes to 20 hours. In preferred embodiments of the process treatment times frequently range from 20 to 25 minutes. Regardless of the stabilization temperature selected within the range of about 200 to 320° C., the presence of the acrylic fibrous material or film in impregnated form while in intimate association with the stabilization promoting agent results in an accelerated stabilization reaction for a given temperature.

The stabilized acrylic fibrous materials or films formed in accordance with the present process are black in appearance, retain essentially the same configuration as the starting material, are non-burning when subjected to an ordinary match flame, commonly have a bound oxygen content of at least 7 (e.g. 7 to 12) percent by weight as determined by the Unterzaucher or other suitable analysis, and commonly contain from about 50 to 65 percent carbon by weight.

The theory whereby the agents herein discussed serve to accelerate the stabilization reaction is considered complex and incapable of simple explanation. It is believed, however, that oxygen cross-linking as well as the cyclization reaction are catalyzed and proceed at an accelerated rate.

Since the oxidative cross-linking reaction is accelerated in the present process, one optionally may elect to carry out the stabilization reaction at a less severe temperature than heretofore commonly utilized. Under milder temperature conditions a more uniform stabilized product may be achieved in the absence of undue chain degradation.

The stabilized fibrous material resulting from the stabilization treatment of the present invention is suitable for use in applications where a fire resistant fibrous material is required. For instance, non-burning fabrics may be formed from the same. As previously indicated, the stabilized acrylic fibrous materials are particularly suited for use as intermediates in the production of carbonized fibrous materials. Such amorphous carbon or graphitic carbon fibrous products may be incorporated in a binder or matrix and serve as a reinforcing medium. The carbon fibers may accordingly serve as a lightweight load bearing component in high performance composite structures which find particular utility in the aerospace industry.

The stabilized film resulting from the stabilization treatment is suitable for use in applications where a fire resistant sheet material is required. Such stabilized films may also be utilized as intermediates in the production of carbonized films. Such carbonized films may be utilized in the formation of lightweight high temperature resistant laminates when incorporated in a matrix material (e.g. an epoxy resin).

The following examples are given as specific illustrations of the invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples.

EXAMPLE I

A continuous length of an 800 fil. dry spun acrylonitrile homopolymer continuous filament yarn having a total denier of 1200 was selected as the starting material. The

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yarn was initially dry spun from a solution of the same in N,N-dimethylformamide solvent into an evaporative atmosphere of nitrogen. The yarn was spun as a 40 fil. bundle, and plied to form the 800 fil. yarn which exhibited a twist of about 0.5 t.p.i. The yarn was next drawn at a draw ratio of about 5:1 to a single filament tenacity of about 4 grams per denier by stretching while passing over a hot shoe at a temperature of about 160° C. for a residence time of about 0.5 second.

Twenty meters of the yarn were wound in 12 layers upon a glass bobbin having a diameter of 1.5 inch using a yarn traverse. The bobbin containing the yarn was next immersed for 24 hours in a 60 percent by weight aqueous solution of orthophosphoric acid provided at ambient temperature (i.e. about 25° C.). The impregnation of the yarn was promoted during the immersion step by rotating the bobbin while present in the aqueous solution of orthophosphoric acid.

The bobbin containing the impregnated yarn was removed from the solution and was unwound from the bobbin and continuously passed through a vessel of water provided at ambient temperature (i.e. about 25° C.) for a residence time of about 10 seconds. While passing through the vessel of water, excess phosphoric acid was removed from the fiber surface.

The washed yarn was next packaged by loosely winding upon a perforated bobbin and was allowed to dry by standing in air at ambient temperature (i.e. about 25° C.) for 18 hours. During the drying step water was evaporated leaving the fibrous material in intimate association with about 0.3 percent by weight phosphoric acid.

The impregnated and dried fibrous material was next stabilized on a continuous basis by heating in a circulating air atmosphere provided in a Lindberg muffle furnace having a length of 4 feet. The muffle furnace had an internal diameter of 1 inch and was provided with variable temperature control means whereby a temperature gradient was provided along its length. Axially aligned within the muffle furnace was a section of copper tubing having an internal diameter of 0.5 inch which extended 1.5 inches beyond each end of the muffle furnace. The yarn was continuously unwound from a motor driven bobbin while under a tension of 50 grams and was passed through the copper tubing of the muffle furnace while suspended therein at a rate of about 2.4 inches per minute. While passing through the heating zone, the yarn was subjected to a temperature gradient wherein the temperature of the air with which it was in contact increased from about 250° C. to about 300° C. at a rate of about 6° C. per minute, and from about 300 to about 310° C. at a rate of about 3° C. per minute where it was maintained for about 7 minutes. The total residence time within the heating zone was about 20 minutes. As the stabilized yarn exited from the heating zone, it was passed to a traverse take-up.

The resulting stabilized yarn was black in appearance, flexible, had a textile-like hand, retained its original fibrous configuration essentially intact, was non-burning when subjected to an ordinary match flame, retained strength after glowing in a match flame, and had an oxygen content in excess of 11 percent by weight.

In a control run, an identical sample of the acrylonitrile homopolymer yarn was passed through the muffle furnace in an identical manner with the exception that it had not been previously impregnated with phosphoric acid. The resulting yarn had an oxygen content of only 7 percent by weight indicating that the stabilization reaction failed to progress to the degree indicated in Example I wherein the phosphoric acid served to promote the same.

