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[54] **ACRYLONITRILE YARN**

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[63] Continuation of Ser. No. 864,225, Oct. 6, 1969, abandoned.

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[58] **Field of Search** ..... 57/140 R, 157 MS; 260/29.6 AN; 264/210 F, 206, 182; 28/1 V

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[57] **ABSTRACT**

Tensile properties of acrylonitrile yarn dry spun from low boiling solvent are improved by heat treating the yarn while held at constant length. The treated yarn can be used as a precursor yarn to produce yarn of unusually high hot-wet modulus coupled with extremely low permanent set value.

3 Claims, No Drawings

ACRYLONITRILE YARN

This is a continuation of application Ser. No. 864,225, filed Oct. 6, 1969, now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to improved shaped articles formed of acrylonitrile polymers. More particularly, the present invention relates to a process for improving many desired properties of continuous mono- and multifilament yarns formed of acrylonitrile polymers, the yarns so-produced and shaped articles manufactured therefrom. In greater detail, one aspect of this invention concerns an inexpensive, rapid method involving a minimum of process steps for treating an essentially solvent-free as-spun acrylonitrile yarn, especially a dry spun yarn, prior to further processing to produce a yarn characterized by enhanced tensile strength and other desired properties. More particularly, yarn coherency, elongation at the break and tensile factor properties are improved by the method of this aspect of the invention, which method is also the first process step of a multi-step method for producing an acrylonitrile yarn characterized by excellent hot-wet performance properties.

Acrylonitrile fibers can be formed, for example, by melt spinning, wet spinning and dry spinning methods. However, because of polymer degradation, chain cleavage and the like factors which frequently occur during melt spinning operations as a result of the relatively high temperatures of the order of 250°C and above which are required to melt acrylonitrile polymers of fiber-forming quality, dry and wet spinning procedures are generally preferred for use in acrylonitrile fiber-forming operations. Until recently, the preferred methods for spinning acrylonitrile polymers have involved dry and wet spinning techniques utilizing a spinning solution containing fiber-formable acrylonitrile polymers admixed with a high boiling solvent. In wet spinning, the spinning solution is extruded into a liquid coagulant which is a non-solvent for the polyacrylonitrile while in dry spinning extrusion is carried out into a heated chamber or spinning column.

With the use of the relatively high boiling solvents, which boil at temperatures significantly above acrylonitrile yarn spinning temperatures, the spun yarns must be washed one or more times for spinning solvent removal. Typical high boiling solvents, i.e., boiling at about 200°C and above, useful for forming acrylonitrile polymer spinning solutions are dimethylformamide, dimethylacetamide, gamma-butyrolactone and the like. In fact, the economic problems of adequately washing continuous filament yarn formed from high acrylonitrile polymers to produce acceptable solvent levels in the yarn that is a solvent level which does not adversely affect wanted yarn properties such as tensile strength, elongation, texturability and the like, have prevented the marketing of continuous filament acrylic yarn in substantial quantities in this country. At this time, as-spun acrylonitrile yarn is gathered into a high denier tow to facilitate more economical washing and subsequently cut into staple form prior to spinning into staple spun yarn.

Of late, a dry spinning technique for forming continuous filament acrylonitrile yarn has become economically feasible through the discovery of relatively low boiling, i.e., 75°–125°C, solvent systems for high acrylonitrile polymers, which solvents function efficaciously at solids levels acceptable for fiber-forming operations. Thus, the prior art washing steps and other special solvent removal steps are eliminated. This invention is particularly directed to benefiting dry spun acrylonitrile yarn formed from low boiling solvent systems which substantially evaporate from the yarn to an insignificant yarn content in the spinning column. The preparation of a low boiling solvent system for high acrylonitrile polymer is disclosed in copending commonly-assigned application of Champ Ser. No. 764,484, filed Oct. 2, 1968, now abandoned and the use thereof in dry spinning is disclosed in copending, commonly assigned application of Champ and Bohrer, Ser. No. 764,380, filed Oct. 2, 1968, now U.S. Pat. No. 3,655,857, which applications are hereby incorporated into this disclosure.

