

[54] **PROCESS FOR THE THERMAL
STABILIZATION OF
POLYACRYLONITRILE FIBERS AND
FILMS**

[75] Inventors: **Andrew H. Di Edwardo**, Parsippany;
Klaus H. Gump, Gillette, both of
N.J.

[73] Assignee: **Celanese Corporation**, New York,
N.Y.

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[56] **References Cited**

UNITED STATES PATENTS

3,242,000	3/1966	Lynch	8/115.5 X
3,427,120	2/1969	Shindo et al.	423/477 X
3,647,770	3/1972	Gump et al.	423/447 X
3,729,549	4/1973	Gump et al.	8/115.5 X

FOREIGN PATENTS OR APPLICATIONS

1,502,253	10/1967	France	423/447
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Primary Examiner—Leon D. Rosdol

Assistant Examiner—Harold Wolman

[57]

ABSTRACT

An improved process for the thermal stabilization of an acrylic fibrous material or film is provided. The fibrous precursor or film is impregnated with 0.5 to 10 per cent stannous chloride by contact with a solution of the same provided at a moderate temperature, dried to remove the solvent, and heated in a gaseous atmosphere containing 30 to 100 per cent by weight molecular oxygen at a more highly elevated temperature until a stabilized fibrous material or film is formed. The presence of the stannous chloride in combination with the gaseous atmosphere containing more than the usual concentration of molecular oxygen (e.g. 10 to about 20 per cent by weight) has been found to result in a substantially improved process. More specifically, the resulting stabilized acrylic fibrous materials and films exhibit enhanced physical properties (i.e. strength and modulus), and the stabilization reaction is accelerated in a controlled manner in the substantial absence of undesirable fiber coalescence. 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.

16 Claims, No Drawings

PROCESS FOR THE THERMAL STABILIZATION OF POLYACRYLONITRILE FIBERS AND FILMS

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. 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 fibers of acrylonitrile homopolymers and copolymers in an oxygen-containing atmosphere involves (1) a chain scission and oxidative cross-linking reaction of adjoining molecules, (2) dehydrogenation reactions, as well as (3) 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 processes of commonly assigned U.S. Pat. Ser. Nos. 777,901, filed Nov. 21, 1968, of K. H. Gump and D. E. Stuetz (now U.S. Pat. No. 3,592,595) 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° C.; U.S. Pat. No. 109,672, filed Jan. 25, 1971, of E. C. Chenevey and R. M. Kimmel (now U.S. Pat. No. 3,708,326); and U.S. Pat. No. 200,183, filed Nov. 18, 1971, of K. H. Gump and D. E. Stuetz.

U.S. Pat. No. 3,242,000 to J. A. Lynch discloses an unrelated process for producing carbonized textile products from acrylic textile products wherein a refractory metal oxide barrier coating is formed upon the surface of fabrics employing a heat treatment atmosphere which contains at least some oxygen (e.g. about 10 to about 20 per cent oxygen).

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 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 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 per cent carbon by weight, and generally at least about 95 per cent 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. Pat. Ser. No. 777,275, filed Nov. 20, 1968, of Charles M. Clarke (now abandoned) 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 an acrylic shaped 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 an improved process wherein the thermal stabilization of an acrylic fibrous material or film is accelerated in a controlled and non-deleterious manner.

It is an object of the invention to provide an improved process for the thermal stabilization of an acrylic fibrous material or film which produces a stabilized product exhibiting enhanced physical properties, i.e., strength and modulus.

It is an object of the invention to provide an improved process for the stabilization of acrylic fibers which is carried out in an enriched oxygen-containing atmosphere on an expeditious basis in the absence of expected fiber coalescence.

