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3,779,983

**ACRYLIC FIBERS AND FILMS WHICH PARTICULARLY ARE SUITED FOR THERMAL STABILIZATION**

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No Drawing. Filed June 1, 1972, Ser. No. 258,788

Int. Cl. C08f 27/06

U.S. Cl. 260—45.7 S

12 Claims

**ABSTRACT OF THE DISCLOSURE**

An improved process is provided for the production of stabilized acrylic fibers and films. A minor quantity of an alkali metal salt of an organic sulfonate is provided in intimate association with an acrylic fibrous material or film and is incorporated therein in a non-polymerized form. Upon heating (preferably while present in an oxygen-containing atmosphere) the thermal stabilization reaction is promoted by the presence of the alkali metal salt of an organic sulfonate. The resulting stabilized fibrous material or film is flexible and 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 a fibrous material in an oxygen-containing atmosphere at a moderate temperature for an extended period of time.

U.S. Pat. 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 shaped articles of acrylonitrile homopolymers and copolymers in an oxygen-containing atmosphere commonly 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, in the past the stabilization reaction must by necessity at least initially be conducted at relatively low temperatures (i.e. below about 300° C.), since the cyclization reaction is known to be exothermic in nature and must be controlled if the original configuration of the material undergoing stabilization is to be preserved. Accordingly the stabilization reaction has tended 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 processes of commonly assigned U.S. Pat. Nos. 3,592,595; 3,656,882; and 3,656,883; and the processes of commonly assigned U.S. Ser. Nos. 777,902, filed Nov. 21, 1968 (now U.S. Pat. No. 3,647,770); 109,669 and 109,672 (now U.S. Pat. No. 3,708,326), filed Jan. 25, 1971; and 200-183 and 200,184, filed Nov. 18, 1971.

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 the manufacturers of carbonized fibrous materials. Carbonized fibrous materials are commonly formed by heating a stabilized acrylic fibrous material in an inert atmosphere, such as nitrogen or argon, at a more

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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, of Charles M. Clarke (now abandoned) for a preferred procedure for forming continuous lengths of carbonized and graphitized fibrous materials from a stabilized acrylic fibrous material.

It is an object of the invention to provide an improved process for forming thermally stabilized shaped acrylic articles.

It is an object of the invention to provide an improved process for forming dimensionally stable flexible flame-proofed fibrous materials and films derived from an acrylic polymer.

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 forming stabilized fibrous materials and films derived 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 an acrylic fibrous material or film to a stabilized form possessing substantially 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 in 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 through thermal treatment, that an improved process results by:

(a) Providing the acrylic fibrous material or film in intimate association with about 0.2 to 10 percent by weight of an alkali metal salt of an organic sulfonate, with the alkali metal salt of an organic sulfonate being incorporated therein in a nonpolymerized form and being capable of promoting the thermal stabilization thereof, and

(b) Heating the acrylic fibrous material or film at a temperature of about 240 to 310° C. until a stabilized fibrous material or film is formed which retains its original configuration substantially intact and which is non-burning when subjected to an ordinary match flame.

The acrylic fibrous material or film utilized in the improved process of the present invention consists essentially of (1) an acrylic polymer 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, and (2) about 0.2 to 10 percent by weight of an alkali metal salt of an organic sulfonate with the alkali metal salt of an organic sulfonate being incorporated therein in a non-polymerized form and being capable of promoting the thermal stabilization thereof upon heating.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Stabilized acrylic fibers and films may be conveniently formed in accordance with the process of the present invention by:

(a) Providing a solution of (1) an acrylic polymer 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, (2) a minor quantity of a stabilization promoting agent comprising an alkali metal salt of an organic sulfonate, and (3) a solvent for the acrylic polymer and the alkali metal salt of an organic sulfonate, with the alkali metal salt of an organic sulfonate being dissolved in said solvent in a non-polymerized form,

(b) Forming from the solution an acrylic fibrous material or film having incorporated therein a minor quantity of the alkali metal salt of an organic sulfonate in a non-polymerized form, and

(c) Heating the acrylic fibrous material or film at a temperature of about 240 to 310° C. until a stabilized fibrous material or film is formed which retains its original configuration substantially intact and which is non-burning when subjected to an ordinary match flame.

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 pendent nitrile groups present within the acrylic precursor are substantially uncyclized.