Following extrusion, acrylonitrile yarns in general are subjected to a drawing operation to improve tensile properties by increasing the degree of molecular orientation of the yarn along the longitudinal yarn axis. This drawing operation, which can be a spin draw and/or one or more post-spin drawing steps in combination to reach a desired post spinning draw ratio, is also employed in many instances to promote fiber crystallization to further increase yarn tensile properties. However, acrylonitrile yarns subjected to the above general type of drawing and orientation operation, and particularly yarns dry spun from low boiling solvent systems, have been found to be deficient in certain respects, particularly under hot-wet conditions of 85° to 95°C. These yarns are often characterized by high permanent set values (corresponding to poor elastic recovery), and relatively low tensile properties as measured by hot-wet, stress-strain modulus (hereinafter designated hot-wet modulus); tensile factor and the like tests. In particular, it is difficult to produce an acrylonitrile yarn dry spun from low boiling solvents which retains an acceptable percentage of its room temperature properties, i.e., 23°C tenacity value coupled with good elongation properties, at temperatures of the order of about 95°C while in a wet condition, i.e., poor hot-wet modulus and tensile factor values. These parameters are recognized by those skilled in the art as indicative of the hot-wet performance of acrylonitrile yarns. Good hot-wet performance as is known is desired, if not needed, in many yarn end use applications.

It has been found that in order to produce a dry spun acrylonitrile yarn characterized by the above-described highly desired hot-wet performance properties, it appears to be highly desirable to employ a precursor yarn for the drawing operation characterized by superior elongation properties as measured by elongation at the break. With such yarns, hot-wet modulus can often be predicted from the elongation at the break of the as-spun precursor, other factors being constant; that is, good hot-wet modulus values appear only to be obtainable at the expense of elongation.

The percent elongation at the break values of acrylonitrile continuous filament yarns dry spun from low boiling solvent systems are usually relatively low and should be improved considerably to develop good hot-wet performance properties in the yarn. These low values are believed to be caused in part by the rapid volatilization of low boiling spinning solvent preventing the self-healing of internal and surface flaws such as surface cracks, internal voids; and presence of particulate

matter and the like which are eliminated by the plasticizing action of residual spinning solvent present when the high boiling spinning solvents are employed. Thus, hot-wet performance of such acrylonitrile yarn is not usually improved by stretching operations. Yarn extensibility generally suffers as tenacity is improved as a result of longitudinal drawing. Therefore, it would be highly desirable to employ a precursor yarn for the drawing operation having an abnormally high elongation at the break, e.g., 50 to 100 percent and above, within acceptable tenacity ranges, e.g., above about 1.0 gram per denier for undrawn, as-spun filaments. If good extensibility is retained, without interference with attained tenacity, yarns characterized by high hot-wet modulus and hot-wet tensile factor values could result.

Therefore, it is an object of the present invention to provide a process for producing an undrawn acrylonitrile yarn dry spun from low boiling solvents characterized by an unusually high elongation at the break value coupled with a tenacity value comparable to that of as-spun yarn and the yarn so produced.

It is another object of the present invention to provide a precursor acrylonitrile yarn for a drawing operation exhibiting a high tensile factor; excellent coherency, i.e., essentially void free; increased linear density and the like properties.

It is still a further object of the present invention to provide a process for producing a drawn acrylonitrile yarn characterized by superior hot-wet modulus and tensile factor properties and the yarn so-produced.

An additional object of the invention is to provide a multi-step process involving the initial preparation of an undrawn acrylonitrile yarn dry spun from low boiling solvent displaying an unusually high elongation at the break value, which yarn is then transformed by further steps of said process into a drawn yarn characterized by excellent hot-wet performance properties.

Other objects of the invention will appear obvious to those skilled in the art from the detailed description of the invention hereinafter.