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 superior 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 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 an improved 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 per cent of acrylonitrile units and up to about 15 mol per cent of one or more monovinyl units copolymerized therewith to produce a stabilized product exhibiting enhanced mechanical properties comprises:

- impregnating the fibrous material or film with about 0.5 to 10 per cent by weight of stannous chloride by contact with a solution of the stannous chloride in a solvent incapable of dissolving the fibrous material or film provided at a temperature of about 0° to 100° C. while preserving the original configuration of the fibrous material or film substantially intact,
- drying said fibrous material or film to substantially remove the solvent therefrom, and
- heating the resulting impregnated and dried fibrous material or film in a gaseous atmosphere containing 30 to 100 per cent by weight molecular oxygen provided at a temperature of about 260° to 350° 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.

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 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. a 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 per cent of acrylonitrile units and not more than about 15 mol per cent 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 per cent of acrylonitrile units and up to about 5 mol per cent 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 tpi, and preferably about 0.3 to 1.0 tpi 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 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. Pat. 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 te-

nacity 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 the gaseous atmosphere of enriched molecular oxygen content to accomplish the desired stabilization (as described hereafter), the precursor is impregnated with 0.5 to 10 per cent by weight of stannous chloride (preferably 1 to 5 per cent by weight) by contact with a solution of the same in a solvent incapable of dissolving the fibrous material or film, and is dried to substantially remove the solvent used in the formation of the solution. The nature of the solvent selected may be widely varied. Particularly preferred solvents are water, methanol, and mixtures of methanol and water. It is essential that the solvent have the ability to dissolve the stannous chloride while being incapable of dissolving or otherwise adversely influencing the acrylic material undergoing treatment. Other representative solvents for the stannous chloride and non-solvents for the acrylic fibrous material or film include acetonitrile, tricresylphosphate, and phenylether. Solvents may also be selected which have a tendency to swell the fiber such as mixtures of dimethylformamide and water.

The stannous chloride commonly is dissolved in the solvent in a concentration of about 1 to 10 per cent by weight based upon the total weight of the solution. When contacted with the acrylic fibrous material or film, the stannous chloride solution is provided at a temperature of about 0° to 100° C., and preferably at a temperature of about 10° to 40° C. Relatively brief contact times, e.g. 3 seconds to 5 minutes, are generally adequate. Contact times depend primarily upon the concentration of stannous chloride in the solution, and relative freedom of access of the solution throughout the acrylic material undergoing impregnation. If a fibrous material is provided as a relatively compact assemblage, longer contact times are required. For instance, when an acrylic fibrous material is immersed in an aqueous solution containing 2 per cent stannous chloride based upon the total weight of the solution provided at 25° C. for 5 seconds under conditions wherein ready access is possible, the stannous chloride uptake following evaporation of the solvent is commonly about 9 to 12 per cent by weight. The stannous chloride which is introduced into the solvent to form the solution of same may be either anhydrous [e.g. SnCl_2] or hydrous [e.g. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$]. When stannous chloride is present in the hydrous form, the water of hydration is not included when calculating the concentration of stannous chloride for the purposes of the present specification and appended claims.

The impregnation step of the process may be conducted on either a batch or a continuous basis, and preferably while the fibrous material is maintained at a substantially constant length in the absence of appreciable shrinkage. 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 stannous chloride, 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. Higher solution temperatures than about 100° C. 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, the stannous chloride 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.

Following impregnation the acrylic fibrous material or film is next dried to that the solvent is substantially removed, and the required quantity of stannous chloride 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 (e.g. air) 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 contains about 0.5 to 10 per cent by weight of stannous chloride, and preferably about 1 to 5 per cent by weight of stannous chloride.