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 stabilization promoting agent which is incorporated within the acrylic fibrous material or film prior to the heating of the same is an alkali metal salt of an organic sulfonate. The cation of the salt may be any of the alkali metals, and is preferably sodium or potassium. The alkali metal salt of an organic sulfonate accordingly contains one or more  $\text{—SO}_2\text{OX}$  groups attached to an organic molecule where X is an alkali metal. The alkali metal salt of an organic sulfonate is provided within the acrylic fibrous material or film in a free, non-polymerized form and is chemically uncombined with the acrylic polymer. For instance, if the alkali metal salt of the organic sulfonate contains a polymerizable vinyl group within its molecule it is non-polymerized.

The chemical structure of the alkali metal salt of an organic sulfonate is not critical and may be varied widely so long as it possesses the requisite  $\text{—SO}_2\text{OX}$  functional group. For instance, common anionic detergents of a sulfonate type may be selected for use in the process. These compounds are commonly alkali metal salts of an alkylaryl sulfonate (e.g. an alkylbenzene sulfonate). One or more straight or branched chain alkyl group (e.g. having up to about 30 carbon atoms and preferably 10 to 20 carbon atoms) may serve as a side chain positioned upon an aryl nucleus of the organic sulfonate. The readily available and relatively inexpensive alkali metal salts of alkylaryl sulfonates are preferably selected. Representative alkali metal salts of alkylaryl sulfonates include:

sodium dodecylbenzene sulfonate,  
sodium toluene sulfonate,  
sodium isopropyl naphthalene sulfonate,  
sodium isobutyl naphthalene sulfonate,  
sodium mesitylene sulfonate,

sodium monobutyl diphenyl monosulfonate,  
sodium ethyl benzene sulfonate.

Other representative alkali metal salts of organic sulfonates which may be employed include:

sodium methallyl sulfonate,  
sodium lauryl sulfonate,  
sodium benzene disulfonate,  
sodium betanaphthalene sulfonate,  
sodium polypropylene sulfonate,  
sodium alkenyl-1-sulfonate (see U.S. Patent 3,444,191),  
sodium tetrahydronaphthalene sulfonate.

Sodium methallyl sulfonate is an example of stabilization promoting agents which possesses a polymerizable vinyl group. In the present process such vinyl is non-polymerized and forms no part of the main polymer chain within the acrylic polymer. For instance, the sodium methallyl sulfonate or other polymerizable sulfonate salt is brought into intimate association with the acrylic polymer following the polymerization of the same and in the absence of polymerization catalysts, etc.

The particularly preferred alkali metal salts of organic sulfonates for use in the present process are sodium dodecylbenzene sulfonate, sodium methallyl sulfonate, sodium benzene disulfonate, sodium lauryl sulfonate, etc.

Suitable solvents for use in the present process are capable of dissolving both the acrylic polymer and the alkali metal salt of an organic sulfonate. Representative organic solvents include N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, butyrolactone, and N-methyl-2-pyrrolidinone. The preferred solvents are those which are commonly utilized during the spinning of fibers from acrylonitrile homopolymers and copolymers. The particularly preferred solvents are N,N-dimethylformamide and N,N-dimethylacetamide.

The concentration of the acrylic polymer in the solvent may be varied widely, e.g. about 5 to about 30 percent by weight based upon the weight of the solvent. Preferred concentrations range from 10 to 25 percent acrylic polymer by weight based upon the weight of the solvent.

The alkali metal salt of an organic sulfonate is present in the solution of acrylic polymer in a minor quantity, i.e. about 1 to 20 percent by weight based upon the weight of the acrylic polymer. The concentration employed will vary with the fiber or film forming technique selected as described hereafter. In a preferred embodiment of the process the alkali metal salt of an organic sulfonate is present in a concentration of about 1 to 10 percent by weight based upon the weight of the acrylic polymer.

In a preferred embodiment of the process wherein N,N-dimethylacetamide serves as solvent the solution of acrylic polymer and alkali metal salt of an organic sulfonate additionally contains 0.1 to 5.0 percent by weight based upon the total weight of the solution (0.5 to 2.0 percent in a particularly preferred embodiment) of lithium chloride dissolved therein. The incorporation of lithium chloride serves the function of lowering and preserving upon standing the viscosity of the solution. The desired solution fluidity and mobility for spinning or casting are accordingly efficiently maintained even upon the passage of time.

The solution of the acrylic polymer and the alkali metal salt of an organic sulfonate may be formed by any convenient technique. For instance, the acrylic polymer while in particulate form together with the alkali metal salt of an organic sulfonate may be added to the solvent with stirring while maintained at about 10 to 100° C. (preferably 50 to 90° C.). It is recommended that any heating of the solution in excess of about 100° C. be of limited duration, i.e. no more than a few minutes, so that no substantial degree of cyclization of pendant nitrile groups within the acrylic polymer occurs while dissolved in the solvent.

