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METHOD OF PREVENTING RING DYEING IN AQUAGEL ACRYLONITRILE POLYMER FIBERS BY STEAMING THE FIBERS

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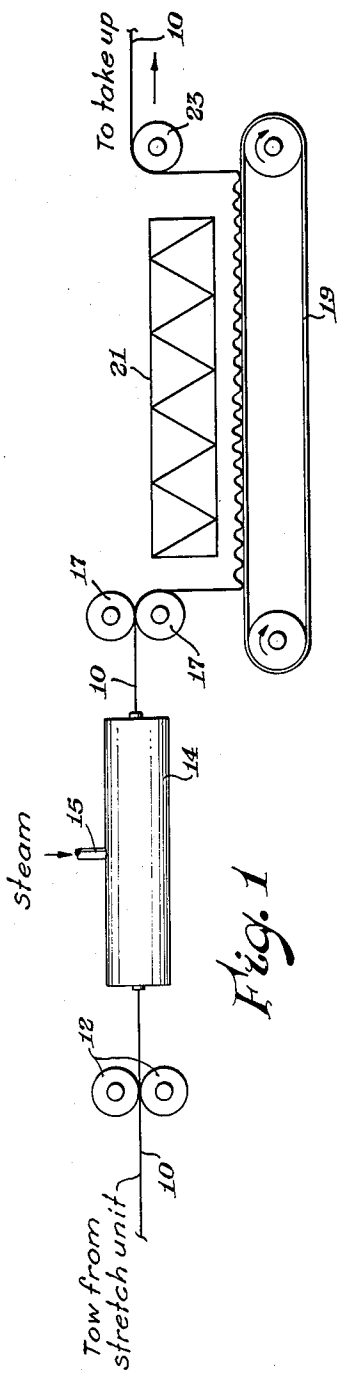


Fig. 1

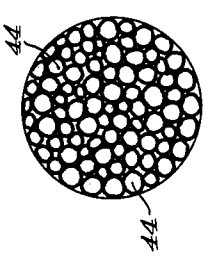


Fig. 4

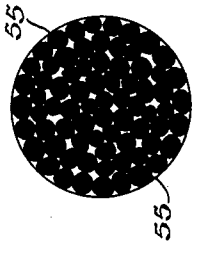


Fig. 5

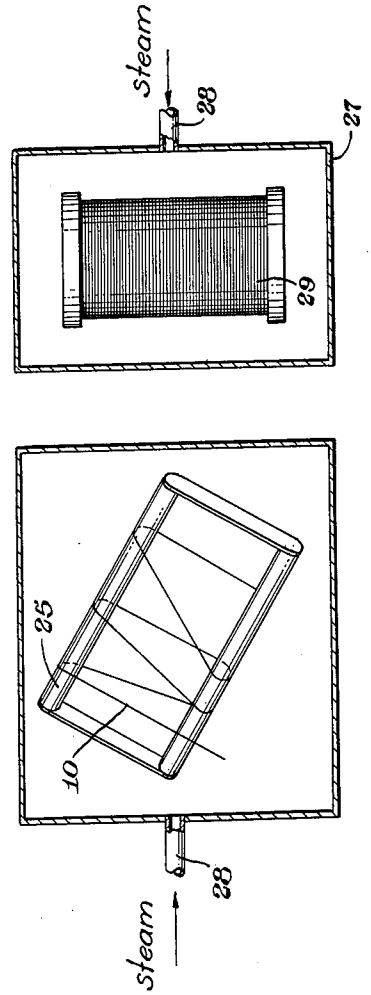


Fig. 3

Fig. 2

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METHOD OF PREVENTING RING DYEING IN AQUAGEL ACRYLONITRILE POLYMER FIBERS BY STEAMING THE FIBERS

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This invention relates to the preparation of improved synthetic textile fibers from polymers and copolymers of acrylonitrile and has particular reference to those containing at least about 85 percent by weight of acrylonitrile polymerized in the polymer molecule, hereinafter referred to as acrylic fibers. More particularly, this invention relates to a method for preparing such fibers in a readily dyeable condition in which they may be more completely and thoroughly penetrated by dyestuffs.

