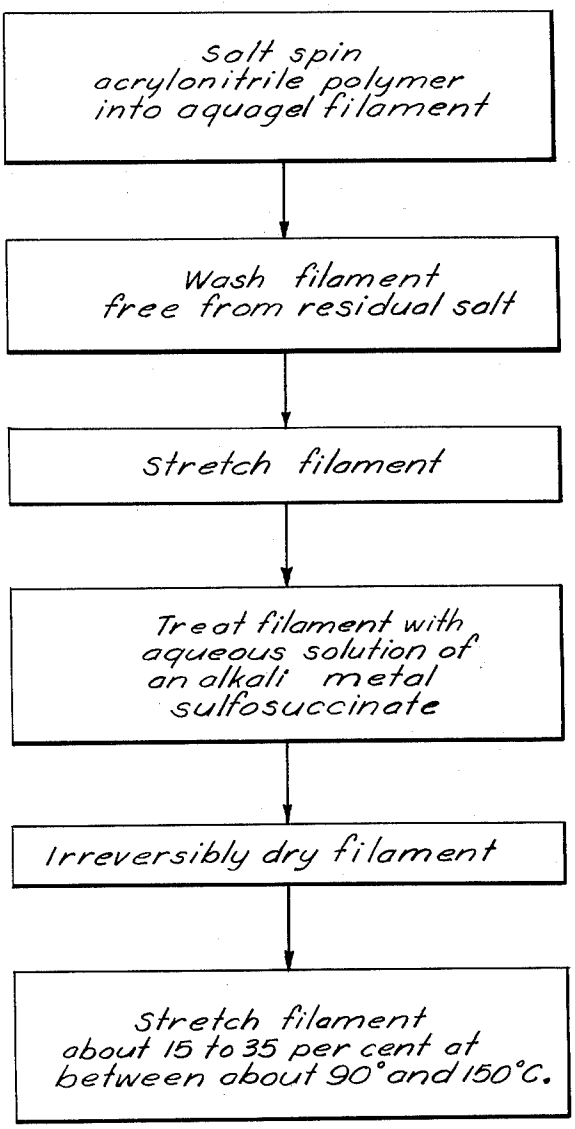
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METHOD OF MAKING HIGH-SHRINK TEXTILE FIBERS

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INVENTORS.
Willis G. Routson
Thomas C. Spence
BY
ATTORNEY

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METHOD OF MAKING HIGH-SHRINK TEXTILE FIBERS

Willis G. Routson, Concord, Calif., and Thomas C. Spence, Yorktown, Va., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

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This invention relates to the production of highly shrinkable synthetic fibers. More specifically, the present invention has reference to shaped or preformed fibers and related filamentous structures, which are comprised of essentially linear acrylonitrile polymer compositions which have been treated while they are in an already fabricated form in order to improve or increase their shrinkability.

Polyacrylonitrile and many of the fiber-forming copolymers of acrylonitrile may advantageously be fabricated into synthetic textile fibers by a wet spinning process of a known variety wherein the fiber-forming polymer composition is salt spun using polyacrylonitrile-dissolving aqueous saline solvents, particularly zinc chloride and its saline equivalents, for preparation of the spinning solution or other composition and non-polymer-dissolving coagulating spin bath solutions of the same salt or salts during the wet spinning operation.

Acrylonitrile polymers, particularly polyacrylonitrile, that are wet spun in such 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, textile fiber product. These aquagels generally contain an amount of water that is at least gravimetrically equal to the hydrated polymer that is contained therein. It may oftentimes be preferable for the water-to-polymer weight ratio in the aquagel to be in the neighborhood of from about 1.5:1 to 2.0:1, respectively. Aquagel structures in which the water-to-polymer ratio prior to irreversible drying and during their manufacturing process is as high as 4.5 to 5:1 may frequently be satisfactorily employed.

