METHOD OF CARBONIZING POLYACRYLONITRILE IMPREGNATED CELLULOSE, CYANOETHYLATED CELLULOSE AND ACRYLONITRILE GRAFT COPOLYMERIZED CELLULOSE TEXTILES

Greville Michell, Spartanburg, S.C., assignor to Deering Milliken Research Corporation, Spartanburg, S.C., a corporation of Delaware


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This invention relates to heat resistant textile materials and more specifically to acrylonitrile treated carbonized textile materials.

Heat resistant fabrics have recently become of vital importance for use in missiles which are subjected to the effects of exceed heat build-up at very high speeds. Since the heat resistance of carbon except in the presence of an oxidizing atmosphere is almost perfect, efforts have been made to produce carbonized fabrics having increased oxidation or flame resistance. Fabrics of this type when employed as a laminate between sheets of organic polymeric materials have found application as liners for missile nose cones and missile exhaust orifices. Carbonization of fabrics, however, results in extreme weight loss, the loss in weight often being correlated to losses in flexibility in the carbonized fabric.

It is therefore an object of this invention to provide a carbonized fabric having increased oxidation or flame resistance.

It is another object of this invention to provide a method for the production of a carbonized fabric wherein carbonization is accomplished without extreme losses in weight and flexibility.

These and other objects of the invention will become apparent from the following description.

In accordance with this invention it has now been discovered that cellulose textile material having high oxidation or flame resistance may be obtained by treating a cellulose fabric with acrylonitrile and then carbonizing the acrylonitrile treated cellulose fabric in a suitable atmosphere whereby the weight loss due to the carbonization of the cellulose is substantially reduced and the flexibility of the carbonized fabric increased. The acrylonitrile treatment may be an acrylonitrile treatment selected from the group consisting of acrylonitrile monomer grafting, acrylonitrile cyanoethylation and polyacrylonitrile solution coating. It is preferred that the acrylonitrile treatment be such that a pickup in excess of from about 5% by weight of acrylonitrile on the fabric is obtained and preferably a pickup of from 10% by weight to 200% by weight. The term "acrylonitrile" or "polyacrylonitrile" as used herein is meant to include acrylonitrile and polyacrylonitrile compositions containing up to 10% by weight of other compatible monomers or polymers or copolymers or terpolymers or admixtures thereof.

While any of the well-known polymer grafting processes for the grafting of acrylonitrile may be employed in the process of this invention, it is preferred to employ a polymer grafting process wherein polymerization is carried out in an aqueous medium at a pH of not greater than 3.5 and in the presence of a ceric salt which is soluble in at least one component of the reaction mixture. The polymer grafting process may be carried out at temperatures between about —5° C. and 100° C. and preferably about between 10° C. and 60° C. It is preferred to utilize in the process conditions in carry out the polymer grafting process, however, either elevated pressure or partial vacuum may be employed. The ceric compound which is utilized in the process may be varied over fairly wide limits. Quantities of from about 10⁻⁶ to about 10⁻¹ moles of ceric ion per mole of polymerizable monomer are satisfactory. The ceric ion may be introduced in the form of a salt such as for instance ceric nitrate, ceric sulfate, ceric ammonium nitrate, ceric ammonium sulfate, ceric ammonium pyrophosphate, ceric iodate, cerium naphthenate, cerium linolate and the like. Ceric compounds which are capable of forming ceric salts in situ are also acceptable, such salts which have been employed being salts such as, for instance ceric hydroxide and the like. It should be understood, however, that oil soluble ceric salts are also operative in the process, such salts being salts such as for instance ceric dihydroxofusacinate, ceric dioctylsulfosuccinate, ceric diheptylsulfogluitate, ceric dicetyl sulfosuflate, ceric dilaurylsulfosuccinate and the like.

The preferred polymer grafting system employed herein involves cellulose as one of the essential components of the redox system. It has been found that oxidation of cellulose by ceric salts produces free radicals capable of initiating vinyl polymerization. The rates of polymerization obtained with this redox system are very high, even at low temperatures, and polymerization is substantially confined to the interior of the cellulose fibers rather than occurring undesirably in the treating medium. The confinement of polymerization to the interior of the fiber is preferably accomplished by forcing the treating medium through the fiber mass unidirectionally, intermittently back and forth throughout the process.