The resulting impregnated and dried acrylic material is heated in a gaseous atmosphere containing 30 to 100 per cent by weight molecular oxygen provided at a temperature of about 260° to 350° C. until a stabilized fibrous product or film is formed which retains its original configuration substantially intact and which is non-burning when subjected to an ordinary match flame. The portion of the gaseous atmosphere other than molecular oxygen, if any, is preferably substantially unreactive with the acrylic fibrous material during the stabilization treatment, e.g. it may include nitrogen, hydrogen, carbon dioxide, carbon monoxide, argon, helium, etc. In a preferred embodiment of the process, the oxygen-containing atmosphere is air enriched with molecular oxygen. Molecular oxygen is preferably present in the gaseous atmosphere in a concentration of 35 to 100 per cent by weight, and most preferably in a concentration of about 40 to 60 per cent by weight. Preferred temperatures for the oxygen-containing atmosphere range from about 290° to 310° C. If desired, the fibrous material or film may be exposed to a temperature gradient wherein the temperature is progressively increased. The presence of an enriched oxygen atmosphere in combination with the presence of stannous chloride has been found to be of prime importance in accomplishing the improved stabilization results discussed hereafter.

For best results during the stabilization reaction uniform contact with the gaseous atmosphere 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 gaseous atmosphere while wound

upon a support to a limited thickness. In a preferred embodiment of the invention, the stannous chloride impregnated acrylic fibrous material or film is continuously passed in the direction of its length through the heated gaseous 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.

The period of time required to complete the stabilization reaction within the gaseous 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 6 minutes to 60 minutes.

The stabilized acrylic fibrous materials or films formed in accordance with the present process are black in appearance, retain substantially 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) per cent by weight as determined by the Unterzaucher, or other suitable analysis, commonly contain from about 50 to 65 per cent carbon by weight, and commonly contain about 0.4 to 8 per cent tin by weight.

The theory whereby the presence of stannous chloride in combination with a greater than usual oxygen concentration in the gaseous atmosphere produces improved stabilization results is considered complex and incapable of simple explanation. The results achieved are considered to be surprising and unexpected. While it has been suggested in the past that acrylic stabilization reactions can be conducted in an atmosphere of air enriched with oxygen, the results of such stabilization conditions have tended to be less than optimum particularly if relatively high stabilization temperatures (e.g. 260° C. and above) are selected because of the increased tendency for an explosive exotherm to occur under such conditions. Such an exothermic reaction at the very least produces a weak and brittle product, and may result in a complete breakage of the acrylic fiber or fragmentation of the acrylic film. It has now been found after extensive experimentation that while stannous chloride has the ability to accelerate the kinetics of the cyclization portion of the stabilization reaction in air, that the presence of this compound has the concomitant tendency to retard the dehydrogenation and oxidative cross-linking portions of the stabilization reaction. Additionally, even when the oxygen concentration of the gaseous stabilization atmosphere is increased, the mechanical properties of the resulting product are surprisingly not diminished, and even more surprisingly are enhanced. For instance, stabilized products formed in the present process in the presence of stannous chloride exhibit a higher tenacity and modulus than if produced in the presence of stannous chloride in air. Not only is the stabilization reaction accelerated, but no substantial fiber coalescence occurs and less fiber weight loss results. The process of the present invention proceeds at an expeditious rate in a controlled fashion with the fiber temperature during the stabilization reaction more closely approximating that

of the gaseous atmosphere while eliminating a deleterious exothermic reaction.

In our commonly assigned U.S. Pat. Ser. No. 248,371, filed concurrently herewith, is disclosed a related process wherein stannous chloride is dissolved within a solution of the acrylic polymer, the solution formed into a fiber or film which contains the stannous chloride in intimate association therewith, and the resulting fiber or film stabilized in a gaseous atmosphere containing more than the usual concentration of oxygen.

The stabilized fibrous material resulting from the stabilization treatment of the present process 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 be also utilized as intermediates in the production of carbonized films. 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 about 960 is selected as the starting material. The yarn exhibits a twist of 0.5 tpi and has been drawn to a single filament tenacity of 2 grams per denier.

The yarn is immersed for 5 seconds in a 5 per cent by weight solution of stannous chloride in methanol by use of a continuous padding apparatus wherein the yarn is maintained at a constant length through the adjustment of the longitudinal tension thereon. The solution is provided at a temperature of about 25° C. while the acrylonitrile homopolymer yarn is immersed therein. While immersed in the solution, the yarn becomes impregnated with about 5 per cent by weight of stannous chloride.

