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PROCESS OF PRODUCING NON-FIBRILLATING ACRYLONITRILE POLYMER FILAMENTS

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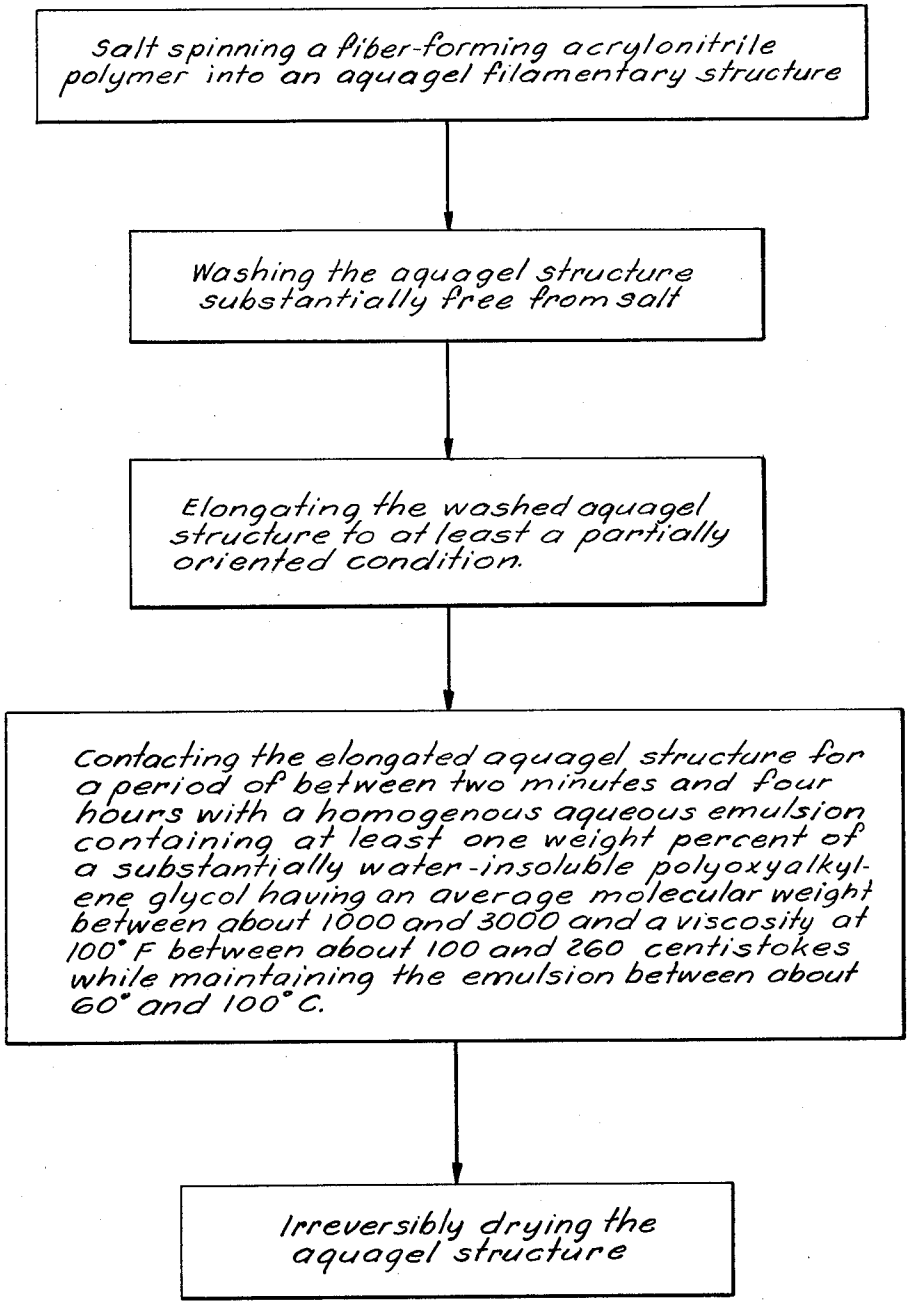

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PROCESS OF PRODUCING NON-FIBRILLATING ACRYLONITRILE POLYMER FILAMENTS

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This invention relates to a process for preparing improved acrylonitrile polymer structures. It relates more particularly to the preparation of non-fibrillating acrylonitrile polymer structures prepared by treating said structures (while in the aquagel form) with certain substantially water-insoluble polyoxyalkylene glycols.

By "structures" as employed throughout the instant specification and claims, is meant fibers, filaments, bundles of filaments, yarns, threads, foils, ribbons, films, and the like. However, for the sake of simplicity of description, the present invention will be described as it is applicable to the production of filaments, including bundles of filaments and fibers, it being understood that this is merely intended in an illustrative sense and the invention should not be limited thereby, but only insofar as the same may be limited by the appended claims.

