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PROCESS FOR PRODUCING UNIFORM POLYACRYLONITRILE FIBERS BY
HEAT RELAXING SOLVENT CONTAINING UNDRAWN FIBERS,
REMOVING SOLVENT AND DRAWING THE FIBERS
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FIG. 1



FIG. 2.

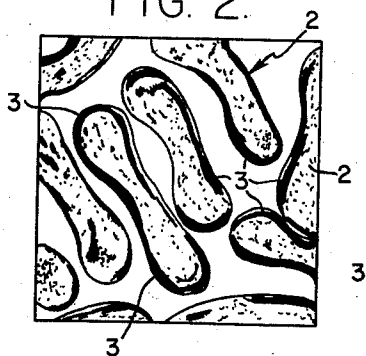
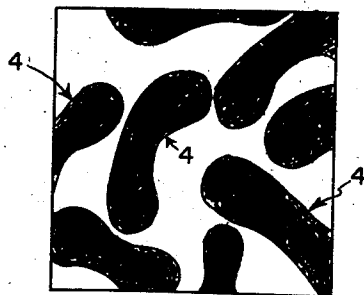


FIG. 3.



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ACRYLONITRILE FIBERS BY HEAT RELAX-
ING SOLVENT CONTAINING UNDRAWN
FIBERS, REMOVING SOLVENT AND DRAW-
ING THE FIBERS**

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This invention relates to improved yarns, filaments, fibers and the like of acrylonitrile polymers. More specifically, the invention is directed to the production of structures of acrylonitrile homopolymers and acrylonitrile copolymers wherein the acrylonitrile content is about 85% or more which structures are more uniform than those produced heretofore especially with respect to dyeability.

One method of manufacturing polyacrylonitrile yarns is by the dry or evaporative spinning of polymer solutions. While most of the solvent is removed in the spinning cell, yarn collected just outside the spinning cell contains solvent and recovery of this solvent is essential for economic operation. However, the recovery of this residual solvent is complicated by the fact that the "as-spun" yarn must undergo further processing to provide it with desirable textile properties.

The most important of these steps is drawing or stretching to several times its "as-spun" length, i. e. to 2 to 10 times or more. The condition of the filaments as they are subjected to this stretch is all important if optimum properties are to be attained in the drawn product, especially such properties as uniform luster and uniform dyeing of the yarn and fabrics made therefrom. One of the essential requirements for uniformity of results is a low and uniform solvent content in the yarn entering the steam stretching chamber. Solvent is most rapidly removed from the yarn by hot water or hot aqueous liquor washing. However, extraction of solvent from "as-spun" yarn using high temperature liquor may cause any existing non-uniformities to "set" in the structure and tenaciously resist subsequent removal or correction.

Therefore, it is an object of this invention to provide a novel process for the production of yarns, filaments, fibers and the like of acrylonitrile polymers containing at least 85% acrylonitrile which yarns and the like are characterized by uniformity of structure and improved uniformity of luster and dyeability in fabrics made therefrom. Other objects of this invention will be apparent from the description that follows:

The objects of this invention are accomplished by shaping an acrylonitrile homopolymer or a copolymer wherein the acrylonitrile content is at least 85% to produce a structure having at the point of collection at least 5% solvent, relaxing the structure, while substantially free of tension, at a high temperature and extracting the residual solvent until the solvent content is no more than about 2.5% by weight (based on the dry weight of the structure) and thereafter drawing the dry structure 2 to 10 times or more. The structures may be subjected to the process of this invention directly after shaping or they may be stored in package form first and then subjected to processing. If the initial solvent content of the structure is low, the relaxing treatment may also serve to remove all or substantially all of the excess solvent. Normally, however, it is necessary to wash the structure with water or dilute aqueous solution of the solvent in which case the structure should be dried before it is subjected to drawing.