Advantageously, aquagel structures of polyacrylonitrile and other fiber-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, as is well known, include various of the thiocyanates (such as calcium thiocyanate), lithium bromide and the salt mixtures that are members of the so-called "lyothopic" series. Such aqueous saline solvents for polyacrylonitrile have been disclosed, among other places, in United States Letters Patents Nos. 2,140,921; 2,425,192; 2,648,592; 2,648,593; 2,648,646; 2,648,648; and 2,648,649.

It may frequently be deemed advantageous and desirable for synthetic fibers to be available having greater shrinkability than that with which they are inherently possessed. 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 loop formation or "arcing-up" 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, comforters, scarfs, etc.

Normal shrinkage of most acrylonitrile polymer fibers when treated with boiling water is 0–5 percent. These fibers can be caused to shrink more, however, by certain conventional unstabilizing treatments as by a rapid stretch with a simultaneous short heating cycle, moist or dry, at about 90 to 150° C. The more stable of the synthetic acrylonitrile polymer fibers derived from aquagels in salt spinning processes generally have a shrinkage of between about 12 and 15 percent when so treated by this conventional treatment. Thus, shrinkage of between about 12 and 15 percent will usually be obtained with fibers from aquagel structures of homopolymeric acrylonitrile, or from polymeric blends with polyacrylonitrile, or from polyacrylonitrile aquagels that have been impregnated with polymeric adjuvants, and from certain of the fiber-forming copolymers and graft copolymers of acrylonitrile. These latter modified polyacrylonitrile fibers will be discussed in more detail at another point.

Certain other of the aquagel fibers derived from acrylonitrile polymers that have been prepared by copolymerizing acrylonitrile with another ethylenically unsaturated monomer may be caused to shrink as much as 16–40 percent by the conventional unstabilizing treatment mentioned above. These fibers are, however, usually inherently more unstable and are caused to be unstabilized by such a treatment to the point that they tend to continue to shrink after the original bulking shrink in subsequent encounters with hot treatments, for instance laundering, etc., a feature usually undesirable for obvious reasons.

It has generally been found in the trade that a shrinkage of about 20 percent produces the optimum high bulk from the standpoint of maximum coverage and stability of the resulting yarn or garment.

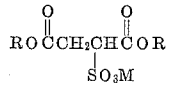
The chief aim and concern of the present invention is to provide synthetic acrylonitrile polymer textile fibers prepared by the indicated salt-spinning process which have generally greater shrinkability without any appreciable increase in instability than the conventional acrylonitrile polymer fibers that are derived from aquagel intermediates in wet spinning operations.

To the attainment of the indicated and corollary ends, high-shrinkable synthetic acrylonitrile polymer textile fibers derived from aquagels that have been salt spun in the indicated manner may be obtained by a method in accordance with the present invention which, surprisingly and simple enough, comprises impregnating (or subjecting to intimate physical contact) an already formed, and at least partially oriented by stretching, acrylonitrile polymer fiber in aquagel form to solutions or dispersions of certain alkali metal salts of dialkyl sulfosuccinates; irreversibly drying the treated aquagel; then subsequently stretching the fiber product about 15–35 percent over its dried length in the presence of heat alone or heat and moisture to the desired characteristically hydrophobic, synthetic textile fiber product having increased shrinkability. The method of the present invention is schematically delineated in the sole FIGURE of the drawing.

Generally, the fibers treated in accordance with the present invention have a shrinkability (as when subjected to steam or boiling water after their irreversible drying and hot stretching) of between about 16 and 20 percent. Thus, the finally obtained fibers can be shrunk by steam or in boiling water by as much as 16–20 percent of the original length in which they were obtained after their final irreversible drying from the aquagel condition and stretching in the presence of heat. Such fibers can advantageously be interblended with normally manufactured acrylonitrile polymer or other varieties of synthetic textile fibers having less inherent shrinkability in order

to advantageously prepare high-bulk yarn constructions.