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 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 structures 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. Those 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.

Filaments produced from acrylonitrile polymers by the wet spinning process have excellent physical properties but do suffer from one serious defect, namely, fibrillation.

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 diameter 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.

Accordingly, it is the primary object of the present invention to provide a method of preparing substantially non-fibrillating textile fibers or like filamentous structures from high acrylonitrile polymers (i.e., those containing at least 85 weight percent of polymerized acrylonitrile in the polymer molecule).

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

In accordance with the present invention, substantially non-fibrillating synthetic polymer textile filaments are prepared by salt spinning acrylonitrile polymers (which polymer contains in the polymer molecule at least about 85 weight percent of acrylonitrile, any balance being another monoethylenically unsaturated monomeric material that is copolymerizable with acrylonitrile), into an aquagel filamentary structure that contains between about 1 and 5 parts by weight of water to each part by weight of dry polymer therein; washing said aquagel structure substantially free from residual salt, and physically elongating the filament aquagel by stretching said aquagel to an at least partially oriented condition; subjecting said aquagel to intimate contact with a homogeneous aqueous emulsion containing at least about 1 weight percent based on the weight of the emulsion, of a substantially water-insoluble polyoxyalkylene glycol (as will be described); maintaining said aquagel in contact with the emulsion at a temperature between about 60° C. and 100° C. for a period of between about 2 minutes to 4 hours; and subsequently irreversibly drying the aquagel filament to a synthetic characteristically hydrophobic textile fiber structure.

In the annexed drawing there is shown a flow sheet in accordance with the herein claimed process.

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 acrylonitrile 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.

Specific polyoxyalkylene glycols that are suitable for instant purposes include, but are not restricted to, polyoxypropylene glycols having an average molecular weight of about 2000; polyoxybutylene glycols having an average molecular weight of about 2000; and suitably mixed poly-

oxyalkylene glycols wherein the polymer chains contain two or more different oxyalkylene units, either as a random sequence (heteric) or as segregated blocks (block copolymers). Ordinarily, water-insoluble glycols having average molecular weights between about 1000 and 3000 are suitable.

The polyoxyalkylene glycols suitably used in the present invention must be present in the aqueous emulsion in a minimum amount of about 1 weight percent based on the weight of the emulsion. The permissible maximum proportion depends on the particular polyoxyalkylene glycol being employed; the ability of the glycol to form a stable homogeneous emulsion with water; and the compatibility of the glycol with the acrylonitrile polymer aquagel. The maximum limit is generally about 20 weight percent, based on the weight of the emulsion. Glycol concentrations greater than about 20 weight percent based on emulsion weight oftentimes form two phase systems with water and are not useful for the present invention.

The amount of polyoxyalkylene glycol present in filaments produced from salt-spun acrylonitrile polymers is dependent upon, and approximately in the same ratio as, the amounts of said glycols present in the aqueous emulsion.

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

For example, polyoxyalkylene glycols of the type here described but having a viscosity at 100° F. less than about 100 centistokes are not sufficiently insoluble in water to provide the ends of the present invention.

Additionally, polyoxyalkylene glycols of the type here described having a molecular weight greater than about 3000 or a viscosity at 100° F. of greater than about 260 centistokes have limited compatibility with the acrylonitrile polymer aquagel and, as a consequence, are not useful for the present invention.

The preparation of the polyoxyalkylene glycols useful in practice of the present invention is well known to those skilled in the art. U.S. 2,056,830 describes a method of preparing polyglycols by partial dehydration of the corresponding simple glycols in the presence of dehydration catalysts. By a "dehydration catalyst" is meant a substance which is capable of prompting splitting of water from a simple glycol, e.g., propylene glycol, with intramolecular formation of glycol ethers when such simple glycol is heated in its presence.

The desirable properties of synthetic textile fibers and like filamentous articles produced by the methods of the present invention are derived by incorporation of the suitable polyoxyalkylene glycols described herein, into the acrylonitrile polymer aquagel structure.

As previously noted, the aquagel structure is generally stretched to an at least partially oriented condition prior to immersing said aquagel structure in the aqueous polyoxyalkylene glycol emulsions described herein. Orientation of the aquagel structure is accomplished to increase the tenacity of the filament of said aquagel structure to a practical point.

It has been observed that non-oriented acrylonitrile polymer aquagel structures which have been treated with the aqueous polyoxyalkylene glycol emulsions, as described herein, and subsequently oriented in the indicated manner, form synthetic textile fibers and like filamentous articles having similar desirable properties.