The solution is preferably filtered such as by passage through a plate and frame press provided with an appro-

appropriate filtration medium, prior to forming a fibrous material or film.

The solution containing the acrylic polymer and the alkali metal salt of an organic sulfonate is preferably converted into a fiber or film through the substantial elimination of the solvent following extrusion through a shaped orifice employing conventional solution spinning techniques (i.e. by dry spinning or wet spinning). As is known in the art, dry spinning is commonly conducted by 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 the solution through an opening of predetermined shape into a suitable coagulation bath. Acrylic films may also be formed by casting wherein a layer of the solution is placed upon a support and the solvent evaporated.

When wet spinning is utilized in the fiber or film forming step of the process, a coagulation bath is selected which is capable of preserving a minor quantity of the alkali metal salt of an organic sulfonate within the resulting fibrous material or film. More specifically, the bath preferably exhibits no propensity to leach out and dissolve the alkali metal salt of an organic sulfonate below the minimum level required to promote the stabilization reaction during the subsequent heat treatment step (described hereafter). Such coagulation bath may inherently possess no substantial tendency to dissolve the alkali metal salt of an organic sulfonate. Alternatively, the coagulation bath which is selected may have its inherent tendency to dissolve the alkali metal salt of an organic sulfonate diminished by preliminarily dissolving a substantial quantity of the alkali metal salt of an organic sulfonate or other compound therein. A preferred wet spinning technique is disclosed in commonly assigned U.S. Pat. No. 3,657,409, which is herein incorporated by reference.

The shaped orifice or spinneret utilized during the extrusion may contain a single hole through which a single filament is extruded, and preferably contains a plurality of holes whereby a plurality of filaments may be simultaneously extruded in yarn form. The spinneret preferably contains holes having a diameter of about 50 to 150 microns when producing relatively low denier fibers having an as-spun denier of about 8 to 24 denier per filament. Alternatively, acrylic films of relatively thin thickness, e.g. about 1 to 10 mils, may be formed, when the extrusion orifice is a rectangular slit. Generally stated, the solution may be formed into an acrylic fibrous material or film having a minor quantity of the stabilization promoting agent incorporated therein utilizing conventional fiber or film forming techniques with a minor quantity of an alkali metal salt of an organic sulfonate being merely added to the polymer dope.

The resulting as-spun fibrous material or film is preferably maintained in a continuous length configuration throughout the process. At an intermediate point prior to heat treatment the fibrous material may alternatively be transformed into another fibrous assemblage, e.g. a tow, fabric, or yarn of greater total denier.

When the fibrous 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. (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 substantially no twist.

The fibrous material may be drawn in accordance with conventional techniques in order to improve its orientation. For instance, the fibrous 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. Pat. Nos. 2,455,173; 2,948,581; and 3,122,412. It is recommended

that fibrous materials prior to the heat treatment (described hereafter) be drawn to a single filament tenacity of at least about 3 grams per denier. If desired, however, the fibrous 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. Additionally, the acrylic films optionally may be either uniaxially or biaxially oriented prior to the heat treatment (described hereafter).

Immediately prior to the heat treatment step the acrylic fibrous material or film commonly contains the alkali metal salt of an organic sulfonate incorporated therein in a concentration of about 0.2 to 10 percent by weight, and preferably in a concentration of about 0.5 to 5 percent by weight.

The acrylic material containing the alkali metal salt of an organic sulfonate incorporated therein is heated at a temperature of about 240 to 310° C. until a stabilized fibrous product or film is formed which is capable of undergoing carbonization, retains its original configuration substantially intact and which is non-burning when subjected to an ordinary match flame. It is preferred that the acrylic material be present in an oxygen-containing atmosphere during the heating, e.g. be present in a gaseous atmosphere containing about 20 to 40 percent by weight molecular oxygen. Inert atmospheres such as nitrogen, argon, and helium may alternatively be provided in the heating zone. In a particularly preferred embodiment of the process the oxygen-containing atmosphere is air. Preferred temperatures for the oxygen-containing atmosphere range from about 240 to 300° C. (e.g. 280 to 300° 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 alkali metal salt of an organic sulfonate containing 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 heating zone while wound upon a support to a limited thickness. In a preferred embodiment of the invention, the acrylic fibrous material or film is continuously passed in the direction of its length through the heating zone while substantially suspended therein. 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 heating zone will be determined by the size of the heating zone and the desired residence time.

