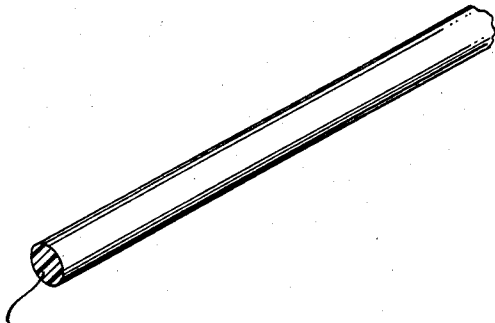


Feb. 7, 1961

G. W. STANTON ET AL
MODIFIED ACRYLONITRILE POLYMER FIBERS WITH
INCREASED SHRINKABILITY AND DYEABILITY
Filed May 7, 1958

2,970,884



*Dye-receptive, highly shrinkable
synthetic textile fiber comprised
of polyacrylonitrile that has been
treated while in the aquagel condition
with a tertiary and/or benzyl alcohol.*

INVENTORS.
George W. Stanton
BY *Ardy Armen*

Lriswold & Lurdick
ATTORNEYS

1

2,970,884

MODIFIED ACRYLONITRILE POLYMER FIBERS WITH INCREASED SHRINKABILITY AND DYEABILITY

George W. Stanton, Walnut Creek, and Ardy Armen, Concord, Calif., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

Filed May 7, 1958, Ser. No. 733,623

9 Claims. (Cl. 18-54)

This invention is germane to the general field of organic chemistry and contributes especially to the polymer art. More specifically, the present invention has reference to shaped articles, particularly fibers and related filamentous structures, which are comprised of essentially linear acrylonitrile polymer compositions which have been modified while they are in an already-fabricated form in order to improve or increase their shrinkability and dyeability, which polymers contain in their molecule recurring alkyl acrylamide units.

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 or 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 "lyotropic" 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.

Synthetic acrylonitrile polymer fibers 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 advantageous and desirable, however, for synthetic fibers 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

2

construction (or in cloth or fabric manufactured from such yarn) are shrunk together, the variation of shrinkage properties produce partial bending and loop 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, comforters, scarfs, etc.

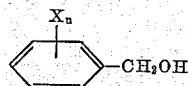
The chief aim and concern of the present invention is to provide synthetic acrylonitrile polymer textile fibers prepared by the indicated salt-spinning process which have generally greater shrinkability than the conventional acrylonitrile polymer fibers that are derived from aquagel intermediates in wet spinning operations. Another design and object of the present invention is to provide synthetic acrylonitrile polymer fibers having enhanced receptivity to many of a wide variety of dyestuffs.

To the attainment of the indicated and corollary ends, dye-receptive, 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 simply 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 alcohols (or their mixtures) in a polar, preferably aqueous, medium in the simultaneous or subsequent presence of strong aqueous acid solutions; then washing the treated aquagel free from the treating reagents; and subsequently irreversibly drying the treated aquagel to the desired characteristically hydrophobic, synthetic textile fiber product having increased shrinkability and enhanced dye-receptivity. 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) of between about 16 and 18 percent. Thus, the finally obtained fibers can be shrunk by steam or in boiling water by as much as 16-18 percent of the original length in which they were obtained after their final irreversible drying from the aquagel condition. Such fibers, one of which is schematically portrayed in the sole figure of the accompanying drawing, 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 treated fibers are also rendered more dyeable with many diverse types of dyestuffs including vat dyes, sulfur dyes, direct dyes, acid dyes, basic dyes, premetalized dyestuffs and the like that frequently are not particularly effective on acrylonitrile polymer fibers, especially fibers consisting entirely of polyacrylonitrile.

