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3,145,186

PROCESS FOR PREPARING ACRYLONITRILE POLYMER FIBERS AND RESULTING PRODUCT

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This invention relates to compositions of matter that are especially adapted for use in spinning acrylonitrile polymer synthetic textile fibers or the like structures. It relates more particularly to spinnable solutions of such polymers in concentrated aqueous salt solutions having certain hydroxyalkyl alkyl cellulose ethers dissolved therein. The invention is also concerned with shaped articles, especially filamentary structures having increased shrinkability, dyeability, and resistance to fibrillation and, to methods for preparation of such compositions and articles.

Polyacrylonitrile and many of the fiber and film-forming copolymers of acrylonitrile may advantageously be fabricated by a wet spinning process wherein the polymer composition is extruded from compositions of the polymer in polyacrylonitrile-dissolving aqueous saline solvents, particularly aqueous solutions of zinc chloride and its saline equivalents. Such a procedure, as is well known in the art is oftentimes referred to as salt-spinning with the fibers (or other shaped articles) obtained thereby being salt-spun. In salt-spinning, the fiber-forming, aqueous saline spinning solution or other composition of the polymer is extruded during the spinning operation into a non-polymer dissolving coagulation liquid, or spin bath, which frequently is a solution of the same salt or salts as are in the spinning solution.

Acrylonitrile polymers (including fiber-forming copolymers), particularly polyacrylonitrile, that are salt-spun in the referred-to manner are generally formed initially as aquagel intermediates. Such intermediates have a water-swollen or hydrated structure prior to their being finally irreversibly dried to the desired, characteristically hydrophobic, product.

Advantageously, the aquagel structure of polyacrylonitrile and other fiber and film forming acrylonitrile polymers may be derived by the extrusion into and coagulation in an aqueous coagulating spin bath of a solution of the acrylonitrile polymer that is dissolved in an aqueous zinc chloride saline solvent therefor. It is usually desirable for zinc chloride to be at least the principal (if not the entire) saline solute in the aqueous saline solvent solution.

If preferred, however, various of the saline equivalents for zinc chloride may also be employed in the aqueous saline solvent medium for the spinning solution and the coagulating bath utilized. These zinc chloride equivalents, as is well known, include various of the thiocyanates (such as calcium thiocyanate) lithium bromide and the salts and salt mixtures that are "solvent" members of the so-called "lyotropic" series as are disclosed, among other places, in U.S. 2,140,921; 2,425,192; 2,648,592; 2,648,593; 2,648,646; 2,648,648; and 2,648,649.

Fabricated acrylonitrile polymer films, textile fibers and like filamentous articles derived from salt-spinning processes are generically described as being capable of lying substantially in a single plane, having at least one major dimension, and at least one minor dimension less than about 0.1 inch, said articles being characterized by having orientation of the molecules parallel to one another and to a major surface of the article. Such articles are often hard and brittle and have a tendency to fibrillate during preparation and subsequent normal usage of the shaped article.

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The term "fibrillation" is used in the textile industry to indicate a type of fiber disintegration or longitudinal fracture generally along the lines of molecular orientation. As a consequence of fibrillation the fiber or filament is longitudinally divided into segments or fibrils. Often, fibrillation may result in a frosty or whitened appearance, even of dyed fibers and fabrics.

The loss of color or change toward white is affected by several variables including the amount of division and size of fibrils produced during processing of the spun product. Fibrils can be of such small diameters that incident light is scattered. Fibrillation of textile fibers and fabric produced therefrom appears to result from transverse forces which ultimately cause a shattering of the fiber along the lines of least resistance, namely longitudinally. Thus, a fiber or related filamentous article having greater characteristic flexibility may often be less prone to fibrillation than a corresponding relatively less flexible article.

Synthetic acrylonitrile polymer fibers and films derived from aquagels in salt spinning processes generally have a normal shrinkage of between about 12 and 14 percent. For most purposes the indicated order of shrinkage is quite satisfactory.

It may frequently be deemed desirable, however, for synthetic fibers and films to be available having greater shrinkability. Thus, in the preparation of high bulk yarns, it is beneficial to combine fibers of high shrinkability with others of relatively low shrinkability. When the mixed fibers in the yarn construction (or in cloth or fabric manufactured from such yarn) are shrunk together, the variation of shrinkage properties produce partial bending and hook formation in the longer fibers. This results in a yarn of high bulk and softness. Textile goods of such characteristics are frequently of great desirability for the manufacture of such articles as sweaters, scarfs, etc. Similarly, films of high shrinkability derived from acrylonitrile polymers are desirable for such uses as bottle closures, etc.