The stannous chloride impregnated yarn upon removal from the solution is dried while at constant length by contact with circulating air in a tubular furnace through which it is passed for 2 minutes wherein the methanol solvent is substantially removed. The temperature within the tubular drying zone is 80° C.

A portion of the yarn containing 5 per cent by weight stannous chloride is next stabilized on a continuous basis by heating in a circulating gaseous atmosphere of air enriched with molecular oxygen provided in a muffle furnace. The total oxygen concentration in the atmosphere is 40 per cent by weight. The gaseous atmo-

sphere is provided at a temperature of 290° C. and the residence time therein is 18 minutes. The yarn is maintained under a longitudinal tension sufficient to maintain a substantially constant length during the stabilization reaction.

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

In a control run an identical sample of the acrylonitrile homopolymer yarn is passed through the muffle furnace in an identical manner with the exception that it has not been previously impregnated with stannous chloride. The resulting yarn is coalesced, extremely brittle, and non-flexible.

The resulting stabilized yarn of Example I is carbonized and graphitized in accordance with the teachings of U.S. Pat. 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 portions of the stannous chloride impregnated yarn are stabilized for 10 minutes in air enriched with molecular oxygen atmospheres containing 40 and 80 per cent by weight molecular oxygen by weight provided at 300° C.

In each instance the stabilized yarn is black in appearance, non-brittle, flexible, has a textile-like hand, retains its original fibrous configuration substantially intact, is non-burning when subjected to an ordinary match flame, retains strength after glowing in a match flame, and has an oxygen content in excess of 9 per cent by weight as determined by the Unterzaucher analysis.

The stabilized yarn produced in the 40 per cent by weight molecular oxygen gaseous atmosphere possesses a single filament tenacity of 1.82 grams per denier, and a Young's modulus of 63.2 grams per denier.

The stabilized yarn produced in the 80 per cent by weight molecular oxygen gaseous atmosphere possesses a single filament tenacity of 2.09 grams per denier, and a Young's modulus of 75.2 grams per denier.

For comparative purposes the process of Example II is repeated with the exception that the gaseous atmosphere is air only and contains 20.9 per cent by weight molecular oxygen. The resulting fibers burn when subjected to an ordinary match flame, are visibly coalesced, exhibit a single filament tenacity of only 0.92 grams per denier, and a single filament Young's modulus of only 47.5 grams per denier.

EXAMPLE III

A rectangular section of acrylonitrile homopolymer film having a thickness of 5 mils is selected as the starting material. The film is impregnated stannous chloride by immersion for 10 seconds in a 5 per cent by weight solution of stannous chloride in methanol. The solution is provided at a temperature of about 25° C. while the acrylonitrile homopolymer film is immersed therein.

While immersed in the solution the film becomes impregnated with about 3 per cent by weight of stannous chloride.

The stannous chloride impregnated film upon removal from the solution is dried by placement in a circulating air oven for 30 minutes wherein the methanol solvent is substantially removed. The temperature within the drying zone is 80° C. The resulting impregnated and dried film is next suspended for 8 minutes in an oven provided with a circulating air enriched with molecular oxygen atmosphere containing 40 per cent by weight molecular oxygen and maintained at 300° C. wherein it is converted to a stabilized form while retaining its original configuration substantially intact. The resulting stabilized film is black in appearance, non-brittle, flexible, non-burning when subjected to an ordinary match flame, and contains a bound oxygen content in excess of about 7 per cent by weight as determined by the Unterzaucher analysis.

In a control run an identical sample of the acrylonitrile homopolymer film is heated in the oven in an identical manner with the exception that it has not been impregnated with stannous chloride. The resulting film is brittle and without any physical strength.