The alkali metal dialkyl sulfosuccinates that may be utilized in the practice of the present invention include those described by the generic structure:



wherein R is an alkyl radical containing from about 4–14 carbon atoms, and M is an alkali metal, i.e. sodium, potassium, and lithium. Thus, amongst the various sulfosuccinates that may be employed are sodium dioctyl sulfosuccinate (alternatively, sodium bis(octyl) sulfosuccinate), sodium diamyl sulfosuccinate, sodium dibutyl sulfosuccinate, sodium didecyl sulfosuccinate, sodium bis(tridecyl) sulfosuccinate, potassium dioctyl sulfosuccinate, sodium octyl amyl sulfosuccinate, etc., and mixtures thereof. Beneficially and advantageously, sulfosuccinates indicated in the foregoing structure are employed wherein each R is simultaneously the same 4–14 carbon alkyl radical. As indicated, the sulfosuccinates can be employed in either solution or dispersion in order to impregnate the aquagel structure therewith for accomplishment of the desired modification.

The sulfosuccinates may generally be described as being wax-like, water-soluble, hygroscopic solid anionic agents. The water solubility is somewhat dependent on the length of the alkyl radicals. For instance, sodium bis(tridecyl) sulfosuccinate is soluble to 0.5 percent in cold water but easily dissolved to higher levels by warming. Sodium dioctyl and diamyl sulfosuccinates are even more readily dissolved. Sodium dioctyl sulfosuccinate is readily dissolved to form a gel to 50 percent solids.

The treatment may be accomplished by impregnating the washed and oriented aquagel fiber in an aqueous bath of the sulfosuccinate shrinking agent. Or, padding, spraying, wiping or some such similar application may be used. Actual intimate contacting of the aquagel with an aqueous solution of the shrinking agent is most desirable. Concentrations of the sulfosuccinates in the applicating solutions may be between about 0.1 and about 10 percent by weight, and preferably 0.5–2 percent. The temperature of the treating bath may be between about 15–100° C. and preferably between 90–100° C. The amount of the sulfosuccinate picked up by the aquagel while passing through the treating bath will depend on the concentration of the bath, the temperature and the time in the bath. For a treatment with a 1 percent solution at the boil, an aquagel fiber in contact with the bath for about 2 seconds will have approximately 3–4 percent, based on the dry weight of the fiber (O.W.F.), of the sulfosuccinate treating agent.

After the treatment, the aquagel fiber is irreversibly dried. Ordinarily, acrylonitrile polymer aquagels may be irreversibly dried most satisfactorily at temperatures between about 100 and 150° C. for periods of time between about 30 and 5 minutes.

Following the irreversible drying, the dried fiber is stretched in the presence of heat or heat and moisture. Stretching is usually performed between suitable rollers, the forward rollers rotating at an increased speed over the back rollers to provide sufficient differential tension to stretch the fiber between about 15 and 35 percent. The fiber may be heated while stretching by passing it between two heated plates or next to a single heated plate or other suitable heating elements. The surface temperature of the heating plates or grids is maintained between about 120 and 150° C. Preferably, the fibers are stretched while in an atmosphere of 100–125° C. saturated steam. The stretching may also be accomplished while the fiber is immersed in a water bath maintained at about 90–100° C. The time the fiber is in the hot stretching zone may be about 0.5–5 seconds depending on the temperature and degree of stretch desired.

After drying, the high-shrink fiber product of the present invention may advantageously be incorporated in blends with low shrinking fibers of the same or other general varieties in order to produce high bulk yarn constructions. Thus, the fiber product of the present invention may be blended with lower shrinking fibers of polyacrylonitrile or other fiber-forming acrylonitrile polymers or with lower shrinking fibers of other materials, including fibers of nylon, polyesters ("Dacron") etc. The quantity of high shrink fiber that is incorporated in the blend for such yarn constructions depends upon the bulking effect desired in the final product. Greater relative proportions of the high shrink product ordinarily cause relatively less bulking in the blended yarn. Generally, an amount of between about 30 and 70 weight percent of the high shrink fiber blended with the conventional low shrinking fiber provides satisfactory results. As indicated before, the fibers can be shrunk by steam or boiling water. Usually, during shrinking, and particularly if shrunk in boiling water, the shrinking agents are removed from the fibers and thus present no difficulties in further processing and handling of the fibers or fabric.

