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PROCESS OF PRODUCING UNIFORMLY DYEING POLYACRYLONITRILE FILAMENTS BY HEAT STRETCHING THE WATER WETTED FILAMENTS

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Fig. 1

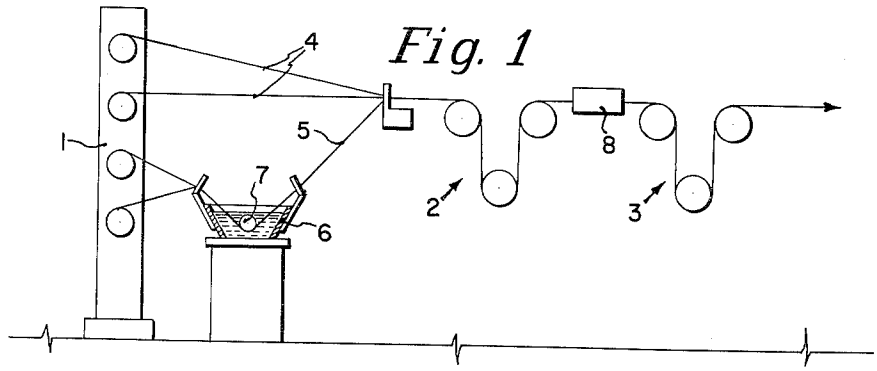


Fig. 2

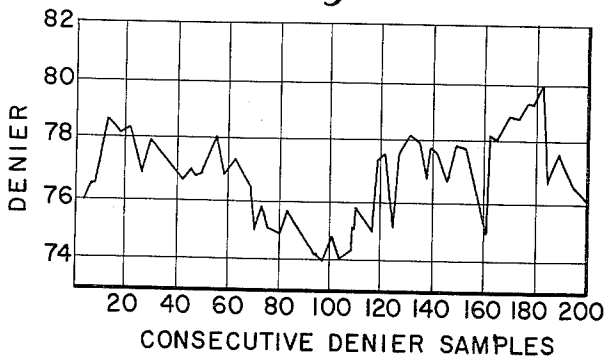
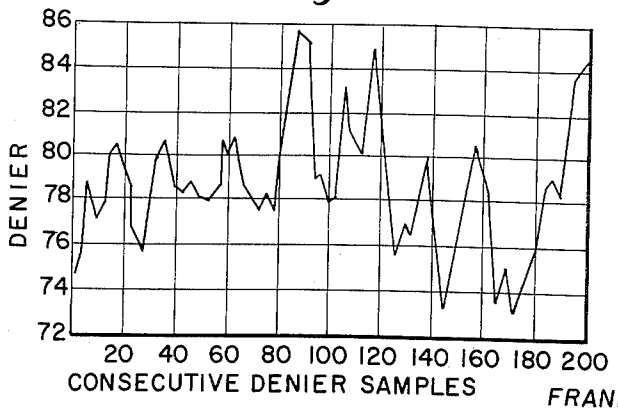


Fig. 3



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PROCESS OF PRODUCING UNIFORMLY DYEING POLYACRYLONITRILE FILAMENTS BY HEAT STRETCHING THE WATER WETTED FILAMENTS

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This invention relates to an improved method of drawing acrylonitrile homopolymer and copolymer yarns, filaments and similar structures to produce attenuated products possessing greater uniformity of size and greater uniformity of dye receptivity.

"As spun" acrylonitrile polymer yarns and the like must be drawn a substantial amount to impart desirable physical properties to them. But, when the yarn from a dry spinning cell is wound up on a bobbin and the residual solvent is extracted by means of aqueous liquor while the yarn is still in package form, unwinding of the yarn, after drying or without drying, and steam drawing it from 2× to 10×, leads to undesirable fluctuations in short length denier measurements. Acrylonitrile polymer yarns when so produced and so processed also exhibit poor dyeing uniformity which has given rise to much research in an effort to eliminate these non-uniformities.