Various methods for preparing and treating acrylic fibers, filaments, yarns, threads, tows, bundles and the like in order to enhance certain of their physical properties are known and practiced in the art. In general, however, the available techniques, including the several known heat treatments, are not particularly beneficial insofar as improving their dyeing characteristics is concerned. None of the known methods and treatments, for example, have any significant capability for improving the tendency of the fibers to be thoroughly penetrated by commonly employed dyestuffs so that they are substantially uniformly and fastly colored by the dyestuff throughout their cross-sections as well as on their surfaces. Fibers which are not thoroughly penetrated and dyed but which merely accept a dyestuff in their peripheral or outer circumferential portions are characterized and known as being "ring dyed." Acrylic fibers, which may frequently have a tendency to fibrillate in the course of normal usage and to thereby expose their interior portions, are objectionable when they are only ring dyed. Fibers that are incompletely colored in this manner exhibit a highly undesirable whitening effect upon fibrillation.

It is, therefore, among the objects of the present invention to provide a method for conditioning acrylic fibers to effect an appreciable and substantial increase in the dyeability of the finished product. It is a further object of the present invention to provide a method for treating or conditioning acrylic fibers which materially and significantly improves and facilitates the penetrability of dyestuffs into and throughout the fibers to avoid ring dyeing as well as improving their overall dye-receptive properties. A still further object of the present invention is to provide a treating method for consummately accomplishing the forementioned objectives which may conveniently be included in the operational sequence of spinning and subsequent processing being employed for manufacturing the fiber, particularly when wet spinning techniques are involved. Another object is to provide a facile method for treating and conditioning acrylic fibers which may be easily accomplished without involving undesirably lengthy treating periods. An additional object of the present invention is to provide a treating and conditioning method which may be practiced economically with relatively simple and readily available apparatus.

These objects and other advantages and benefits may be accomplished in accordance with the treating and conditioning method of the present invention wherein a wet spun acrylic fiber in gel form, after having been washed and hot stretched, is subjected in an incompletely free-to-shrink condition, and advantageously under a positive, shrink-resisting tension, to steam under an absolute pressure of at least about 20 pounds per square inch for a

period of time between about 0.5 second and 0.5 hour. Greater benefit may usually be derived when the conditioning treatment is conducted by subjecting the restrained from completely shrinking fiber to steam under an absolute pressure between about 25 and 60 pounds per square inch for a period of time between about 1 second and 5 minutes. Upon completion of the conditioning treatment, the fiber is dried in either a relaxed condition or under tension. It may then be thoroughly dyed with excellent penetration of the dystuff by using conventional techniques for the application of a wide variety of dyes. The dyed fibers that may be obtained do not have ring dyed characteristics to any appreciable extent.

Better and more level dyeability may often be obtained in the thermally conditioned fibers when they are finally dried at moderately elevated drying temperatures. The temperature that is employed for drying the fibers may be between room temperature and about 160° C., although a moderate drying temperature between about 110° C. and 150° C. may frequently be employed with a greater advantage.

Further features and advantages of the present invention will be apparent in the following description, taken in connection with the accompanying drawing, wherein:

FIGURE 1 schematically represents an embodiment of a method for treating and conditioning a wet spun acrylic fiber in gel form to improve its dye-receptivity and through dyeing characteristics in accordance with the present invention;

FIGURES 2 and 3 are schematic representations of other techniques that may be employed for practice of the invention; and

FIGURES 4 and 5 illustrate the improvement in dyeability which is attained by practice of the present invention.

With initial reference to FIGURE 1, there is shown a tow **10** or like bundle of wet spun, continuous filament acrylic fibers in an undried aquagel form being drawn from preceding processing operations (not illustrated) by and between a pair of nip rolls **12**. Any conventional wet spinning steps may be included in the processing that precedes the thermal conditioning treatment. For example, extrusion, coagulation, washing and stretching may be included in such a preliminary sequence. These may be performed according to any desired and suitable continuous or non-continuous arrangement regardless of whether or not the spinning steps are directly or continuously coupled with the treatment of the present invention. The acrylic fiber in the tow **10** may be polyacrylonitrile or an acrylonitrile copolymer containing at least about 85 percent by weight of acrylonitrile polymerized in the polymer molecule. Advantageously, the fibers may be wet spun from an aqueous, salt-containing spinning solution into an aqueous, salt-containing coagulating liquid and may also have received at least partial orientation by having been stretched, preferably in a hot aqueous medium.