Accordingly, it is the primary object of the present invention to provide compositions of matter especially adapted for use in forming synthetic films and textile fibers or like structures comprising solutions of high acrylonitrile polymers (i.e. those containing at least 85 weight percent of polymerized acrylonitrile in the polymer molecule).

A further object is to provide shaped articles from the compositions of the invention which have increased flexibility, resistance to fibrillation, increased shrinkability, and enhanced receptivity to many of a wide variety of dyestuffs.

A still further object is to provide a process of producing the compositions and articles of the present invention.

Other and related objects will become evident from the following specification and claims.

In accordance with the present invention synthetic films and textile fibers having the desired properties described herein, are produced from a polymeric spinning solution comprising an acrylonitrile polymer containing in the polymer molecule at least about 85 weight percent of acrylonitrile dissolved in an aqueous saline solvent solution, preferably where zinc chloride is the principal (if not entire) saline solute, wherein the aqueous saline solvent has additionally dissolved therein at least about 10 weight percent preferably between about 15 weight percent and 20 weight percent of the acrylonitrile polymer, of certain hydroxyalkyl alkyl cellulose ethers, as will be described.

The acrylonitrile polymer employed in practice of the present invention is, advantageously, polyacrylonitrile, although, as is readily apparent, any of the well known

fiber- and film-forming copolymers thereof that contain, polymerized in the polymer molecule, at least 85 weight percent of acrylonitrile with at least one other ethylenically unsaturated monomer that is copolymerizable with acrylonitrile may, beneficially, be utilized. The acrylonitrile polymer employed is soluble in an aqueous saline solvent for polyacrylonitrile which, usually, has therein at least about 50-60 weight percent of zinc chloride or its saline equivalents. U.S. 2,776,946, among many other reference sources, sets forth many of the monomers which may be copolymerized or interpolymerized with acrylonitrile to produce binary or ternary acrylonitrile copolymers that are useful in the practice of this invention.

The hydroxyalkyl alkyl cellulose ethers employed in practice of the present invention are those water-soluble ethers which advantageously contain from 2 to 3 carbon atoms in each of the hydroxyalkyl substituents and, from 1 to 2 carbon atoms in each of the alkyl substituents, each hydroxyalkyl alkyl cellulose ether containing from about 15 to 35 percent alkoxyl substitution and from about 2 to 14 percent hydroxyalkoxyl substitution as determined by the analytical methods described in Lenieux and Parves, Canadian J. Research, B-25, 485, (1947) using the method of Samsel and McHard, Ind. Eng. Chem., Anal. Ed., 14, 750, (1942) to determine methoxyl.

Mixed cellulose ethers, such as those suitable for the purposes of the present invention, are sold according to viscosity grade. By viscosity grade is meant the viscosity in centipoises of a 2 percent aqueous solution of the cellulose ether measured at 20° C.

It has been found that any of the available viscosity grades are operable in the instant invention. Thus, mixed cellulose ethers having viscosities of about 10 centipoises or less up to about 18,000 centipoises may be used. It is also possible to use mixtures and combinations of viscosity grades for the purposes of the present invention.

Representative of such cellulose ethers useful in the present invention are hydroxyethyl methyl cellulose hydroxypropyl methyl cellulose hydroxyethyl ethyl cellulose, and hydroxypropyl ethyl cellulose. Because of its availability and its unusually good community of properties hydroxypropyl methyl cellulose is preferred. Such ethers and the preparation thereof are described in U.S. 2,831,852 and 2,949,452.

The hydroxyalkyl alkyl cellulose ethers suitably used in the present invention must be present in the polymer solution in a minimum amount of about 10 weight percent based on the weight of the acrylonitrile polymer. The permissible maximum proportion depends on the particular hydroxyalkyl alkyl cellulose ether being employed and the limit of its compatibility with the aqueous saline solution, as well as the polymeric material contained therein. The maximum limit is generally about 30 weight percent, based on the weight of the acrylonitrile polymer.

The amount of hydroxyalkyl alkyl cellulose ether present in shaped articles produced from salt-spun acrylonitrile polymers is dependent upon, and in the same ratio as, the amounts of said ethers incorporated in the spinning solution.

It has been observed that only the ethers as defined herein are suitable for achieving the ends of the present invention.

For example, a commercially sold methyl ether of cellulose containing from about 26 to 33 percent methoxyl substitution was unsatisfactory for the purpose of the present invention.

Still further, methyl cellulose materials which are soluble only in alkali solutions, e.g. aqueous solutions containing from about 2 percent by weight of an alkali, are also unsatisfactory for the purpose of the present invention.

The desirable properties of shaped articles produced by the methods of the present invention are believed to be derived from reaction of the suitable hydroxyalkyl alkyl cellulose ethers described herein with acrylonitrile

polymers, said reaction taking place in a heated aqueous saline spinning solution.