The period of time required to complete the stabilization reaction within the heating zone is generally inversely related to the temperature of the gaseous atmosphere therein, 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 (if any) in the atmosphere. Treatment times in the heating zone accordingly commonly range from about 7 to 180 minutes. For instance, representative residence times at specific temperatures are as follows.

| Temperatures, ° C.: | Residence time, minutes |
|---------------------|-------------------------|
| 240                 | 180                     |
| 260                 | 65                      |
| 280                 | 35                      |
| 310                 | 7                       |

Regardless of the stabilization temperature selected within the range of about 240° to 310° C., the presence of the alkali metal salt of an organic sulfonate within the acrylic fibrous material or film results in a controlled and accelerated stabilization reaction at a given temperature

which precludes mass exothermic reactions from taking place.

The stabilized acrylic fibrous materials or films formed in accordance with the present process are black in appearance, dimensionally stable, flexible, retain essentially the same configuration as the starting material, are non-burning when subjected to an ordinary match flame, when heated in an oxygen-containing atmosphere 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 alkali metal salts of an organic sulfonate serve to accelerate the stabilization reaction is considered complex and incapable of simple explanation. It is believed, however, that the cyclization reaction is catalyzed and caused to proceed at an accelerated rate in a controlled manner.

When a shaped acrylic article, e.g. an acrylonitrile homopolymer fiber or film, which has not undergone any previous thermal stabilization is heated in air from room temperature (i.e. 25° C.) at a rate of 15° C./minute, a weight loss of about 25 percent is observed when a temperature of about 325 to 330° C. is reached. This weight loss is accompanied by a spontaneous exotherm which is attributed to the cyclization of pendant nitrile groups and a simultaneous chain scission reaction with the evolution of low molecular weight products, e.g. NH<sub>3</sub>, NCN, CH<sub>4</sub>, CH<sub>3</sub>CN, etc. Alternatively, if the shaped acrylic article has incorporated therein 1 to 10 percent of an alkali metal salt of an organic sulfonate, upon undergoing an identical thermal treatment a weight loss of only about 10 percent is observed when heating up to about 325 to 330° C. Accordingly, the process of the present invention makes possible a lower weight loss during the stabilization reaction, as well as accelerates the same. The resulting stabilized products if subsequently converted to carbon fibers or films likewise produce a higher eventual carbon yield.

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

871 parts by weight polyacrylonitrile homopolymer, 4.36 parts by weight sodium methallyl sulfonate, and 79 parts by weight lithium chloride are slurried in 3000 parts by weight N,N-dimethylacetamide at room temperature. The slurry is heated to 100° C. in 65 minutes while present in a closed vessel and held at that temperature for about 29 hours. The resulting dope containing the acrylonitrile homopolymer and the sodium methallyl sulfonate dissolved in N,N-dimethylacetamide is passed through a conventional filter press while at 100° C. The low shear

viscosity (Brookfield) of the resulting spinning solution after degassing is found to be 135 poises at 27° C.

The solution while at room temperature (i.e. 25° C.) is fed to a standard cup type spinneret of 80 holes each having a diameter of 100 microns. The solution is then passed at a rate of 7.1 cc./min. into a coagulation bath consisting of 66 parts by weight ethylene glycol and 34 parts by weight N,N-dimethylacetamide which is provided at 50° C. The extrusion velocity is 11.1 meters/minute, and the velocity as the fiber exits from the coagulation bath is 15 meters/minute thereby accomplishing a slight draw in the coagulation bath.

The resulting fiber is washed with water at 14° C., drawn at a draw ratio of 2:1 while immersed in glycerin provided at 90° C., washed with water at 14° C., dried, and subsequently drawn at a draw ratio of 5:1 while passing over a hot shoe at 150° C. The resulting fiber possesses a single filament tenacity of about 3.5 grams per denier, contains about 0.5 percent by weight of free sodium methallyl sulfonate incorporated therein, and the pendant nitrile groups of the acrylonitrile units present therein are substantially uncyclized.

The fiber is next stabilized on a continuous basis by passage for 12 minutes through a circulating heated air atmosphere provided in a tube furnace having a temperature of 300° C. while axially suspended therein.

The resulting stabilized yarn is capable of undergoing carbonization, shiny black in appearance, flexible, has a textile-like hand, retains its original fibrous configuration substantially intact, is non-burning when subject to an ordinary match flame, retains strength after glowing in a match flame, and has an oxygen content in excess of 8 percent by weight as determined by the Unterzaucher analysis.