The wet spun and stretched tow **10** of acrylic fibers is passed from the bight of the nip rolls **12** under sufficient tension to be restrained from shrinking or at least to be incompletely free-to-shrink through a steam tube **14** or equivalent chamber to a second set of nip rolls **17**. Advantageously, the consecutive roll pairs **12** and **17** are operated at about the same peripheral rate of speed so that the fibers in the tow **10** are restrained completely or nearly completely from shrinking during their passage through the steam tube **14**. The desired steam pressure may be maintained by admitting steam to the steam tube through a supply conduit **15**. The fibers are subjected to the steam for a predetermined time during their residence in or passage through the steam tube. Generally, for fibers of a given size, higher steam pres-

sures permit the employment of relatively shorter treating times. While the fibers can be subjected to steam under considerable pressure in the practice of the invention, care should be taken to avoid such high pressures and the associated high temperatures as may tend to dissolve the fiber while it is in the aquagel condition.

The treated and thermally conditioned tow **10** is passed from the nip rolls **17** to be randomly placed free from tension on a conveyor belt **19**. They are carried on the conveyor belt **19** through a drying oven **21** of any suitable type for drying. The treated fiber may also, if desired, be dried while it is under tension. After being dried, the tow **10** is passed over a guide roll **23** to suitable take-up or collection means. The treated and dried fiber is readily dyeable with excellent penetration by commonly employed dyestuffs. It may be dyed by conventional techniques to deep and level shades with acetate, acid, direct and vat dyestuffs. In addition, it has excellent physical properties.

The conditioning treatment of the invention to enhance dye-receptivity may also be accomplished by subjecting the fiber to the steam while it is stationarily maintained under tension by any suitable supporting means. Thus, as is illustrated in FIGURE 2, the tow **10** may be wound or supported upon a suitable frame or other support **25** which is adapted to maintain it under tension in an incompletely free-to-shrink or totally restrained from shrinking condition while being subjected to the steam under pressure from a conduit **28** in a suitable chamber **27**. Or, as is depicted in FIGURE 3, the tow **10** may be wound on a bobbin **29** or other support to be treated according to the method of the invention in the form of a thread package. In such cases, it is desirable to employ a relatively widely spaced winding pattern and to avoid excessive thicknesses in the wound layers to facilitate uniform exposure to the steam in a satisfactory manner of all the fibers being treated in the wound package.

In FIGURE 4 there is portrayed a replica showing greatly enlarged cross sections of acrylic fibers showing ring dyed effects. Observations of this nature are readily apparent and commonly made with highly magnified photomicrographs or upon microscopic examination of fiber cross-sections. Each of the fibers **44** is ring dyed, having accepted the dye-stuff in only their peripheral portion, as is represented by the darkened circumferential areas of the fiber cross sections. Such fibers, as mentioned, whiten undesirably upon fibrillation which is likely to occur in the course of normal usage. In comparison, fibers which have been treated and thermally conditioned for improved dye-receptivity in accordance with the present invention would, after being dyed, exhibit a thoroughly and completely dyed cross-section such as is illustrated in the fibers **55** in FIGURE 5. Acrylic fibers having such a high penetrability by and through acceptance of the dyestuff are not likely to have undesirable characteristics due to fibrillation.

The following examples wherein, unless otherwise indicated, all parts and percentages are to be taken by weight will further illustrate the method for improving dyeability of acrylic fibers of the present invention.

Example I

A spinning solution was prepared by dissolving about 1 part of polyacrylonitrile, having an average molecular weight between about 25 and 30 thousand, in about 9 parts of a 60 percent solution of zinc chloride in water. The spinning solution, having a viscosity of about 2000 poises at 25° C., was extruded through a 10 mil, 300 hole spinnerette into a coagulating liquid comprised of a solution of about 43.5 percent zinc chloride in water. The temperature of the coagulating liquid was about 15° C. The extruded, coagulated spinning solution formed an aquagel filamentary structure which was washed in distilled water at room temperature until the salt content of the aquagel did not exceed about 0.5 percent, based on the dry weight of the polyacrylonitrile. The washed aquagel structure was oriented by being stretched to a total length of about 12 times its original length in a series of drawing operations during its washing after withdrawal from the coagulating bath.

A first portion (Sample A) of the wet stretched aquagel was dried directly in air at room temperatures. A second portion (Sample B) of the aquagel was directly dried for 5 minutes at 150° C. in such a manner as to be in a completely relaxed condition. Two other portions (Samples C and D) were treated and conditioned in accordance with the invention prior to drying after being tightly wound on a rigid stainless steel frame, on which they were restrained from shrinking, by being subjected to saturated steam in a pressure vessel. The steam was employed under a pressure of about 25 pounds per square inch (gauge) which was attained within about a minute after the wound samples had been placed in the vessel. Samples C and D were subjected to the steam under the full 25 pounds pressure for a period of about ten minutes before being removed from the pressure vessel. Sample C was dried under tension at 150° C. for 5 minutes while remaining wound tightly on the frame. Sample D was removed from the frame and dried for 5 minutes at 150° C. in a completely free-to-relax condition.