SUMMARY OF THE INVENTION

It has now been found that an undrawn acrylonitrile yarn characterized by a tenacity of at least 0.5 grams per denier, designated hereinafter gpd, preferably over 0.6 gpd, e.g., 1.0–1.5 gpd, and an elongation at the break of at least 15 to 25 percent, preferably 25 to 50 percent and often over 100 percent, suitable for drawing into a yarn exhibiting excellent hot-wet properties can be prepared by forming an essentially solvent-free acrylonitrile yarn by dry spinning from a low boiling solvent, said yarn having a tenacity as stated and an elongation at the break of below about 15 percent, preferably below about 10 percent, and improving said yarn by heating said yarn at a temperature above its glass transition point, preferably above 100°C., for at least about 30 seconds while maintained at constant length. In a preferred embodiment of the invention the yarn is heat treated below about 175°C. for about 1 minute under a tension required for maintenance of constant fiber length conditions. This precursor yarn is then further treated by hot drawing at a draw ratio of from about 2–8:1, preferably about 4.5:1–6.5:1, followed by heat setting while held at constant length at a temperature above that employed at any previous point during the process and preferably above any temperature the yarn will encounter during subsequent processing, i.e., conversion operations or use. The final product is an acrylonitrile yarn characterized by a hot-wet modulus at 95°C. of at least above 6.5 gpd, preferably over 7.8 to 8.0 gpd and, under the same hot-wet testing conditions, an elongation at the break of at least 36 percent, preferably over 40 percent, a tenacity of at least 1.32, preferably above 1.35 gpd, a tensile factor of at least 8.00, preferably above 8.50 and essentially 0 percent permanent set following a 10 percent extension.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to acrylonitrile monofilament and multifilament yarn. Therefore, by the term "acrylonitrile yarn" and the like as used herein is meant continuous monofilament and multifilament yarn, to the exclusion of spun staple yarn, formed of acrylonitrile polymers. The continuous filament substrate can be formed of modacrylic polymer, that is, polymers containing at least 40 percent acrylonitrile up to about 85 percent acrylonitrile, but more preferably will be formed of high acrylonitrile polymers containing at least about 85 percent or more acrylonitrile, by weight. Such polymers are well known in the art and normally are used in filament production as copolymers, terpolymers and higher copolymerized products. Typically, varying amounts of other copolymerizable monomers are added to produce the co- and terpolymers. Typically, ethylenically unsaturated monomers, such as methylacrylate, methyl methacrylate, vinyl acetate, vinylidene chloride, styrene, sulfonic acid materials such as sodium methylallyl sulfonate, disodium allyl phosphate and the like can be used. In modacrylics, the proportion of the comonomer is substantially higher, thereby lowering the amount of acrylonitrile used in the polymerization reaction. With high acrylics, the amounts of copolymerized monomer is up to about 15 percent, but more generally in the range of about 0.1 to 10 percent by weight. While sulfur-containing monomers are preferred to enhance the dyeability of the end polymer, other dye-enhancing compounds can be used such as those containing a phosphorous group or other dye enhancing group, as are well known in the art.

As-spun or undrawn continuous acrylonitrile filaments, dry spun in low boiling solvents, that is, filaments which have only been subjected to a drawing-down operation while being positively pulled from the spinnerette, as opposed to a separate drawing operation in which the point of reference would not be that of the spinnerette, are generally characterized by relatively poor tensile properties, particularly elongation at the break. For this reason, the as-spun filaments are stretched to develop higher tensile strength suitable for textile conversion operations, i.e., knitting and weaving processes. However, if high tenacity values are obtained, usually requiring a high draw ratio, elongation suffers, particularly when tested at elevated temperatures such as those encountered by textile articles of manufacture during, e.g., finishing, dyeing and washing operations. Therefore, it would be advantageous to have available an as-spun fiber characterized by a high elongation at the break value allowing the employment of higher draw ratios for the development of better tensile properties by a stretching operation and which would retain improved elongation properties following

drawing when tested under hot-wet performance conditions.