In general, the cyanoethylation process employed in this invention may be any of the well-known cyanoethylation procedures employed in the treatment of cellulose textile materials. Cyanoethylation procedures employed may be employed involve the immersion of a cellulose textile material while in a Beck or a package dyeing machine in a dilute solution of a base, centrifuging or squeezing to remove excess basic solution and then reacting the basic textile material with a large excess of acrylonitrile at the reflux temperature of the acrylonitrile-water azotrope. If the amount of acrylonitrile reactant is carefully controlled, that is to say, if large excesses of acrylonitrile are not applied which will, of course, necessitate removal and recovery of unreacted acrylonitrile, the acrylonitrile component may be applied by means of a scotch roll.

When a polyacrylonitrile solution is coated onto the cellulose fabric, the coating operation employed may be any of the coating operations which are well known to the art, that is to say, the coating operation may take the form of dip coating, padding, spraying or the like.

In general, the carbonization or pyrolysis of the acrylonitrile treated cellulose fabric is carried out by placing the fabric in a Hoskins oven or other apparatus having the ability to attain the desired temperature range in the proper atmosphere and heating at a temperature from about 300° C. to about 3000° C. or higher. When the fiber being carbonized or pyrolyzed is treated with substantial amounts of acrylonitrile, it is desirable that the carbonization atmosphere contain at least some oxygen. Oxygen, however, should not be present in quantities sufficient to promote combustion. Where, however, relatively small quantities of acrylonitrile are present in the cellulose fabric, it is desirable for the carbonization atmosphere to be an inert atmosphere such as for instance a nitrogen or argon atmosphere or a reducing atmosphere such as for instance carbon monoxide or hydrogen. Where the atmosphere is a reducing or inert atmosphere, oven temperatures of from about 300° C. to about 3000° C. or higher are employed. Where the carbonizing atmosphere is an oxygen containing atmosphere, it is preferred that temperatures of from about 180° C. to about 550° C. be employed. Temperatures and time limits, however, must be such that combustion of the fabric is not promoted.
It should be understood that the acrylonitrile treated cellulosic fabric of this invention may be subjected to additional coating and impregnating operations which will enhance the flexibility and oxidation or flame resistance of the fabric. Additional treatments of the aforementioned type are the impregnation of the acrylonitrile treated cellulosic fabric with compounds having refractory metal oxides, and the coating of the acrylonitrile treated cellulosic fabric with refractory metal oxides. The term "refractory" as employed herein is meant to include in addition to those compounds considered refractory in the classical sense, those compounds having thermal stability at temperatures of 300° C. or greater.

The following specific examples for the preparation of acrylonitrile treated cellulosic textile fabrics which are suitable for carbonization are given for purposes of illustration and should not be considered as limiting the spirit or scope of this invention.

**EXAMPLE I**

A 38 x 38 viscose filament fabric is stripped of every fourth warp and fill yarn in order to give an open fabric of construction 29 x 29 and weight of 108 grams. The fabric is then wound on a perforated spool and placed in a miniature package dyeing machine. After scouring with a 0.2% Surfacton N-95 (surface active agent marketed by Jefferson Chemical Corporation) at 180° F. for 20 minutes, the fabric is rinsed and brought to room temperature. The package dyeing machine containing the scoured fabric is then charged with the solution of acrylonitrile (40 grams) in water (1500 milliliters) at 73° F. and the solution circulated through the fabric. Fifty milliliters of tenth molar ammonium nitrate in normal nitric acid is then added with continuous stirring. Forty grams of acrylonitrile is then added dropwise over a thirty minute period. By appropriate external cooling, the temperature of the treating solution is allowed to rise gradually to 90° F. over a total reaction time of two hours. The treating solution is then drained and the fabric rinsed successively with water, 2% sodium bicarbonate solution, again with water and with 1% acetic acid solution and again with water. After drying in air, the treated fabric is found to weigh 139 grams (a weight increase of 29%) and to have a final construction of 34 x 34. Swatches of the original 38 x 38 fabric and the treated 34 x 34 fabric were then carbonized in pure nitrogen by slowly heating the fabrics to 800° C. in a Hoskins oven, the temperature being maintained for a 30 minute period. The untreated fabric was found to have suffered an 80% weight loss on carbonization and to have a tensile strength of 2.20 lbs. The acrylonitrile treated fabric was found to have suffered a 71% weight loss upon carbonization and to have a tensile strength of 2.52 lbs.