More specifically, the suitable hydroxyalkyl alkyl cellulose ethers described herein must be added to the acrylonitrile containing, aqueous saline spinning solution with subsequent heating of said spinning solution for periods of at least about 30 hours, preferably from about 60 to 80 hours, at a temperature ranging from about 60° to 80° C. to obtain the ends of the present invention.

Temperatures in excess of about 80° C. will appreciably darken the polymeric spinning solution and the shaped articles formed therefrom.

Temperatures less than about 60° C. are not sufficient to provide the desirable results described herein.

It has been observed that hydroxyalkyl alkyl cellulose ethers of the type here described but which have been preheated in an aqueous solution containing about 60 weight percent of zinc chloride (prior to the incorporation of the fiber and film-forming acrylonitrile polymer), do not suitably provide the ends of the present invention.

The following examples, wherein all parts and percentages are to be taken by weight, illustrate the present invention but are not to be construed as limiting its scope.

EXAMPLE 1

In each of a series of experiments, separate charges of about 35 grams of a solution consisting of 10 percent polyacrylonitrile, 54 percent zinc chloride, and 36 percent water, all based on the total weight of the solution, were placed in each of a number of bottles.

Varying percentages of several hydroxypropyl methyl cellulose ethers having a methoxyl content of from about 19 to 24 percent and a hydroxypropyl content of from about 4 to 12 percent were individually added to the individual samples with stirring until a homogeneous solution was, in each case, obtained. The resulting samples were placed in a standard laboratory oven maintained at a temperature of about 80° C., wherein said samples remained for periods of from about 60 to 65 hours.

In each experiment the individual oven-treated spinning solutions were extruded through a spinnerette having about 300 individual orifices (each orifice having a diameter of about 3 mils), into an aqueous non-polymer dissolving zinc chloride coagulating bath. The aquagels formed therein were then individually spun into a multiple filament aquagel tow and collected on a magnesium bar covered with aluminum foil and the resulting individual aquagel tows water washed until substantially free of zinc chloride.

There was thereby obtained a series of aquagel filament tows containing about 1 part water for each part of polymer therein. These aquagel filament tows were oriented by being stretched to a length of about 10 to 12 times their original extruded length and allowed to air dry at normal room temperatures.

Each filament tow was then finally irreversibly dried for about 5 minutes at about 140° C. and tested for resistance to fibrillation.

Each of the resulting fibrous materials were combed out flat; and cemented at each end of a glass slide. Each of the glass slides were fastened to the pan of a "Welsh" triple-beam laboratory balance. The "Welsh" balance was mounted on a milling vice, by means of which, each fiber sample was traversed under a vibrating ball in a test of fibrillation resistance.

In each of the tests, five passes of the tool were made at right angles to the fiber axis (about 1/8 inch apart) under loads of 1, 4, 16, 64, and 128 grams, respectively. Rating of fibrillation resistance was by visual and microscopic inspection.

Fibers which gave no perceptible fibrillation at 64 grams or more were rated "excellent." Those which fibrillated noticeably at 16 grams or less were rated "fair to poor."

Fibrillation ratings for fibers containing varying percentages of the hydroxypropyl methylcellulose ethers as herein described are reported in the following Table 1.

Table 1

Sample	Percent Hydroxypropyl Methyl Cellulose Based on Polymer Weight	Viscosity in Centipoises of 2 Percent Aqueous Solution at 20° C.	Load in Grams to Noticeable Fibrillation	Rating
1-----	None	-----	16	Fair.
2-----	10	100	64	Excellent.
3-----	20	100	64	Do.
4-----	30	100	64	Do.
5-----	10	15,000	64	Do.
6-----	20	15,000	64	Do.
7-----	30	15,000	64	Do.

EXAMPLE 2

The shrinkability of film samples was determined according to the following tests.

In each of a series of experiments the individual, oven-treated, spinning solutions described in Example 1, were cast on "Pyrex" glass plates using a stainless steel drawbar. The resulting films were coagulated by holding the coated plate in a stream of water at ambient temperature.

Within 1 or 2 minutes after casting, the films were detached from the glass plates and thoroughly water washed until free from zinc chloride.

The films prepared in this manner were aquagels which were each then oriented by stretching while immersed in an aqueous medium at a temperature of at least 65° C. Plasticizing was preliminarily indicated in each case when a material could be drawn with less force than required for an equivalent but untreated material (the same cross section and with the same temperature).

The resulting, oriented films were dried overnight at room temperature and subsequently measured. Each of the films were then immersed in boiling water for about 10 minutes after which the film was re-measured, and the percent shrinkability calculated.

