United States Patent Office

3,143,437

Patented Aug. 4, 1964

3,143,437

TREATMENT OF POLYACRYLONITRILE TEXTILE MATERIALS

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No Drawing. Filed Jan. 27, 1960, Ser. No. 4,876
Claims priority, application France Feb. 2, 1959
9 Claims. (Cl. 117—138.8)

This invention relates to the production of a so-called "permanent" finish on polyacrylonitrile textile articles.

By the expression "polyacrylonitrile textile articles" is meant threads, fibres and the like consisting of polymers of which at least 85% is acrylonitrile, and woven, knitted or made-up articles based on these yarns fibres or the like.

It is known to produce a hardened finish on synthetic plastic filaments by heating the filaments with a solution having a dissolving action at room temperature, for example by treating cellulose acetate articles with acetone.

It is an object of this invention to provide a method of producing a permanent finish on polyacrylonitrile textile articles.

According to the present invention there is provided a process for the treatment of polyacrylonitrile textile articles to impart a permanent finish thereto which comprises impregnating the polyacrylonitrile textile articles with a composition consisting of a latent solvent for the said textile and a polymer which is soluble, at least at elevated temperature, in the said latent solvent, said impregnation being effected at a temperature below that at which the textile spontaneously dissolves in said latent solvent, and thereafter drying the impregnated articles at a temperature at least equal to the temperature at which the said textile dissolves in the said latent solvent. Optionally excess liquid may be removed from the textile, e.g., by centrifuging, before the textile is dried.

By the term "latent solvent" used in this invention is meant a liquid which does not spontaneously dissolve the textile below a certain temperature but does dissolve the textile at higher temperatures. With such a "latent solvent" it is possible to keep the textile in the latent solvent below the said temperature for at least one hour without modification and then to effect dissolution by simply heating the mass. It is to be noted that solutions thus obtained may remain homogeneous when cooled down, i.e., the textile does not spontaneously dissolve at the lower temperature but may not separate from its solution at higher temperatures when that solution is cooled.

In the case of textiles consisting of an acrylonitrile homopolymer, such liquids are, for example, dimethylformamide, dimethylacetamide, dimethylsulphoxide and γ-butyrolactone. Mixtures of such liquids may also be employed.

The polymer introduced into the said liquid may be of any desired nature; for example, it may be a cellulose derivative or a completely synthetic polymer (e.g., a polyolefine, vinyl polymer or acrylic polymer). A soluble polymer containing from 85% to 100% of acrylonitrile and up to 15% of another copolymerisable ethylenically unsaturated monomer is particularly suitable.

The concentration of the polymer in the latent solvent may vary in accordance with the desired effect. It is generally advantageous for it to be present in fairly low concentration, for example in a concentration between 0.1% and 15%, preferably of from 1% to 5%. The polymer may be dissolved in the latent solvent by any appropriate means, for example by heating for a quarter of an hour at 80° C.

The impregnation temperature employed depends upon the nature of the polyacrylonitrile textile and that of the latent solvent employed. It must be lower than the temperature at which the textile dissolves in the said latent solvent.

In the preferred method of carrying out the present invention, the polyacrylonitrile textile article is immersed in the treatment solution at a temperature below that at which the textile would dissolve in the latent solvent, the excess liquid is removed, for example by centrifuging, and the article is then dried. The drying temperature may vary within fairly wide limits and may even without difficulty be higher than 100° C., for example, 130° C.

The stiffness of the finish obtained will vary in accordance with the concentration of the polymer in the treatment solution employed. It is thus possible to adjust the stiffness of the finish in accordance with the desired effect by varying the concentration of the polymer in the treatment solution. In accordance with the ultimate object, the process according to the invention may be combined with a particular shaping operation such as folding, crimping, calendering or embossing, which shaping operation may be carried out before, during or after immersion in the treatment solution, but always before the drying of the finish.

The finish obtained is permanent in the sense in which that word is applied to textile finishes. For example, it resists all washing, dyeing and even bleaching treatments, and it resists rubbing. If the product dissolved in the finishing liquid is itself a polymer based on acrylonitrile, the articles obtained have maximum homogeneity and possess to the highest degree the stability peculiar to this class of polymers.

The following examples will serve to illustrate the invention. All percentages referred to are by weight.