The alcohols that may be utilized in the practice of the present invention include tertiary alcohols of the generic structure:



wherein each R independently has from 1 to about 4 carbon atoms with the limitation that the total number of carbon atoms in all three R substituents is from 3 to 7 and benzyl alcohols of the general structure:



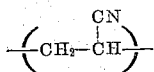
(II)

wherein each X is independently selected from the group consisting of hydrogen, chlorine, bromine or an alkyl radical containing from 1 to about 4 carbon atoms and n has a whole number value from 0 to 5. Thus, amongst the various alcohols which may be employed are tertiary-amyl alcohol of the structure: $C_2H_5(CH_2)_2COH$; tertiary-butyl alcohol of the structure: $(CH_3)_3COH$; 3-methyl-

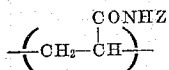
pentane-3-ol of the structure: $(C_2H_5)_2CH_2COH$; 2-methyl-pentane-2-ol of the structure: $C_3H_7(CH_3)_2COH$; 3-ethyl-pentane-3-ol of the structure: $(C_2H_5)_3COH$; 3-methyl-hexane-3-ol of the structure: $C_3H_7C_2H_5CH_3COH$; 2-methyl-hexane-2-ol of the structure: $C_4H_9(CH_3)_2COH$; p-chloro-benzyl alcohol; 2,4-dibromo-benzyl alcohol; 2-chloro-4-methyl-benzyl alcohol; and the like. Advantageously, tertiary-amyl alcohol, tertiary-butyl alcohol, or benzyl alcohol are employed. As indicated, the alcohols can be employed in either solution or dispersion in order to impregnate the aquagel structure therewith for accomplishment of the desired modification.

Among the acids that may be utilized with utmost benefit is sulfuric acid in aqueous solutions having a concentration of from 40 to 95 percent, advantageously from 60 to 90 percent, and more advantageously about 70 percent by weight of H_2SO_4 . If desired, other strongly dissociated inorganic acids of equivalent strength in aqueous solution to the mentioned sulfuric acid may also be utilized, particularly such acids as hydrochloric acid.

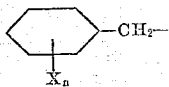
The treatment may be accomplished by impregnating the washed and oriented aquagel fiber in an aqueous or undiluted bath of the alcohol followed by acid treatment. Alternatively, and with equal advantage, the aquagel fiber can be treated in a single bath containing a mixture of the alcohol and acid. Beneficially, the aquagel fiber is impregnated during the treatment with a sufficient quantity of the alcohol to convert between about 5 and 25 mole percent, preferably between about 8 and 20 mole percent, of the substituent nitrile groups in the acrylonitrile polymer structure to alkyl amide groups so as, in effect, to obtain a copolymer containing between about 75 and 95 mole percent of recurring units derived from acrylonitrile of the structure:



and from about 5 to 25 mole percent of recurring alkyl acrylamide units of the structure:



wherein Z, as is apparent, is a substituent whose precise characteristics depend upon the particular alcohol used for modification of the acrylonitrile polymer. Thus, when alcohols of Formula I are involved Z is $-\text{CR}_3$; with benzyl alcohols it is:



As will be evident to those who are skilled in the art, the precise quantity of alcohol impregnated in the aquagel depends upon the amount of water permitted to remain in the aquagel structure before the impregnation step as well as the particular alcohol being utilized for the modifying operation. In many cases, however, an amount of alcohol between about 5 and 50 percent by weight, based on the weight of an aquagel containing about 2 parts of water to each part of dry polymer therein, will provide satisfactory and beneficial results in the practice of the invention. The conversion may be effected at any temperature between about 0-15 and 110° C., although it is generally most convenient and quite satisfactory to accomplish the modification at about room temperature or in the range between about 20 and 30° C. The necessary time for accomplishing the modification depends upon the temperature employed and the quantity of alcohol in the aquagel fiber. Generally, the treatment can be accomplished within 24-48 hours and, under optimum reaction-favoring conditions, is usually performable in as little as 5-1 minutes.

After the treatment, the modified acrylonitrile polymer aquagel fiber is washed thoroughly with water to

remove all or substantially all of the treating reagents, taking particular care to rid the aquagel of any residual acid. Following the washing, the treated fiber is irreversibly dried to produce the desired high-shrink and dyeable, characteristically hydrophobic, synthetic textile fiber product. 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.

After drying, the dyeable, 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.

It is ordinarily most desirable to employ and modify 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. In this connection, it is advantageous for the acrylonitrile polymers that are modified by 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, the aquagel structures that are modified by the present practice can also be utilized when they contain interblended therewith up to about 20 weight percent of various dye-assisting polymeric adjuvants, including poly-N-vinyl-pyrrolidone 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 modified 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.