It is desirable to employ polyacrylonitrile aquagels in the practice of the present invention. If desired, however, certain of the fiber-forming copolymers and graft copolymers of acrylonitrile and graft copolymers on polyacrylonitrile can be utilized in place of polyacrylonitrile including those which form fibers having the same tendency for shrinkage as homopolymeric acrylonitrile. Thus, copolymers of at least about 80 percent acrylontrile with other monoethylenically unsaturated monomers such as vinyl chloride, vinylidene chloride, styrene, vinyl pyridenes, etc., are contemplated.

In this connection, it is advantageous for the acrylonitrile polymers that are used in the practice of the present invention to be high polymers having a molecular weight in the range (say, roughly from 25 to 60 thousand or so) that is generally contemplated by those skilled in the art as being most desirable for fiber-forming acrylonitrile polymers.

In addition, and highly desirable, the aquagel structures that are modified by the present practice contain interblended therewith up to about 20 weight percent of various dye-assisting polymeric adjuvants, including homopolymers or copolymers of such monomers as N-vinyl lactams, for instance, N-vinyl pyrrolidones and N-vinyl caprolactams; N-vinyl-3-morpholinones; N-vinyl-2-oxazolidones, such as N-vinyl-2-oxazolidinone and N-vinyl-5-methyl-2-oxazolidinone; N-vinyl methylalkylsulfonamides such as N-vinyl-N-methyl-methyl-sulfonamide; and the like or equivalent dye-receptors, that have been blended in the aquagel structure by extrusion of a fiber-forming polymer blend or by impregnation of the dye-assisting adjuvant after initial fabrication of the aquagel. Likewise, the aquagels may also, if desired, be further impregnated prior to their final irreversible drying with polymeric dye-assisting adjuvants or other beneficial treating agents for the fibrous product.

The invention is further illustrated by the following examples in which all parts or percentages are by weight unless otherwise indicated.

Example 1

A spinning solution comprised of about 10 parts of polyacrylonitrile dissolved in about 90 parts of a 60 percent aqueous solution of zinc chloride was salt-spun by being extruded through a spinnerette having 750 individual orifices, each of which had a diameter of about 6 mils, into an aqueous coagulating bath that contained about 43 weight percent of zinc chloride dissolved therein to be spun into a multiple filament aquagel tow. The coagulated tow was washed substantially free from salt after being withdrawn from the coagulating bath and oriented by being stretched to a length of about 12 times its original extruded length and impregnated with an aqueous solution of poly-N-vinyl-2-pyrrolidone (PVP) so

as to contain about 7 percent (O.W.F.) of the dye-assisting adjuvant. The aquagel tow was then passed through a boiling aqueous 1 percent by weight solution of sodium dioctyl sulfosuccinate. The time the fibers were in the solution was about 2 seconds. The fibers, on leaving the shrinking agent applicating bath, contained about 3 percent (O.W.F.) of the agent. The fiber tow was then irreversibly dried at 140° C. for about 6 minutes. Following this, the tow was passed through a steam tube, in which was maintained saturated steam at atmospheric pressure, and stretched 31 percent. The residence time in the tube was about 1 second. When the fibers were placed in boiling water for 15 minutes and dried at 80° C., they shrank 19.5 percent. Essentially none of the shrinking agent remained on the fibers.