The samples were dyed for about one hour at the boil, following a conventional technique, using 4 percent Calcodur Pink 2BL (a direct dyestuff), based on the weight of the fiber. Sample A was only very faintly dyed in its peripheral portions. Sample B did not accept the dyestuff to an appreciable extent. Both Sample C and Sample D, however, which had been treated and thermally conditioned to enhance their dye-receptivity and facilitate their thorough dyeability according to the present invention, were brightly dyed in comparison to Samples A or B. In addition, neither Sample C nor D showed evidence, upon photomicrographic examination of having been ring dyed but accepted the dye thoroughly throughout their cross-sections. These visual observations were substantiated by reflectance readings made with a Beckman spectrophotometer, the results of which are set forth in the following tabulation. The spectrophotometer was used to measure the amount of light from a standard source that was reflected from the dyed samples. The numerical reflectance value given represents a relative comparison of the amount of light reflected from each of the dyed samples with that reflected from a standard white tile reflector. Lower reflectance values are taken as a reliable indication of better dyeability.

Sample No.:	4 percent Calcodur Pink 2BL reflectance value
A	77
B	100+
C	24
D	24

In addition, several of the physical properties of the treated samples (C and D) were observed to be at least commensurate with, if not noticeably improved over, those of the untreated samples. This is indicated by the comparisons set forth in the following table:

Sample	A	B	C	D
Tenacity, gms./denier	4.0	4.2	4.5	4.2
Yield, gms./denier	0.90	1.10	0.95	1.15
Loop Strength, gms./denier	1.1	1.5	2.0+	2.0+
Elongation, percent	38	33	29	16

Example II

A wet spun, stretched aquagel fiber tow similar to that employed in the first example was treated and thermally conditioned in a continuous manner to improve its dyeability in accordance with the present invention by pass-

ing it directly, after the final hot stretching step, through a steam tube before being dried in a relaxed condition at 150° C. The stretched aquagel fiber tow was passed through the steam tube, which had a length of about 3 feet and contained steam under a pressure of about 25 pounds per square inch (gauge), at a linear rate of about 54 feet per minute. The residence time of the tow passing through the steam tube was about 3.34 seconds. The tow entered and was withdrawn from the steam tube at the same linear rate of speed so that it was not additionally stretched nor was it permitted to shrink during its exposure. The treated and thermally conditioned tow was found to have a very white appearance and was obtained in a good open condition. The treated fiber accepted Calcodur Pink 2BL dye quite readily. A good color yield without ring dyeing was obtained upon a 4 percent dyeing with the dyestuff. The reflectance value of the treated and dyed fiber was found to be about 35. It had a tenacity of about 4.2 grams per denier, a yield point of about 0.96 gram per denier and an elongation of about 33 percent.

Similar results may be obtained when acrylic fibers are treated and thermally conditioned to improve their dye-receptivity under other conditions within the scope of the invention.

It is to be fully understood that the present invention is to be construed and interpreted not by the foregoing didactic description and specification but in the light of what is set forth and defined in the appended claims.

What is claimed is:

1. A conditioning method for improving the dyeability of wet salt-spun and stretched so as to be at least partially oriented fibers comprised essentially of fiber-forming acrylonitrile polymers that contain in the polymer molecule at least about 85 weight percent of polymerized acrylonitrile which method comprises subjecting said fibers, while they are in aquagel form and under positive, non-elongating tension in an incompletely free-to-shrink condition, to steam under an absolute pressure between about 20 pounds per square inch and a higher pressure less than that under which said aquagel fibers would dissolve for a period of time between about 0.5 second and 0.5 hour; then drying said treated fibers.

2. A method in accordance with the method set forth in claim 1, wherein said fibers are subjected to steam under an absolute pressure between about 25 and 60 pounds per square inch for a period of time between about 1 second and 5 minutes.

3. A method in accordance with the method set forth in claim 1, wherein said fibers are dried at a temperature between about 110° C. and 150° C.

4. A method in accordance with the method set forth in claim 1, wherein said fibers are polyacrylonitrile.

5. A method in accordance with the method set forth in claim 1, wherein said fibers are wet spun and stretched so as to be at least substantially completely oriented.

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