In order to further illustrate the invention, 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 42 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 prior to being collected or dried. There was thereby obtained an aquagel fiber containing about 2 parts of water for each part of polymer therein. Several samples of the polyacrylonitrile aquagel, each containing about 10 grams on a dry weight basis of the polymer, were then individually wound on separate, perforated stainless steel cylinders. Each of the samples (excepting for two control samples) were then immersed in individual 500 ml. baths of various alcohols for about one hour at room temperature. After

this, the samples were removed and permitted to drain before subsequently being immersed in 500 ml. baths of 70 percent aqueous sulfuric acid for 30 minutes at about 24 C. During the acid immersion, the temperature of each of the acid solutions was noted to rise about half a centigrade degree. After the acid treatments, each of the modified aquagel fiber samples were washed several times with distilled water until no trace of residual acid could be noted. They were then irreversibly dried for 5 minutes at 140° C. and tested for shrinkability.

Several additional samples of aquagel fiber were similarly prepared and treated excepting that each of the samples contained about 10 percent by weight, based on the dry weight of the polymer therein, of K-54 poly-N-vinyl-2-pyrrolidone (PVP) which was incorporated therein by impregnation from an aqueous bath in order to improve the dye-receptivity of the finally obtained fiber structure.

The results are set forth in the following tabulation, wherein samples 1 and 7 are blanks which received no treatment and samples 2 and 8 were treated merely by immersion in the acid without prior alcohol impregnation. Samples 6 and 12 employed an alcohol not in accordance with the present invention for purposes of additional comparison.

The shrinkability of the fiber samples was determined according to the following tests:

Determination of shrinkage of treated fibers.—The dried fiber in tow form was stretched to 1.25 times its original length by passing it between two electrically heated aluminum plates 6 inches long. The plates were set about 3/32 inch apart and were heated to 175° C. The linear speed of the tow entering the stretching zone was 30.5 feet per minute. The fibers stretched under these conditions were shrunk in a steam chamber by the following steaming cycle:

- One minute purge at atmospheric pressure
- One minute to raise pressure to 10 p.s.i.g.
- Two minutes to hold at 10 p.s.i.g.
- Fifteen seconds to release to atmospheric pressure

The steam shrunk fibers were dried at 40° C. The initial length of the fiber tow to be shrunk was 90 cm. The distance was marked on the tow sample by tying two pieces of string about the tow, 90 cm. apart, while the tow was under a tension of about 0.1 gm. 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:

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

The percent shrink values were usually reproducible to ± 0.2 percent.

TABLE I

Shrinkage properties of polyacrylonitrile wet-stretched gel treated with various alcohols and sulfuric acid

Sample	Treatment of wet-stretched gel	Net increase in amide, g.p.s.	Shrinkage
1	None	0	13.9
2	H ₂ SO ₄	4	13.0
3	t-Amyl alcohol + H ₂ SO ₄	14	17.2
4	t-Butyl alcohol + H ₂ SO ₄	13	17.3
5	Benzyl alcohol + H ₂ SO ₄	57	
6	n-Butyl alcohol + H ₂ SO ₄	4	13.3
7 ¹	None	11	12.5
8 ¹	H ₂ SO ₄	12	
9 ¹	t-Amyl alcohol + H ₂ SO ₄	15	16.7
10 ¹	t-Butyl alcohol + H ₂ SO ₄	17	16.1
11 ¹	Benzyl alcohol + H ₂ SO ₄	40	17.4
12 ¹	n-Butyl alcohol + H ₂ SO ₄	12	12.2

¹ Impregnated with PVP before treatment.

Similar results are obtained when the foregoing is repeated excepting to use mixed acid-alcohol baths for the modifying treatment or to utilize other of the alcohols and acids indicated to be within the scope of the invention, as well as when aquagels spun from other salt systems (including any of those mentioned in the foregoing) are treated.