The shrinkage was calculated by the following formula

$$\text{Percent Shrink} = \frac{\text{Original Length} - \text{Final Length}}{\text{Original Length}} \times 100$$

The films containing hydroxypropyl methylcellulose as described herein were characterized by a shrinkability of about 60 to 65 percent whereas equivalent, but untreated films were characterized by a shrinkability of about 12 to 14 percent.

EXAMPLE 3

The dye-receptivity of fiber samples was determined according to the following test.

In each of a series of experiments, the oriented, irreversibly dried, filament tows described by Example 1, were separately immersed in a boiling aqueous solution containing about 1 percent by weight of Irgalan Violet 5 RL dye (C.I. acid violet 73).

Each tow was rinsed in water and dried at normal room temperature.

Dye-receptivity of the dried filament tows was measured visually.

Filament tow samples containing hydroxypropyl methylcellulose as described herein, were characterized by a noticeably enhanced dye-receptivity as compared to equivalent, untreated samples.

Similar desirable plasticizing efficiency, resistance to fibrillation, increased shrinkability, and enhanced dye-receptivity is obtained using any concentration between about 10 weight percent to 30 weight percent of polymer weight of at least one hydroxyalkyl alkyl cellulose ether wherein each hydroxyalkyl substituent of each ether con-

tains from 2 to 3 carbon atoms and each alkyl substituent contains from 1 to 2 carbon atoms, each hydroxyalkyl alkyl cellulose ether containing from about 15 to 35 percent alkoxy substitution and from about 2 to 14 percent hydroxyalkoxy substitution.

Similar good results are obtained when fiber- and film-forming acrylonitrile polymers containing at least 85 weight percent of polymerized acrylonitrile and up to 15 weight percent of one or more of such copolymerizable materials as vinyl chloride, vinyl acetate, methyl and other alkyl acrylates or methacrylates, the vinyl pyridines, allyl alcohol, and many others well known to those skilled in the art are admixed with the polyoxyalkylene glycols suitable for use in practice of the present invention.

What is claimed is:

1. In the process of producing essentially non-fibrillating, dye receptive, shrinkable synthetic acrylonitrile polymer textile fibers by dissolving a fiber forming acrylonitrile polymer in an aqueous saline solvent therefor to form a salt spinning solution, which polymer contains in the polymer molecule at least about 85 weight percent of acrylonitrile with any balance being another monoethylenically unsaturated monomeric material that is copolymerizable with acrylonitrile; spinning said fiber forming acrylonitrile polymer containing salt spinning solution into an aquagel filamentary structure substantially free from residual salt; and subsequently irreversibly drying said aquagel structure to a synthetic characteristically hydrophobic textile structure; the improvement consisting of (1) dissolving in said fiber forming acrylonitrile polymer containing salt spinning solution, prior to spinning said solution into said aquagel filamentary structure, of between about 10 and 30 weight percent, based on the weight of said fiber forming acrylonitrile polymer, of at least one hydroxyalkyl alkyl cellulose ethers having from 1 to 2 carbon atoms in each alkyl substituent, from 2 to 3 carbon atoms in each hydroxyalkyl substituent, from 15 to 35 percent alkoxy substitution and from about 2 to 14 percent hydroxyalkoxy substitution, and (2) heating the fiber forming acrylonitrile polymer and hydroxyalkyl alkyl cellulose ether containing spinning solution for a period of at least about 30 hours at a temperature between about 60° C. and 80° C.

2. The process of claim 1, wherein the hydroxyalkyl alkyl cellulose ether is hydroxypropyl methylcellulose containing from about 19 to 24 percent methoxyl substitution and from about 4 to 12 percent hydroxypropyl substitution, said hydroxypropyl methylcellulose having a viscosity at 20° C. in a 2 percent aqueous solution of said hydroxypropyl methylcellulose of about 100 centipoises.

3. The process of claim 1, wherein the hydroxyalkyl alkyl cellulose ether is hydroxypropyl methyl cellulose containing from about 19 to 24 percent methoxyl substitution, and from about 4 to 12 percent hydroxypropyl substitution, said hydroxypropyl methyl cellulose having a viscosity at 20° C. in a 2 percent aqueous solution of said hydroxypropyl methyl cellulose of about 15,000 centipoises.

4. The process of claim 1, wherein said fiber forming acrylonitrile polymer is polyacrylonitrile.

5. The process of claim 1, wherein said aqueous saline solvent is a solution of zinc chloride.

6. A flexible, essentially non-fibrillating, dye receptive, shrinkable filamentary structure prepared by the process of claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS

2,140,921	Rein	Dec. 20, 1938
2,538,051	Schick	Jan. 16, 1951
3,060,139	Greminger et al.	Oct. 23, 1962

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, list of References Cited, add the following:

3,097,055 Routson et al.----- July 9, 1963

Signed and sealed this 17th day of November 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
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Commissioner of Patents