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In the figures:

Figure 1 illustrates, in cross-section, filaments prepared by previous methods which filaments have dyeing localized on the center portions of the filaments;

Figure 2 shows other prior art filaments having structure which leads to dyeing localized in the outer sections; and

Figure 3 shows cross-sections of filaments prepared in accordance with this invention which filaments have a structure leading to uniform dyeing.

The following examples are given to illustrate this invention. In these experiments, density values have been used to measure yarn uniformity. While a high average density is desired, it is even more important that the deviation from this be small. Average densities of the order of 1.17 with standard deviations of no more than 0.007 are desired. They are attained by this invention; yarns having such properties dye with acceptable uniformity.

Example I

Sixteen different lots of "as-spun" 475 denier, 30 filament yarn were produced by dry spinning an N,N-dimethylformamide solution of acrylonitrile homopolymer under varying conditions of solvent evaporation so that the N,N-dimethylformamide content of the yarns as wound up at the spinning machine varied from 17% to 60% based on the dry solvent-free weight of the yarn. Samples of each of these yarns were relaxed by exposing them free of tension in an atmosphere saturated with N,N-dimethylformamide vapor at a temperature of 105° C. for 20 minutes while this relaxing treatment was omitted from other samples of each of these yarns. Subsequently, all of these yarn samples were subjected while free of tension to solvent extraction with dilute aqueous N,N-dimethylformamide liquor at about 100° C. and dried while free of tension. The average density value for the relaxed yarn samples was 1.160 g./ml. with a standard deviation in densities of only 0.0069; for the yarn samples not subjected to relaxing the average density was 1.129 g./ml. with a larger standard deviation in densities of 0.0106.

Example II

Another similar test on acrylonitrile homopolymer yarn was performed, the relaxing time being increased from 20 minutes to 1 hour to 2 hours at 105° C. The density results were somewhat higher, e. g., 1.171 g./ml. while the standard deviation in densities was 0.0070.

Example III

Samples of "as-spun" yarn produced by dry spinning an N,N-dimethylformamide solution of a copolymer of acrylonitrile (94%) and methyl acrylate (6%), when subjected to solvent extraction at about 100° C. with and without previous hot relaxation as in Example I except the time of relaxation was 60 minutes, furnished the following data on densities and standard deviation of densities. The relaxed yarns had an average density of 1.177 g./ml. with a standard deviation in densities of 0.004 whereas the unrelaxed yarns had an average density of 1.158 g./ml. with a standard deviation in densities of 0.008.

From these data it is immediately apparent that a far higher level of density results from yarns that are hot relaxed prior to solvent extraction. More importantly, it may be noted too that the standard deviation of densities for the unrelaxed yarns is at least about 50% greater than for the heat relaxed yarns. This means that the yarns relaxed before solvent extraction are much more uniform in density. Subsequent dyeing tests on the yarn samples heat relaxed and then extracted at 100° C. and

dried have shown this density uniformity to be strongly indicative of uniform dyeing.

Another measure of uniformity is through comparison of dyed cross sections of the filaments. Samples are prepared by mounting the filaments in wax and cutting 10 micron cross sections with a microtome. The cross sections are mounted on a thin layer of Mayer's albumin on a glass microscope slide and the albumin coagulated by holding the slide at a slight angle while carefully running 95% alcohol over the surface of the slide. The slide is then dried and dipped into naphtha to dissolve the wax and again dried. Thereafter the sample may be dyed by any of the usual dyeing techniques applicable to the dyeing of acrylonitrile polymer structures and photomicrographs made therefrom.

One of the most prominent evidences of nonuniformity in "as-spun" yarn extracted in water at near 100° C. is the variation in structure revealed by dyed cross sections of filaments or fibers. Some of the sections become deeply dyed in voids, predominantly in the core of the filaments 2, hereinafter referred to as "inside" voids, while others are dyed in voids just inside the outer periphery of the filaments, hereinafter referred to as "outside" voids 3. These two types of defects are shown in Figures 1 and 2, respectively. The difficulty is further complicated by the fact that a given package of yarn may contain both types of voids. However, when the yarns are heat relaxed before solvent extraction the nonuniformities revealed in the dyed cross sections are substantially eliminated. This is illustrated in Figure 3, the cross-section showing the filaments 4 to be uniformly dyed. The process of this invention not only removes voids previously preferentially available to the dye, but it converts the character of the polymeric material so that all of it takes up the dye and does so uniformly.