In contrast with the foregoing, polymers prepared by other methods adapted to provide about the same chemical composition in the resulting fiber did not produce fibers that evidenced any noticeable increase in shrinkability. Thus, when polyacrylonitrile was reacted with tertiary butyl alcohol while the polymer was dissolved in the aqueous 60 percent zinc chloride spinning solution containing about 10 percent by weight of the fiber-forming polymer, the resulting textile fiber products had about the same order of shrinkability as the untreated fiber samples illustrated in samples 1 and 7. In these experiments, the spinning solution was prepared to pH 3 (measured at 10:1 dilution in distilled water) with HCl before solution polymerization of the monomer to provide the fiber-forming polymer composition. Ten percent by weight of tertiary butyl alcohol was added to several samples of the polymer solution, based on the weight of the polyacrylonitrile dissolved therein. The alcohol was added as an equal weight solution with 60 percent aqueous zinc chloride to prevent coagulation of the polymer solution. The reaction of the alcohol with the polyacrylonitrile was accomplished at temperatures between 60 and 80° C. None of the filamentary or film materials produced by salt-spinning of such modified fiber-forming compositions prepared finally manufactured products that showed more than about 12-14 percent shrinkability.

In another series of experiments, two fiber-forming acrylonitrile copolymers were prepared, each containing about 91 weight percent of acrylonitrile copolymerized in the polymer molecule. One of the comonomers utilized was N-t-butylacrylamide. The other was N-t-octylacrylamide. When fibers were prepared from each of the copolymers in accordance with the above described salt spinning process, the resulting products exhibited shrinkage properties no different from untreated polyacrylonitrile fibers.

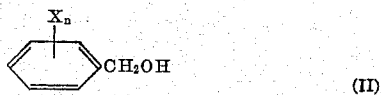
The scope and purview of the present invention is to be gauged in the light of the hereto appended claims rather than from the foregoing didactic description and specification.

What is claimed is:

1. Method of preparing a dye-receptive and 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 14 percent after exposure to water at about 100° C., which polymer contains in the polymer molecule at least about 80 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 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 (a) at least one alcohol selected from the group consisting of tertiary alcohols and benzyl alcohols having the respective formulae:



and



wherein each R in said tertiary alcohol is an independently selected alkyl radical that contains from 1 to about 4

7

carbon atoms with the limitation that the total number of carbon atoms in all three substituents is from 3 to 7; and wherein each X in said benzyl alcohol is selected from the group consisting of hydrogen, chlorine, bromine and alkyl radicals containing from 1 to about 4 carbons and n has a whole number value from 0 to 5, said alcohol being employed in sufficient quantity to convert between about 5 and 25 mole percent of the nitrile groups in said acrylonitrile polymer to acrylamide substituents; and (b) an aqueous solution of a strong dissociated inorganic acid containing about 40 to 95 percent by weight of the acid and selected from the group consisting of sulfuric acid, hydrochloric acid, and their mixtures; maintaining said aquagel in contact with said acid solution at a temperature between about 0 and 110° C. until between about 5 and 25 mole percent of said nitrile groups in the acrylonitrile polymer are converted to acrylamide substituents; washing the treated aquagel with water until it is free of residual acid; and subsequently irreversibly drying said aquagel fiber to a synthetic characteristically hydrophobic textile fiber structure.

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

3. The method of claim 1, wherein said alcohol is tertiary-amyl alcohol.

4. The method of claim 1, wherein said alcohol is tertiary butyl alcohol.

5. The method of claim 1, wherein said alcohol is benzyl alcohol.

6. The method of claim 1, wherein said acid is an

8

aqueous solution of sulfuric acid having a concentration of H_2SO_4 of between about 60 and 90 percent by weight.

7. The method of claim 1, wherein said aquagel fiber is contacted with said alcohol and said acid solution in respective sequential treating baths.

8. The method of claim 1, wherein said aquagel fiber is contacted with said alcohol and said acid solution in a single bath containing a mixture of the alcohol and the acid.

9. The method of claim 1, wherein said aquagel is maintained in contact with said acid at a temperature between about 20 and 30° C. for a period of time of at least about 5 minutes until between about 8 and 20 mole percent of the nitrile groups in the recurring acrylonitrile units are converted to acrylamide substituents.

References Cited in the file of this patent

UNITED STATES PATENTS

20	1,984,417	Mark et al. -----	Dec. 18, 1934
	2,431,956	Moody -----	Dec. 2, 1947
	2,579,451	Polson -----	Dec. 18, 1951
	2,611,929	Hoxie -----	Sept. 30, 1952
25	2,645,556	Bashford et al. -----	July 14, 1953
	2,776,271	Coover et al. -----	Jan. 1, 1957
	2,850,477	Ham -----	Sept. 2, 1958

FOREIGN PATENTS

30	519,628	Canada -----	Dec. 20, 1955
----	---------	--------------	---------------