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 improved process for the thermal 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 per cent of acrylonitrile units and up to about 15 mol per cent of one or more monovinyl units copolymerized therewith to produce a thermally stabilized product exhibiting enhanced physical properties comprising:

- a. impregnating said fibrous material or film with about 0.5 to 10 per cent by weight of stannous chloride based upon the weight of said acrylic fibrous material or film by contact with a solution of said stannous chloride in a solvent incapable of dissolving said fibrous material or film provided at a temperature of about 0° to 100° C. while preserving the original configuration of said fibrous material or film substantially 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 a gaseous atmosphere containing 30 to 100 per cent by weight molecular oxygen provided at a temperature of about 260° to 350° C. until a thermally stabilized fibrous material or film is formed which is black in appearance, retains its original configuration substantially intact, contains a bound oxygen content to at least 7 per cent by weight, and which is non-burning when subjected to an ordinary match flame, with any portion of said gaseous atmosphere other than molecular oxygen being substantially unreactive with the material undergoing stabilization.

2. An improved process of claim 1 in which the precursor is a fibrous material.

3. An improved process of claim 1 in which the precursor is a film.

4. An improved process of claim 2 in which said acrylic fibrous material is an acrylonitrile homopolymer.

5. An improved process of claim 2 in which said acrylic fibrous material is an acrylonitrile copolymer containing at least about 95 mol per cent of acrylonitrile units and up to about 5 mol per cent of one or more monovinyl units copolymerized therewith.

6. An improved process of claim 1 in which said solution of said stannous chloride is provided at a temperature of about 10° to 40° C. during said impregnation step (a).

7. An improved process of claim 1 in which said solvent for said stannous chloride is water.

8. An improved process of claim 1 in which said solvent for said stannous chloride is methanol.

9. An improved process of claim 1 in which said drying step (b) is conducted at a temperature of about 10° to 40° C.

10. An improved process of claim 1 in which said resulting impregnated and dried fibrous material or film contains said stannous chloride in a concentration of about 1 to 5 per cent by weight based upon the weight of said acrylic fibrous material or film immediately prior to heating in said gaseous atmosphere containing 30 to 100 per cent molecular oxygen by weight.

11. An improved process of claim 1 in which said gaseous atmosphere contains about 35 to 100 per cent molecular oxygen by weight.

12. An improved process for the thermal stabilization of an acrylic fibrous material selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers containing at least 85 mol per cent of acrylonitrile units and up to about 15 mol per cent of one or more monovinyl units copolymerized therewith to produce a thermally stabilized product exhibiting enhanced physical properties comprising:

- a. impregnating said fibrous material with about 1 to 5 per cent by weight of stannous chloride based upon the weight of said acrylic fibrous material by contact with a solution of said stannous chloride wherein the solvent is selected from the group consisting of water, methanol, and a mixture of methanol and water with the solution being provided at a temperature of about 10° to 40° C.,
- b. drying said fibrous material to substantially remove the solvent therefrom, and
- c. heating said resulting impregnated and dried fibrous material in a gaseous atmosphere containing 35 to 100 per cent by weight molecular oxygen provided at a temperature of about 290° to 310° C. while maintaining a substantially constant length until a thermally stabilized fibrous material is formed which is black in appearance, retains its original configuration substantially intact, contains a bound oxygen content of at least 7 per cent by weight, and which is non-burning when subjected to an ordinary match flame, with any portion of said gaseous atmosphere other than molecular oxygen being substantially unreactive with the material undergoing stabilization.

13. An improved process of claim 12 in which said acrylic fibrous material is an acrylonitrile homopolymer.

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14. An improved process of claim 12 in which said acrylic fibrous material is an acrylonitrile copolymer containing at least about 95 mol per cent of acrylonitrile units and up to about 5 mol per cent of one or more monovinyl units copolymerized therewith.

15. An improved process of claim 12 in which said

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drying step (b) is conducted at a temperature of about 10° to 40° C.

16. An improved process of claim 12 in which said gaseous atmosphere contains about 40 to 60 per cent molecular oxygen by weight.

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