The acrylonitrile polymer aquagels must be immersed in the aqueous polyoxyalkylene glycol emulsions described herein, for periods of between about 2 minutes and 4 hours, preferably from about 5 to 10 minutes, at a temperature ranging between about 60° C. and 100° C., to obtain the ends of the present invention.

Temperatures less than about 60° C. are not sufficient to provide the desirable results described herein, and immersion periods greater than about 4 hours may at least partially hydrolyze the polyoxyalkylene glycol constituent of the homogeneous emulsion.

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

Example 1

In each of a series of experiments, a charge 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, was placed in a bottle.

The spinning solution was 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 aquagel formed therein was spun into a multiple filament tow and collected on a magnesium bar covered with aluminum foil. The resulting aquagel filament tow was then water washed until substantially free of zinc chloride.

There was thereby obtained an aquagel filament tow containing about 1 part water for each part of acrylonitrile polymer therein. The aquagel filament tow was oriented by being stretched to a length of about 10 to 12 times its original extruded length.

The oriented tow was then cut in individual shorter lengths and several of the individual shorter lengths individually boiled for a period of about 5 minutes in a homogenized aqueous emulsion containing about 5 weight percent based on emulsion weight, of a substantially water-insoluble polyoxypropylene glycol having an average molecular weight of about 2000 and a viscosity at 100° F. of about 164 centistokes.

Each of the resulting fibrous materials were dried: 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 ⅛ 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."

Each of the polyacrylonitrile fibrous materials treated with the aqueous polyoxyalkylene glycol emulsions as described herein, fibrillated only slightly under loads of 64 to 128 grams and, consequently, had a fibrillation rating of "excellent."

Equivalent, but untreated polyacrylonitrile fibrous materials fibrillated noticeably under a load of 16 grams and, consequently, were assigned a fibrillation rating of "fair to poor."

Similar desirable resistance to fibrillation is obtained using any concentration between about 1 and 20 weight percent based on emulsion weight of the polyoxypropylene glycol described herein.

In like manner similar desirable resistance to fibrillation is obtained using any concentration between about 1 and 20 weight percent based on emulsion weight of a polyoxybutylene glycol having an average molecular weight of about 2000 and a viscosity at 100° F. of about 258 centistokes (such glycol being a viscous liquid which is less than about 0.1 percent soluble in water at 25° C.).

On the other hand, polyoxypropylene glycols having a viscosity at 100° F. of less than about 100 centistokes, and polyoxyethylene glycols having a molecular weight ranging from about 200 to 2000, and corresponding viscosities at 100° F. of more than about 20 centistokes to

that of a solid material, are insufficiently insoluble in water and are not useful for the present invention.

Polyoxypropylene glycols that have an average molecular weight greater than about 3000 and a corresponding viscosity at 100° F. greater than about 260 centistokes are insufficiently compatible with most acrylonitrile polymers of interest to be useful for the present invention.

Similar good results, as noted above in Example 1 carried out in accordance with this invention, 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. Method of preparing a non-fibrillating synthetic acrylonitrile polymer textile fiber which method comprises:

(*a*) salt spinning a fiber-forming acrylonitrile polymer, which polymer contains in the polymer molecule at least about 85 weight percent of acrylonitrile, any balance being another monoethylenically unsaturated monomeric material that is copolymerizable with acrylonitrile, into an aquagel filamentary structure that contains between about 1 and 5 parts by weight of water to each part by weight of dry polymer therein;

(*b*) washing said aquagel structure substantially free from residual salt;

(*c*) physically elongating said aquagel structure by stretching it to an at least partially oriented condition;

(*d*) subjecting for from 2 minutes to about 4 hours the so-formed aquagel fiber to intimate contact with a homogeneous aqueous emulsion containing at least 1 weight percent of a substantially water-insoluble polyoxyalkylene glycol having an average molecular weight between about 1000 and 3000 and a viscosity at 100° F. between about 100 and 260 centistokes, said emulsion maintained at a temperature between about 60° C. and 100° C.; and

(*e*) subsequently irreversibly drying said aquagel fiber to a synthetic characteristically hydrophobic textile fiber structure.

2. The method of claim 1, wherein the substantially water-insoluble polyoxyalkylene glycol is present in amounts between about 1 and 20 weight percent, based on the weight of the homogeneous emulsion.

3. The method of claim 1, wherein said polyoxyalkylene glycol is polyoxypropylene glycol with an average molecular weight of about 2000 and a viscosity at 100° F. of about 164 centistokes.

4. The method of claim 1, wherein said polyoxyalkylene glycol is polyoxybutylene glycol with an average molecular weight of about 2000 and a viscosity at 100° F. of about 258 centistokes.

5. The method of claim 1, wherein said acrylonitrile polymer is polyacrylonitrile.

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