The samples depicted in the figures are selected from a single lot of yarn prepared as described under Example IV.

Example IV

A copolymer of acrylonitrile (94%) and methyl acrylate (6%) was dry spun from solution in N,N-dimethylformamide and collected as a multifilament yarn on a bobbin. The individual filament size was about 16 denier. Samples of this yarn representative of both inside and outside cracking were separated into 2 sets and processed as follows: One set of samples was heat relaxed for 1 hour by suspending small skeins of the yarn in a beaker immersed in boiling water and containing a pool of N,N-dimethylformamide out of contact with the yarn but to provide an atmosphere of solvent around the yarn to minimize solvent loss during this treating period. The second set of samples was not subjected to any relaxing treatment. All of these samples were then extracted in water at 96° C. for 1 hour to free them of solvent after which they were dried and the dyed cross sections prepared as earlier described.

The Figures 1 and 2 relative to the unrelaxed yarn samples clearly show large undyed areas. In the case of yarns exhibiting "inside" voids only the core portions take up the dye while in the samples exhibiting "outside" voids the dye take up is almost exclusively at or near the peripheral surfaces of the filaments. In contrast to these two pictures the Figure 3 relative to the relaxed samples shows that both types of yarn structure are converted to a uniform structure with very little variation from filament to filament. Similar uniformity was obtained by relaxing the yarns in air for 1 hour. For example, skeins were suspended in an empty vessel which was placed in a larger vessel containing a heated liquid, such as, boiling water. The air surrounding the skeins was thus heated and relaxation of the yarn was effected.

Example V

Other copolymer yarns wherein the acrylonitrile con-

tent is at least 85% behave in general much the same as the yarns previously discussed. The following copolymers are prepared and dry spun from solution in N,N-dimethylformamide to produce multifilament yarns.

- (a) Acrylonitrile 92%, methyl methacrylate 8%
- (b) Acrylonitrile 90%, vinyl acetate 10%
- (c) Acrylonitrile 93%, methyl vinyl ketone 7%
- (d) Acrylonitrile 95%, dimethyl itaconate 5%
- (e) Acrylonitrile 92%, t-butyl acrylamide 8%
- (f) Acrylonitrile 94%, methyl acrylate 6%
- (g) Acrylonitrile 90%, vinyl acetate 9%, styrene sulfonate 1%

These yarns are relaxed 1 hour at 105° C. in an atmosphere containing N,N-dimethylformamide vapor and thereafter trough extracted in counter current flowing water at 98° C. to a solvent content of about 1.5%. The yarns were then dried at 105° C. and pressure steam drawn 8x and hot relaxed 12%. All the yarns so prepared exhibit deep and uniform dyeings free of short length nonuniformities. Furthermore, dyeing of cross sections from these drawn yarns demonstrated that the structures are very much alike from filament to filament whereas like cross-section dyeings of similar yarns not relaxed before being extracted in hot water reveal many non-uniformities of structure.

The hot relaxing may be accomplished in a number of ways. As shown above, the yarn while free of tension may be heated in air at temperatures of about 100° C. to about 150° C. or in an atmosphere containing vapor of the solvent present in the structure. The amount of solvent vapor in such an atmosphere may be such that it partially or completely saturates the atmosphere. Other atmospheres include glycerol and oil. In general, any inert medium having a boiling point high enough to obtain the desired temperatures may be used. Solvents other than N,N-dimethylformamide may be used; for example, N,N-dimethylacetamide, gamma-butyrolactone, tetramethylene cyclic sulfone and the solvents disclosed in such patents as U. S. 2,404,714 to U. S. 2,404,727 are generally applicable.