Example I

A woven fabric consisting of polyacrylonitrile thread is completely immersed at 20° C. in a previously prepared solution containing 20 g. per litre of polyacrylonitrile in dimethylformamide. In order to obtain good penetration the fabric is left immersed for half an hour. The excess liquid is then removed by centrifuging. The weight of liquid retained is 28%. The article is dried for 2 hours at 60° C. and then for half an hour at 120° C.

The fabric obtained possess a light-weight permanent finish, but the textile properties of the threads are not modified, as may be seen by determination of their tensile strength. The breaking elongations of the threads employed are as follows:

	Untreated fabric	Treated fabric
Elongation (Percent):		
Warp	20.1	20.5
Weft	20.9	21

Example II

The procedure of Example I is followed but using a treatment solution containing 50 g. per litre of polyacrylonitrile in dimethylformamide.

The measured weight of liquid retained is 0.8%.

This small quantity is sufficient to give a very firm finish which resists washing, dyeing and bleaching treatment and possesses the same properties of chemical, photochemical and biological resistance as the support fabric. The breaking elongations of the threads are as follows:

	Untreated fabric	Treated fabric
Elongation, Percent:		
Warp	20.1	20.8
Weft	20.9	20.9

Example III

A tube consisting of Helanca type polyacrylonitrile thread, having an internal diameter of 8 mm. and a length of 1.50 m., obtained in accordance with the method of copending United States application No. 661,015, filed February 19, 1957, now U.S. Patent No. 3,011,527, and intended for use as an arterial prosthesis, is pulled on to glass rod having an external diameter of 7.8 mm. and a length of 0.50 m.

Folds are formed in the tube by drawing it along the rod, the two ends being tied.

The folds are set by steam treatment for a quarter of an hour at 100° C. and for a quarter of an hour at 120° C.

The set tube withdrawn from the glass rod has circular pleats and is soft.

It is immersed at 25° C. in a solution containing 2% of polyacrylonitrile in dimethylformamide and then centrifuged. The weight of liquid retained is 35%. After drying for one hour at 120° C., the tube obtained is very firm, while retaining satisfactory flexibility and the necessary porosity. More especially, it can be very readily curved without flattening and is particularly suitable for the replacement of diseased arteries, that is, for the operation known as heterografting.

It may be bleached and sterilised with boiling water or by steam treatment without modification of its properties, and behaves in the living organism exactly in the manner of a corresponding untreated prosthesis.

Example IV

A fabric consisting of polyacrylonitrile thread is immersed for half an hour in a solution at 0° C. containing 10 g. per litre of polyacrylonitrile in dimethylsulphoxide. After centrifuging to retain a liquid content of 35%, the fabric is dried for two hours at 60° C. and then for half an hour at 120° C. The fabric obtained has a satisfactory light-weight finish.

Example V

A fabric consisting of polyacrylonitrile thread is immersed in a solution, at 0° C., containing 10 g. per litre of a copolymer consisting of 90% of acrylonitrile and 10% of methyl methacrylate in γ-butyrolactone. The fabric is left immersed for half an hour and the excess liquid is removed by centrifuging. The weight of liquid retained is 35%. The product is dried for two hours at 60° C. and for half an hour at 120° C.

The fabric obtained has a satisfactory light-weight finish.

Example VI

A tube having an internal diameter of 7.3 mm. woven from Helanca type polyacrylonitrile thread obtained in accordance with the method of copending United States application No. 661,015, filed February 19, 1957, now U.S. Patent No. 3,011,527, but in which the two high-shrinkage polyacrylonitrile threads and four Helanca type polyacrylonitrile threads are alternately introduced as weft yarns in the course of the weaving, is pulled on to a glass rod having a diameter of 6.8 mm. and then steam-treated for 15 minutes at 135° C. to shrink the high-shrinkage yarn.

A tube having small circular pleats due to the shrinkage is obtained, which is dried for 15 minutes at 120° C.

It is immersed in a solution, at 25° C., containing 5% of polyacrylonitrile in dimethylformamide. The tube is then centrifuged to retain a liquid content of 35%.

The tube is then replaced on the glass rod and longitudinally drawn together into folds. The folds form regularly on the existing small circular pleats. The two ends are tied on the glass rod.

The assembly is then heated in an oven for half an hour at 120° C.

On removal of the glass rod, a circularly pleated tube is obtained, which is elastic in the longitudinal direction and fairly rigid in the radial direction and which does not flatten when bent.