It is, therefore, an object of this invention to provide an improved method for processing acrylonitrile polymer or copolymer yarns that have been initially collected as wound packages or which formed yarns contain non-uniformities that give rise to short length denier inequalities in the drawn yarn. Another object of this invention is to provide a yarn or filament conditioning step just prior to drawing that gives improved drawing uniformity from "as spun" yarn collected in package form as reflected by more uniform short length denier and greater dyeing uniformity of the drawn yarn or fabrics made therefrom. A still further object of this invention is to improve draw continuity by eliminating filament flaring due to static and subsequent filament strip-backs at the steam drawing cell. Other objects will be apparent from the description that follows.

In the figures:

FIGURE 1 shows the application of the process of this invention to yarn on the run i.e., while moving rapidly;

FIGURE 2 is a graph showing the uniformity in denier obtained by the process of this invention; and

FIGURE 3 shows graphically the non-uniformity that is normally obtained by prior art processes.

The objects of this invention are accomplished by unwinding packaged yarn or filaments, uniformly wetting the unwound yarn or filaments with water or aqueous solution and then drawing in an atmosphere of steam. Most effectively this wetting of the yarn takes place while moving rapidly, but any condition that permits the yarn to uniformly imbibe a substantial quantity of water is effective as will be explained more fully hereinafter. The temperature of the aqueous material may vary widely as, for instance, from room temperature up to 100° C. The duration of application has little or no effect as long as the time is sufficient for uniform impregnation under the tension being imposed and may be as short as 1/25 second or as long as 24 hours or more. The tension at the time of impregnation is uniformly applied to the yarns and is generally not very great. Pure water or water containing up to 10% of other soluble materials, such as a solvent, may be impregnated into the yarn. The various organic solvents disclosed in U.S. Patents 2,404,714 to 2,404,727 may be present in the bath. Also, inorganic salts may be present such as calcium chloride, zinc chloride and sodium thiocyanate, these salts being used in concentrated solutions as solvents or being used in wet spinning procedures. There may be present also materials which are not solvents for the polymers such as alcohol, glycerol or acetone. Normally, the bath contains only vaporizable material and is preferably water. Preferably steam drawing is effected with low or atmospheric pressure steam.

That uniform impregnation of the yarn with an aqueous medium just prior to drawing produces unexpectedly and surprisingly good uniformity of short length denier and of dyeing is borne out by a number of varied experiments. All evidence points to the necessity of substantially uniform water take-up by the yarn, and, therefore, the tension and/or pressure on the yarn must be substantially uniform throughout its entire length during the wetting treatment. Apparently, the "as spun" package of yarn or any other relatively dense package structure has too tight a structure or there are variations in the tension on the yarn so that uniform take-up of water throughout the length of the yarn is prevented. In the process of this invention the yarn is free to imbibe water readily, for it is in the form of a running yarn or a loose skein.

The improvement in denier and dyeing uniformity is from 100% to 200% and results from soaking a relaxed skein of package-washed yarn or by passing the yarn on the run through a few inches of water just prior to steam drawing. Yarns similarly processed but not subjected to this water wetting step before drawing fail to show this improvement. As-spun yarn which had not been subjected to any prior washing treatment also is improved in dyeing uniformity when passed through a water bath on the run prior to drawing. No improvement at all was realized by soaking the yarn package (after washing to remove residual solvent) for a period of two days in water at 30° C. and then steam drawing. Similarly extending the solvent extraction time, i.e. pressure washing with water, to 10 hours as compared with a normal extraction time of about 3½ hours gave no improvement in denier nor in dyeing uniformity. Furthermore, skeins of yarn unwound from the water-washed package and allowed to hang free for a period of time before drawing yielded a non-uniform dyeing, drawn yarn as did yarn processed directly from the package.

From these and other experiments it is apparent that uniform water wetting of acrylonitrile polymer and copolymer yarns substantially improves short length denier uniformity and dyeing uniformity. Water analyses of washed package yarn and yarn removed from the package and impregnated with water while free to readily imbibe it shows that the water content is very substantially increased by this latter step. Based on the dry weight of the yarn the average water content of the washed yarn removed from the spin package is about 40% while the

content of the yarn unwound from the package and thereafter impregnated with water is about 100% by weight.