In a control run, an identical sample of the acrylonitrile homopolymer yarn is passed through the tube furnace in an identical manner with the exception that it contains no sodium methallyl sulfonate incorporated therein. The control sample exhibited a violet exotherm which was accompanied by disintegration.

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

#### EXAMPLE II

Example I is repeated with the exception that the solution contains 45 parts by weight of sodium dodecyl benzene sulfonate in place of the sodium methallyl sulfonate. The resulting fiber contains about 5 percent sodium dodecyl benzene sulfonate incorporated therein which serves to promote the stabilization reaction.

#### EXAMPLE III

Example I is repeated with the exception that the solution contains 45 parts by weight of sodium polypropylene sulfonate in place of the sodium methallyl sulfonate. The resulting fiber contains about 5 percent sodium polypropylene sulfonate incorporated therein which serves to promote the stabilization reaction.

#### EXAMPLE IV

Example I is repeated with the exception that N,N-dimethylformamide is substituted for the N,N-dimethylacetamide solvent and the acrylonitrile homopolymer fiber containing sodium methallyl sulfonate incorporated therein in a concentration of about 0.5 percent by weight is formed by extruding the solution while at 140° C. through a spinneret into a dry spinning column. The column contains circulating nitrogen at 180° C. which substantially evaporates the N,N-dimethylformamide. Substantially similar results are achieved upon stabilization.

## EXAMPLE V

Example I is repeated with the exception that the solution of acrylonitrile homopolymer and sodium methallyl sulfonate is extruded through a rectangular slit having a height of 8 mils into ethylene glycol to form a film.

Following washing and orientation the resulting film containing about 0.5 percent by weight of free sodium methallyl sulfonate is suspended for 15 minutes in a circulating air oven provided at 300° C. wherein it is converted to a stabilized form while retaining its original configuration substantially intact.

The resulting stabilized film is capable of undergoing carbonization, shiny black, flexible, non-burning when subjected to an ordinary match flame, and contains an oxygen content of about 8 percent by weight as determined by the Unterzaucher analysis.

## EXAMPLE VI

A thin layer of the solution of acrylonitrile homopolymer and sodium dodecyl benzene sulfonate of Example II is placed upon a flat support and the N,N-dimethylacetamide solvent evaporated by contact with circulating hot air provided at 90° C.

Following washing and orientation the film contains about 5 percent sodium dodecyl benzene sulfonate by weight, and is stabilized as described in Example V to produce substantially similar results.

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. An acrylic fibrous material or film consisting essentially of (1) an acrylic polymer 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, and (2) about 0.2 to 10 percent by weight of an alkali metal salt of an organic sulfonate, with said alkali metal salt of an organic sulfonate being incorporated therein in a non-polymerized form and being capable of promoting the thermal stabilization thereof upon heating.

2. An acrylic shaped article according to claim 1 wherein said acrylic material is a fibrous material.

3. An acrylic shaped article according to claim 1 wherein said acrylic material is a film.

4. An acrylic fibrous material or film according to claim 1 wherein said alkali metal salt of an organic sulfonate which is capable of promoting the thermal stabilization of said acrylic polymer is sodium methallyl sulfonate.

5. An acrylic fibrous material or film according to claim 1 wherein said alkali metal salt of an organic sul-

fonate is present in a concentration of about 0.5 to 5 percent by weight.

6. An acrylic fibrous material or film consisting essentially of (1) an acrylic polymer 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, and (2) about 0.2 to 10 percent by weight of an alkali metal salt of an alkylaryl sulfonate, with said alkali metal salt of an alkylaryl sulfonate being incorporated therein in a non-polymerized form and being capable of promoting the thermal stabilization thereof upon heating.

7. An acrylic shaped article according to claim 6 wherein said acrylic material is a fibrous material.

8. An acrylic shaped article according to claim 6 wherein said acrylic material is a film.

9. An acrylic fibrous material or film according to claim 6 wherein said alkali metal salt of an organic sulfonate is present in a concentration of about 0.5 to 5 percent by weight.

10. An acrylic fibrous material or film according to claim 6 wherein said alkali metal salt of an alkylaryl sulfonate contains at least one alkyl group having up to about 30 carbon atoms.

11. An acrylic fibrous material or film according to claim 10 wherein said alkali metal salt of an alkylaryl sulfonate contains at least one alkyl group having 10 to 20 carbon atoms.

12. An acrylic fibrous material or film according to claim 11 wherein said alkali metal salt of an alkylaryl sulfonate which is capable of promoting the thermal stabilization of said acrylic polymer is sodium dodecylbenzene sulfonate.

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U.S. Cl. X.R.

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