The resulting stabilized yarn of Example I was carbonized and graphitized in accordance with the teachings of U.S. Ser. No. 777,275, filed Nov. 20, 1968, now abandoned, of Charles M. Clarke, which are herein incorporated by reference. The graphite yarn exhibited satisfactory tensile properties,

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EXAMPLE II

Example I was repeated with the exception that the yarn was immersed for 22 hours in a 30 percent by weight aqueous solution of orthophosphoric acid.

Substantially similar results were achieved.

EXAMPLE III

Example I was repeated with the exception that the yarn was immersed for 24 hours in equal parts of orthophosphoric acid and acetonitrile solvent.

Substantially similar results were achieved.

EXAMPLE IV

Example I was repeated with the exception that the yarn was immersed for 24 hours in 37 percent by weight aqueous solution of hydrochloric acid.

Substantially similar results were achieved.

EXAMPLE V

Example I was repeated with the exception that the yarn was immersed for 24 hours in a 5 percent by weight aqueous solution of p-toluene sulfonic acid.

Substantially similar results were achieved.

EXAMPLE VI

Example I was repeated with the exception that the yarn was immersed for 16 hours in a 5 percent by weight aqueous solution of 2,4-xylene sulfonic acid.

Substantially similar results were achieved.

EXAMPLE VII

Example I was repeated with the exception that the yarn was immersed for 16 hours in a 5 percent by weight aqueous solution of oxalic acid.

Substantially similar results were achieved.

EXAMPLE VIII

Example I was repeated with the exception that the yarn was immersed for 48 hours in a 5 percent by weight aqueous solution of benzoic acid.

Substantially similar results were achieved.

EXAMPLE IX

Example I was repeated with the exception that the yarn was immersed for 24 hours in a 5 percent by weight aqueous solution of o-nitrobenzoic acid.

Substantially similar results were achieved.

EXAMPLE X

A rectangular section of biaxially oriented acrylonitrile homopolymer film having a thickness of 2 mils is selected as the starting material. The film is impregnated with a formic acid stabilization promoting agent by immersion for 48 hours in a 5 percent by weight aqueous solution of formic acid provided at room temperature (i.e. about 25° C.). The impregnated film is next rinsed by immersion for 1 minute in water provided at room temperature (i.e. about 25° C.), and dried at ambient conditions for 12 hours. The resulting dried film is next suspended for 60 minutes in a circulating air oven provided at 270° C. wherein it is converted to a stabilized form while retaining its original configuration essentially intact. The resulting stabilized film is non-burning when subjected to an ordinary match flame, is black in appearance, and contains a bound oxygen content in excess of about 7 percent by weight as determined by the Unterzaucher analysis.

Although the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.

We claim:

1. A process for the stabilization of an acrylic fibrous material or film selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers

containing at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith comprising:

- (a) impregnating said fibrous material or film with a catalytic quantity of a stabilization promoting agent selected from the group consisting of hydrochloric acid, phosphoric acid, sulfuric acid, nitric acid, methane sulfonic acid, aromatic sulfonic acids, and carboxylic acids having a pK_A value below about 4.5 by contact with a solution of said agent in a solvent incapable of dissolving said fibrous material or film having a temperature of about 0 to 100° C. while preserving the original configuration of said fibrous material or film essentially intact,
 - (b) drying said fibrous material or film to substantially remove said solvent therefrom, and
 - (c) heating said resulting impregnated and dried fibrous material or film in an oxygen-containing atmosphere at a temperature of about 200 to 320° C. until a stabilized fibrous material or film is formed which retains its original configuration essentially intact and which is non-burning when subjected to an ordinary match flame.
2. A process according to claim 1 wherein the precursor is a fibrous material.
 3. A process according to claim 1 wherein the precursor is a film.
 4. A process according to claim 2 wherein said acrylic fibrous material is an acrylonitrile homopolymer.
 5. A process according to claim 2 wherein said acrylic fibrous material is an acrylonitrile copolymer containing at least about 95 mol percent of acrylonitrile units and up to about 5 mol percent of one or more monovinyl units copolymerized therewith.
 6. A process according to claim 2 wherein said acrylic fibrous material has been drawn to a single filament tenacity of at least about 3 grams per denier.
 7. A process according to claim 2 wherein said acrylic fibrous material is a continuous multifilament yarn.
 8. A process according to claim 1 wherein said solution of said agent has a temperature of about 10 to 40° C. during said impregnation step (a).
 9. A process according to claim 1 wherein said stabilization promoting agent is phosphoric acid.
 10. A process according to claim 1 wherein said stabilization promoting agent is an aromatic sulfonic acid.

11. A process according to claim 1 wherein said aromatic sulfonic acid is p-toluene sulfonic acid.

12. A process according to claim 1 wherein said carboxylic acid is formic acid.

13. A process according to claim 1 wherein said solvent is water.

14. A process according to claim 1 wherein said solvent is acetonitrile.

15. A process according to claim 1 wherein said acrylic fibrous material or film is rinsed to remove any excess stabilization promoting agent adhering to its surface immediately following said impregnation step (a).

16. A process according to claim 1 wherein said drying step (b) is conducted at a temperature of about 10 to 40° C.

17. A process according to claim 1 wherein said resulting impregnated and dried fibrous material or film contains said stabilization promoting agent in a concentration of about 0.1 to 5 percent by weight immediately prior to heating in said oxygen-containing atmosphere.

18. A process according to claim 1 wherein said oxygen-containing atmosphere is air and said resulting impregnated and dried fibrous material or film is heated by the continuous passage therethrough in the direction of its length.

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