**EXAMPLE II**

A bleached, mercerized and scoured cotton poplin is passed over a thin roll partially immersed in a sodium hydroxide solution containing 2% sodium 2-ethylhexyl sulfonate as a wetting agent. The peripheral speed of the roll is varied relative to the linear speed of the fabric so that the amount of solution applied can readily be adjusted to any desired value. The cloth is formed in a tight roll immediately following its contact with the surface of the sodium hydroxide applying roller and thereafter is, as soon as possible, wrapped in a sheet of vinyl plastic material and allowed to age at room temperature for approximately 2 hours. At the end of this aging period, the material is unwrapped and put over a second scotch roller having its lower edge imbedded in acrylonitrile. The acrylonitrile treated material is again formed into a tight roll and wrapped with a sheet of vinyl plastic material and aged at room temperature. After aging the material is washed in a 2% acetic acid solution and rinsed with clear water and then dried. A swatch of the original bleached, mercerized and scoured poplin material and a swatch of the acrylonitrile treated poplin material are then carbonized in pure nitrogen by slowly heating the fabrics to 800° C. in a Hoskins oven, the temperature being maintained for a 30 minute period. The untreated fabric was found to have suffered a higher weight loss and to have a lower tensile strength than the acrylonitrile treated fabric.

**EXAMPLE III**

A 38 x 38 viscose filament fabric is stripped of every fourth warp and fill yarn in order to give an open fabric of construction 29 x 29 and weight of 108 grams. The fabric is then wound on a perforated spool and placed in a miniature package dyeing machine. After scouring with a solution of 0.2% Surfacton N-95 (surface active agent marketed by Jefferson Chemical Corporation) at 180° F. for 20 minutes, the fabric is rinsed and brought to room temperature. The fabric is then treated with 10% by weight solution of polyacrylonitrile in dimethyl formamide. The polyacrylonitrile fabric is then passed between a pair of squeeze rolls and dried at room temperature. The pickup of polyacrylonitrile on the fabric is found to be about 10% by weight based on the dry weight of the fabric. The original 38 x 38 fabric and the treated fabric were then carbonized in pure nitrogen by slowly heating the fabrics to 800° C. in a Hoskins oven, the temperature being maintained for a 30 minute period. The untreated fabric was found to have suffered a greater weight loss upon carbonization and to have a lower tensile strength upon carbonization than the acrylonitrile treated fabric.

Having thus disclosed the invention, what is claimed is:

1. A method for the preparation of low weight loss carbonized textile materials comprising treating a cellulosic textile material with acrylonitrile so that said cellulosic textile material will have a pickup of about at least 5% acrylonitrile based on the weight of the initial textile material, drying said treated cellulosic textile material and then carbonizing the acrylonitrile treated cellulosic textile material by heating said textile material in a substantially inert atmosphere that does not support combustion at a temperature in the range of about 300° C. to about 3000° C.

2. The method of claim 1 wherein said cellulosic textile material is a cellulosic textile material selected from the group consisting of cotton, regenerated cellulose and mixtures thereof.

3. A method of the preparation of a low weight loss carbonized textile material comprising immersing a cellulosic textile material in a polyacrylonitrile solution so that said cellulosic textile material will have a pickup of about at least 5% acrylonitrile based on the weight of the initial textile material, drying said treated cellulosic textile material and then carbonizing the polyacrylonitrile treated cellulosic textile material by heating said textile material in a substantially inert atmosphere which does not support combustion at a temperature in the range of about 300° C. to about 3000° C.

4. The method of claim 3 wherein said cellulose textile material is a cellulosic textile material selected from the group consisting of cotton, regenerated cellulose and mixtures thereof.

5. A method for the preparation of a low weight loss carbonized textile material comprising graft copolymerizing about at least 5% weight of acrylonitrile, based on the weight of the textile material, onto a cellulosic textile material and then carbonizing the graft copolymerized cellulosic textile material by heating said textile material in a substantially inert atmosphere which does not support combustion at a temperature in the range of about 300° C. to about 3000° C.
6. The method of claim 5 wherein said cellulose textile material is a cellulose textile material selected from the group consisting of cotton, regenerated cellulose and mixtures thereof.

7. A method for the preparation of a low weight loss carbonized textile material comprising cyanoethylating a cellulose textile material with about at least 5% acrylonitrile based on the weight of the textile material and then carbonizing the cyanoethylated cellulose textile material in a substantially inert atmosphere which does not support combustion at a temperature in the range of about 300° C. to about 3000° C.

8. The method of claim 7 wherein said cellulose textile material is a cellulose textile material selected from the group consisting of cotton, regenerated cellulose and mixtures thereof.

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NORMAN G. TORCHIN, Primary Examiner.
H. WOLMAN, Assistant Examiner.