Uniform room temperature water impregnation of the washed yarn gives a noticeable improvement in denier uniformity. However, greater improvement results as the temperature of the water treatment is increased above about 40° C. In some cases not only is short length dyeing uniformity more improved by higher temperature water impregnation but residual shrinkage of the yarn from various parts of the spin package is uniformized and yarn from the inside of the package and from the outside of the package may be used side-by-side without encountering the characteristic dye junctions frequently present.

The invention is applicable to yarns, filaments and other attenuated structures of homopolymers of acrylonitrile and to copolymers containing a major portion of and preferably upwards of 85% acrylonitrile such as acrylonitrile copolymerized with monoethylenically or diethylenically unsaturated compounds as vinyl acetate, vinyl chloride, vinylidene chloride, methyl vinyl ketone, styrene, vinylpyridine, acrylic acid and its esters, such as methyl acrylate, ethylenesulfonates, 1-propylenesulfonates, styrenesulfonates, and the like. The copolymers may be comprised of two or three or more copolymerizing compounds such as 85% to 99% acrylonitrile and with or without minor amounts of other copolymerizable compounds. In place of copolymers, mixed polymers comprised of at least 85% acrylonitrile may be used. Useful polymers are given in many patents such as U.S. 2,404,714 through U.S. 2,404,727, U.S. 2,486,641 and others.

Thus, the process of this invention comprises improving the physical properties and dyeability of a filament or yarn made from an acrylonitrile polymer by uniformly impregnating it with water prior to drawing. The impregnation is done by contacting the filamentary material with an aqueous bath containing at least about 90% water and having a temperature from about room temperature to about 100° C., preferably about 40° C. to about 100° C. The extent of drawing is at least about 2 times the original length of the filaments, 2 to 10× usually being applied though greater drawing may be used if desired. Preferably, the polymers are those containing at least 85% acrylonitrile for it is with these polymers that the optimum properties desired in the final textile articles, as for example, weather resistance, are obtained. Of the many media which may be used, water by itself is preferred.

The following examples illustrate this invention further and are given without any intention of being limited thereby.

Example I

A copolymer of 94% acrylonitrile and 6% methyl acrylate having an intrinsic viscosity of about 1.7 dissolved in N,N-dimethylformamide as a 25% solution was dry spun by the usual method and collected on a bobbin outside the spinning cell as 330 denier 30 filament yarn containing about 25% residual solvent. The yarn packages formed were subjected to pressure washing with 2% dimethylformamide aqueous wash liquor at 25° C. for 3.5 hours at the end of which time the dimethylformamide content of the yarn had been reduced to about 2% based on the dry yarn weight.

As schematically shown in the attached drawing (FIGURE 1) the "as spun" packages of this yarn were placed on a creel **1** and unwound and drawn by means of two sets of a plurality of rolls **2** and **3**. The drawing may be done as shown in U.S. Patent 2,568,920, the yarns being heated between roller sets **2** and **3**. Yarns **4** were passed directly from the creel to the drawing unit while another set of yarns **5** was passed from the creel through four or five inches of water bath **6** at 25° C. (by means of a freely rotatable grooved roller guide **7** submerged in the bath) and thence to the drawing apparatus. The tension on the yarn in the water bath was about 10 grams total which was only slightly more than the tension on the control yarn passing directly to the drawing unit. The draw rolls were set to give 5× draw and 9.98% relaxation before the yarn was wound up and the steam pressure in the drawing cell **8** was maintained at 3 pounds per square inch gauge. The results of this experiment are shown by the data that follows.

Treatment	Straight T, g.p.d./E, percent	Loop T, g.p.d./E, percent	Residual Shrinkage, percent	Denier CDV,[1] percent	$\bar{X}$
No Dip	2.87/16.7	2.51/14.4	5.9	2.7	78.4
Dip (25° C.)	2.86/16.1	2.48/13.8	6.1	1.9	78.2

[1] CDV—coefficient of denier variation of 25 consecutive 9-cm. lenths. $\bar{X}$—average denier.

Advantageously, the water dip had no appreciable effect on the drawn yarn properties with the exception of residual shrinkage which was increased slightly, but the coefficient of denier variation was markedly affected, being considerably lowered.