If desired, the effect can be further enhanced by a steam treatment for half an hour at 135° C.

Example VII

A tube consisting of Helanca type polyacrylonitrile thread having an internal diameter of 8 mm. and a length of 1.50 m., obtained in accordance with the method of copending United States application No. 661,015, filed February 19, 1957, now U.S. Patent No. 3,011,527, is immersed, at 20° C., in a solution containing 5% of polyacrylonitrile in dimethylformamide. The excess liquid is removed by centrifuging to retain a liquid content of 38%. The tube is then pulled on to a glass rod having a diameter of 7.8 mm. and a length of 0.50 m. and drawn together into folds; the two ends are then tied on the rod.

Drying is then effected for half an hour at 120° C., which is sufficient to produce both a good drying of the finish and a good setting of the folds. The tube obtained is elastic and has good radial firmness. It may, more especially, be very readily curved without flattening and is particularly suitable as a substitute for diseased arteries.

It may be bleached and sterilised with boiling water or by steam treatment without modification of its properties.

Example VIII

A fabric consisting of polyacrylonitrile thread is immersed at 25° C. in a solution containing 5% of polyvinyl chloride in dimethylformamide. The excess liquid is removed by centrifuging to retain a liquid content of 35%. The fabric is then dried for half an hour at 120 °C.

A good, very resistant finish is obtained.

Example IX

A woven fabric consisting of polyacrylonitrile thread is immersed, at 25° C., in a solution containing 5% of secondary cellulose acetate in dimethylformamide.

The excess liquid is removed so as to retain a liquid content of 38%, and the fabric is then dried for half an hour at 120° C.

A good stiff finish is obtained without, however, destroying the porosity of the fabric.

Example X

A woven fabric consisting of polyacrylonitrile thread is immersed for half an hour, at 25° C., in a solution containing 5% of a polyvinyl acetate, having a molecular weight of 33,000, in dimethylformamide.

The excess liquid is removed so as to retain a liquid content of 35%, and the fabric is dried for half an hour at 120° C.

A good, stiff, very resistant finish is obtained.

I claim:

1. A process for the treatment of acrylonitrile polymer textile fabrics to impart a permanent finish thereto, which comprises subjecting textile fabrics formed of a polymer containing at least 85% of acrylonitrile to impregnation with a solution of a thermoplastic polymer in a liquid at a temperature at which the liquid is a non-solvent for the textile fabrics and drying the textile fabrics at a temperature at which the liquid is a solvent, therefor, thereby coating the fibres of which the fabric is composed with the said thermoplastic polymer.

2. A process according to claim 1, wherein the textile fabric is subjected to impregnation with a solution in dimethylformamide of a polymer which is soluble in dimethylformamide at least at elevated temperatures.

3. A process according to claim 1, wherein the textile fabric is subjected to impregnation with a solution in γ-butyrolactone of a polymer which is soluble in γ-butyrolactone at least at elevated temperatures.

4. A process according to claim 1, wherein the textile fabric is subjected to impregnation with a solution in di-

methylsulphoxide of a polymer which is soluble in dimethylsulphoxide at least at elevated temperatures.

5. A process according to claim 2, wherein the said impregnating polymer is also an acrylonitrile polymer containing at least 85% of acrylonitrile and is present in the impregnating solution in a concentration of 0.1 to 15% by weight of the solution, and the impregnated fabric is dried at a temperature above 80° C.

6. A process according to claim 5, wherein the said impregnating polymer is also an acrylonitrile polymer containing at least 85% of acrylonitrile and is present in the impregnating solution in a concentration of 0.1 to 15% by weight of the solution, the impregnation is effected at a temperature of at most 0° C., and the impregnated fabric is dried at a temperature above 20° C.

7. A process according to claim 4, wherein the said impregnating polymer is also an acrylonitrile polymer containing at least 85% of acrylonitrile and is present in the impregnating solution in a concentration of 0.1 to 15% by weight of the solution, the impregnation is effected at a temperature of at most 0° C., and the impregnated fabric is dried at a temperature above 20° C.

8. A process according to claim 1, wherein the textile

fabric is formed into a desired configuration in which it is maintained during the drying operation.

9. Process according to claim 8, wherein the textile fabric is a tube woven of high bulk acrylonitrile polymer thread which is drawn together to form pleats and is held in the pleated form during the drying operation.

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