The structures are relaxed while under little or no tension. This is done while the structures, for example, filaments, are in skein form or while they are on the run as, for example, while they are being advanced by rollers or while lying on an advancing belt. The time required in the heat relaxing treatment will depend to some extent on the polymer that makes up the structure, upon the temperature and upon the solvent content of the structure. If the solvent content is relatively high the time required is relatively low. Thus with high solvent content as short a time as 5 seconds is sufficient, the temperature being 150° C. On the other hand with low solvent content and a temperature of 105° C., the treatment should be for about 2 hours. It is of course recognized that shorter or longer times may be applied depending upon the circumstances; normally the time will be between 20 minutes and 2 hours. Similarly, the amount of stretching may vary. Normally the structures are drawn from about two to about ten times their original length. The extent of the stretching may be less or greater, but generally it is desired to stretch at least 2 times and normally there is no need to stretch more than 10 times the original length.

Similarly, the practice of this invention can be applied effectively not only to the acrylonitrile polymers and copolymers hereinbefore disclosed but also to other copolymers such as those mentioned in U. S. Patents 2,404,714 to 2,404,727, and copolymers which may be present in the yarns include those of acrylonitrile and isobutylene, butadiene or divinylbenzene. The other constituent may be mono- or di-ethylenically substituted, and any structure containing at least 85% acrylonitrile in the polymer may be processed by this invention. In fact, any containing a major amount of acrylonitrile is oper-

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able; of most interest are those structures that are derived from about 85% or more by weight of acrylonitrile. The structures that are used in the process of this invention may be prepared by dry spinning, wet spinning or plasticized melt spinning techniques. The structures prepared for processing in accordance with this invention may be filaments, yarns, ribbons, films and similar shaped articles.

Knitted and woven fabrics prepared from homopolymer and copolymer continuous filament or spun staple yarns produced as hereinbefore set forth are more uniform in appearance and when dyed with basic acid or dispersed dyes in accordance with accepted procedures the dyed fabrics are uniform in color. The improvement in dyeing uniformity which follows from the practice of this invention is the outstanding benefit realized and this improvement is indeed important if not essential for the continued commercial acceptance of acrylonitrile polymer yarns.

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

I claim:

1. A process for the preparation of an acrylonitrile polymer fiber from an undrawn spun polymer which contains at least 5% by weight of an inert solvent for said polymer, at least 85% of acrylonitrile with a maximum of 15% of copolymerizable monomers in the polymer molecule and which is capable of being drawn at least about two times its original length, the said process comprising heating said spun polymer, while it is in a relaxed condition, in an inert non-aqueous medium at a temperature of from about 100° C. to about 150° C. for a period of time of from about 5 seconds to about 2 hours; removing the inert solvent from spun polymer until its solvent content is no more than about 2.5% by weight; and thereafter drawing said spun polymer at least about two times its original length.

2. The process of claim 1 wherein the heating time is from about 20 minutes to about 2 hours.

3. The process of claim 1 wherein said spun polymer

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is drawn from about two to about ten times its original length.

4. The process of claim 1 wherein said polymer is polyacrylonitrile homopolymer.

5. The process of claim 1 wherein said polymer is a copolymer of acrylonitrile and methyl acrylate.

6. The process of claim 1 wherein said polymer is a copolymer of acrylonitrile, methyl acrylate and styrene sulfonate.

7. The process of claim 1 wherein said polymer is a copolymer of acrylonitrile, vinyl acetate and styrene sulfonate.

8. The process of claim 1 wherein said polymer is a copolymer of acrylonitrile and methyl methacrylate.

9. The process of claim 1 wherein said solvent is N,N-dimethylformamide.

10. The process of claim 1 wherein solvent is removed from said spun polymer subsequent to the heating of said spun polymer.

11. The process of claim 1 wherein solvent is removed from said spun polymer by washing with hot aqueous liquor subsequent to the heating of said spun polymer.

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