The improvement in the short-length denier variation with the water dip which corresponds directly with the short-length dyeing non-uniformities in the drawn yarn is shown in FIGURE 2, where measurements on 200 consecutive 9-cm. lengths have been plotted. It will be noted that the sudden large fluctuations seen in the control (FIGURE 3) in yarn denier were greatly reduced. The average maximum periodic fluctuations in the untreated yarn were as large as 7 to 10% (short length section to section); the water dip treatment reduces these to about the 2 to 4% level. The periodicity of the large denier fluctuations corresponds to the distance of the yarn between the shoulders of the "as spun" package. Similar periodicity has been calculated for the short-length dyeing non-uniformities as found in dyed knitted tubings.

The intensity of the dyeing non-uniformity has been correlated directly to the degree of variation in short-length denier. The dip treatment before draw is a simple, practical method for correcting these variations as they occur in the "as spun" package. This is illustrated in the following table:

Intensity of Dyeing Barre	Treatment	5× Drawn Yarns—CDV (200)
Greatest	No Dip	3.4
Improved	Dip 25° C.	2.0
Intermediate	No Dip	3.3
Improved	Dip 25° C.	2.1
Best	No Dip	2.3
Improved	Dip 25° C.	2.0

Example II

Washed "as spun" yarn such as described in Example I was subjected to water dip treatment before drawing 5× in an atmospheric steam draw cell and relaxation of 10%. In this example the water bath was heated to 40° C. in one case and to 90° C. in another. The results were as follows:

Treatment	Straight T, g.p.d./E, percent	Loop T, g.p.d./E, percent	Residual Shrinkage, percent	Denier, CDV, percent	$\bar{X}$
Dip 40° C.	3.07/14.8	2.69/13.5	8.3	1.5	76.3
Dip 95° C.	3.22/15.5	2.77/13.5	6.8	1.6	73.0

The 95° C. dip as compared to the 40° C. dip reduced the residual shrinkage of the drawn yarn by about 18%. Tenacities of the 95° C. dip yarns were increased about 5%.

Example III

A homopolymer of acrylonitrile having an intrinsic viscosity of about 1.9 was dissolved in N,N-dimethylformamide and dry spun as 710 denier 40 filament yarn.

The yarn from the spinning cell was suitably finished and collected with a small amount of twist on pirns. The pirns of yarn were pressured washed for 90 minutes to reduce the solvent content of the yarn to about 0.5% based on the dry yarn weight. Yarns from the same part of each washed package were drawn 4.5× in the atmospheric steam draw cell immediately after one of three following conditioning steps: (1) no dip, (2) 40° C. water dip, and (3) 95° C. water dip. The drawn yarns were relaxed about 10% to give a 180 denier drawn yarn.

Uniformity of dyeing was compared with three types of dyes on knitted tubings made from these yarns; a basic green dye (Color Index No. 662), and acid blue dye (Foreign Prototype 12) applied by the cuprous-ion dyeing technique, and a blue dispersed dye (Foreign Prototype 62). In all cases the "no-dip" items exhibited extreme short-length dyeing nonuniformities whereas the 40° C. and 95° C. water dip yarns dyed substantially uniformly. With all the classes of dyes the water dip increased the dye shade and dyeing rates. For example, the basic dye rate for the "water-dip" yarns was increased about 40% as compared to the "no-dip" yarn.

Example IV

Four different terpolymers of acrylonitrile, methyl acrylate and potassium styrenesulfonate were prepared under different conditions to give a range of molecular weights as well as variations in composition. These polymers were dissolved in N,N-dimethylformamide and dry spun to a bobbin wind-up package, which was water extracted to free the yarn from solvent and the yarn was then drawn from 5× to 6.5× in atmospheric steam.

Yarns from the same part of each washed package were drawn under three conditions. (1) No dip; (2) 40° C. dip; and (3) 95° C. dip. Uniformity of dyeing was compared on knitted tubings dyed with a basic green dye (Color Index No. 662). In all cases short length uniformity was improved with the dip treatment and the best results were obtained when the 95° C. dip was used.