The percent shrinkage was determined by first tying two pieces of string about the tow a given distance apart while the tow was under a tension of about 0.1 gram per denier. After shrinking, the tow was again put under a tension of 0.1 gram per denier and the distance between the markers measured. The shrinkage was then calculated by the following formula:

$$\text{Percent shrink}=\frac{\text{Original length}-\text{final length}}{\text{Original length}}\times 100$$

Example 2

The procedure of Example 1 was repeated excepting to reduce the concentration of the sulfosuccinate to 0.1 percent. The resulting fibers shrank 16.8 percent.

Example 3

A fiber tow was made according to the procedure of Example 1 except that the treatment with the sodium dioctyl sulfosuccinate was eliminated. The fibers were stretched 31 percent under the same conditions, immersed in boiling water for 15 minutes and dried at 80° C. The tow shrank 15.0 percent.

Example 4

Another fiber sample was made and treated according to the first procedure excepting to substitute a 1 percent solution of sodium diamyl sulfosuccinate for the dioctyl sulfosuccinate. The fibers shrank 16.2 percent.

Example 5

A sample of the tow of Example 1, after irreversibly drying, was passed between two electrically heated aluminum plates 6 inches long and stretched 31 percent. The plates were spaced about $\frac{3}{32}$ inch apart and were heated to about 140° C. The exposure time of the fibers between the heated plates was about 1 second. After boiling and drying as before the fibers shrank 18.5 percent.

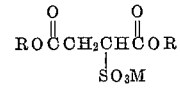
Example 6

The procedure of Example 5 was repeated excepting to eliminate the treatment with sodium dioctyl sulfosuccinate. The fibers shrank 12 percent.

Results commensurate with the foregoing are obtained when other of the indicated alkali metal salts of dialkyl sulfosuccinates and when the indicated acrylonitrile copolymers and acrylonitrile polymers containing other of the dye-assisting adjuvants are used analogous to the methods illustrated and indicated elsewhere in the specification.

What is claimed is:

1. Method of preparing a highly shrinkable synthetic acrylonitrile polymer textile fiber which method comprises salt spinning a fiber-forming acrylonitrile polymer that is adapted to provide fibers which do not shrink more than 15 percent after exposure to water at about 100° C., which polymer contains in the polymer molecule at least about 80 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, said aquagel having incorporated therein between about 2 and 15 weight percent, based on the dry weight of the combined polymer composition, of a polymer of a monomer selected from the group consisting of a N-vinyl lactam, a N-vinyl-3-morpholinone, a N-vinyl-2-oxazolidinone, and a N-vinyl-methylalkyl-sulfonamide; washing said aquagel substantially free from residual salt and physically elongating said fiber by stretching it to an at least partially oriented condition; subjecting said aquagel fiber to intimate contact with an aqueous solution of a sulfosuccinate of the structure:



wherein R is an alkyl radical containing from about 4 to 14 carbon atoms, and M is an alkali metal consisting of sodium, potassium and lithium; irreversibly drying said aquagel fiber to a synthetic characteristically hydrophobic fiber structure; and subsequently stretching said fiber structure about 15 to 35 percent while heating said structure between about 90 and 150° C.

2. The method of claim 1, wherein the sulfosuccinate is a symmetrical dialkyl sulfosuccinate.

3. The method of claim 1, wherein the sulfosuccinate is sodium dioctyl sulfosuccinate.

4. The method of claim 1, wherein the sulfosuccinate is sodium diamyl sulfosuccinate.

5. The method of claim 1, wherein said aqueous solution contains 0.1–10 percent, based on the weight of the solution of the sulfosuccinate.

6. The method of claim 1, wherein said aqueous solution contains 0.5–3.0 percent, based on the weight of the solution, of the sulfosuccinate.

7. The method of claim 1, wherein said aqueous solution is at a temperature of 90–100° C.

8. The method of claim 1, wherein said heating of said structure between about 90 and 150° C. is performed in the presence of an aqueous medium selected from the group consisting of aqueous liquids and aqueous vapors.

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

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