Example V

Dye junctions between drawn yarn from the inside and from the outside cake windings of the "as spun" yarn can be substantially reduced or completely eliminated by a hot 95° C. dip treatment. For instance, when 8 spin cakes of yarn were preliminarily processed as described in Example II and given a water dip treatment at 40° C. prior to drawing 5× the average in-out dye junction was 2.5 shades. When yarns from the same eight cakes were subjected to a 95° C. water dip just prior to drawing 5× no visible in-out dye junctions could be found. Thus, while water dip at any temperature just prior to drawing improves short length denier variations only at elevated temperatures such as 80° C. and above is there also a visible effect on in-out dye junctions.

Characterization of the drawn yarns leading to in-out dye junctions has shown a strong correlation between residual shrinkage and dye shade, particularly for the 200/80 denier counts. Deep dye shades and increased dye rates are closely associated with high residual shrinkages. In the following table the average residual shrinkages for 44 cakes shows the effectiveness of the 95° C. dip in uniformizing in-out shrinkage variations for drawn 75 denier 30 filament yarn.

RESIDUAL SHRINKAGE

Cake Position	Dip Treatment	
	40° C.	95° C.
Out	9.1	6.9
Middle	8.5	6.8
In	7.6	6.7
Average	8.4	6.8

Similar improvements have been obtained with other copolymers and with the terpolymers of Example IV.

Example VI

A copolymer of the same composition as described in Example I was processed as shown in Example I, except that the "as-spun bobbin" was not pressure washed. In the case where the yarn was passed through the water dip at 25° C. before drawing 5× in steam at 3 p.s.i.g., the short length dyeing uniformity of the yarn in knitted tubing was markedly improved. Similar yarns from the same as-spun package when drawn without the water dip were very non-uniform when dyed. In both instances substantial amounts (10–11%) of residual solvent remained after this treatment. Longer contact times within the water trough are used if the beneficial effects of water dipping prior to drawing as well as extraction are desired.

Similar experiments with the water dip were not effective when the unextracted "as-spun" yarns were drawn in high pressure steam (40 p.s.i.).

By the easily applied treatment of this invention short length denier uniformity and dyeing uniformity is greatly improved. The uniform and substantially complete impregnation of the "as-spun" yarn with water assists in overcoming a tendency for static to build up on the yarns undergoing drawing and as the result there is no filament flaring when these water-dipped yarns are drawn. This noticeably improves the quality of the drawn yarn and the continuity of drawing. By employing high temperature water dip not only are the short length dyeings uniformized but dye junctions between the inside and outside yarn from the spin package are greatly reduced or completely eliminated.

Any departure from the above description which conforms to the present invention is intended to be included within the scope of the claims.

We claim:

1. The process for the production of a filament having improved dyeing properties and being capable of being drawn at least two times which comprises dry spinning a solution in an inert organic solvent of a copolymer having at least an 85% acrylonitrile content and up to 15% of an ethylenically unsaturated monomer copolymerized therewith, winding the as-spun filament into a package, extracting the organic solvent from the filament while on the package with water, unwinding and saturating the said filament containing not more than about 2% of the aforesaid organic solvent with water by passing it under low uniform tension insufficient to produce appreciable permanent stretching through an aqueous medium inert to the said filament and in which the polymer is insoluble, and immediately thereafter drawing the resulting wet filament at least 2 times its original length in an atmosphere of low pressure steam.

2. The process of claim 1 in which the polymer is polyacrylonitrile.

3. The process of claim 1 in which the polymer is a terpolymer of acrylonitrile, methyl acrylate and a styrenesulfonate.

4. The process of claim 1 in which the aqueous medium has a temperature of from about room temperature to 100° C.

5. The process of claim 1 in which the aqueous medium has a temperature between about 40° C. to 100° C.

6. The process for the production of a filament having improved dyeing properties and being capable of being drawn at least two times which comprises dry spinning a solution in an inert organic solvent of a copolymer having at least 85% acrylonitrile content and up to 15% of an ethylenically unsaturated monomer copolymerized therewith, winding the as-spun filament into a package, unwinding and saturating the said filament with water by passing it under low uniform tension through an aqueous bath inert to the said filament

and in which the polymer is insoluble, and drawing the resulting wet filament at least 2 times its original length in an atmosphere of low pressure steam.

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