Therefore, the present invention is initially concerned with modifying the percent elongation at the break of an as-spun acrylonitrile yarn dry spun in low boiling solvent systems without deleteriously affecting the tenacity of the yarn or its ability to be drawn into a tenacious yarn from which wearing apparel, carpeting pile and other textile materials can be manufactured.

Typical acrylonitrile filaments drawn down in a dry spinning operation from low boiling solvent solutions will have a tenacity of from about 0.5 to 1.5 gpd and an elongation at the break of below about 15 percent and most often below about 10 percent, e.g., in the range of about 6 to 8 percent. One aspect of the present invention involves the treatment of such an undrawn as-spun yarn to increase its percent elongation at the break to over 15 percent up to about 50 to 200 percent, and preferably at least over 100 percent for high denier per filament yarn, without appreciably decreasing tenacity. That is, if tenacity is lowered at all, it will only be down to about 10 percent below the as-spun value. In fact, many times there is a slight increase in tenacity along with the many fold increase in elongation.

It has been found that this objective is achieved by treating the described as-spun yarn which is in an essentially solvent free condition at a temperature above the glass transition point of the yarn for at least about 30 seconds while held under a tension required to maintain the fiber at about constant length. It is quite surprising to find that constant length treatment develops the best elongation properties in the dry spun yarn since it has been generally accepted by those skilled in the art that yarn relaxation, that is free to shrink or controlled relaxation conditions allowing molecular relaxation, should consistently develop the best yarn elongation properties. In fact, acrylonitrile yarn dry spun from conventional high boiling solvent systems appears to follow this general principle while yarns of the same composition spun from low boiling solvent systems respond more consistently and with markedly superior results to constant length heat treatment conditions.

In preferred embodiments of this aspect of the invention, the continuous filament substrate is treated for at least about 1 minute at a temperature over about 100°C. while maintained at constant length.

The temperature employed can theoretically range up to about the degradation point of the polymer, i.e., above 175°C. However, no particular advantage is realized with unusually high temperatures over about 150°C. In fact, lower temperatures from about 25° to 50°C. above the glass transition temperature of the fiber give the best elongation properties in many instances. Temperatures at about the high end of the above range are preferred, i.e., 115° to 150°C. for a typical continuous filament yarn formed of a high acrylonitrile polymer.

The glass transition temperature of the polymer as defined herein is the temperature at which appreciable amounts of the amorphous or non-crystalline regions of the fiber attain chain mobility. For filaments formed of high acrylonitrile polymers, this temperature is about 80°C. to 90°C. but can vary somewhat depending upon percentage and type of co-monomer(s) present, polymer intrinsic viscosity and the like factors well-known to those skilled in the art.

The mechanism or reason for improvement in elongation is not fully understood. However, it is believed that a combination of interacting factors may be involved. An as-spun continuous filament acrylic yarn, particularly dry spun from low boiling solvent system, tends to form comparatively brittle, randomly positioned regions along the length of the filaments after solvent removal. These brittle regions can not be stretched to the extent that the non-brittle regions can be drawn and, therefore, cause a premature cracking or rupturing of the filaments. The brittle regions usually contain numerous microvoids which, during stretching, combine into larger cavities which may form the nuclei of areas of filament rupture. Also, it is believed that rupture might be caused by a cleavage occuring along the boundary areas of the brittle regions of the filaments. By heating the filaments to a temperature above the glass transition temperature, amorphous polymer segments of the filaments attain the necessary mobility to fill the microvoid structures, thereby contributing to the prevention of filament rupture during a stretching operation and increasing the extensibility of the substrate. Additionally, the heat treatment permits the relaxation of local stored stresses, particularly since a relatively low tension is applied to the substrate, and segmental rotation leading to an increase in the short range order of crystallinity. Molecules can become more regularly aligned along the fiber axis in a more dense structure. It is believed that all of these factors, and others, contribute to the improvement in tensile properties, i.e., elongation at the break, tensile modulus and tensile factor, increased thermal stability, higher density and the like properties of the treated filaments. Further, following a drawing operation, hot-wet performance properties are enhanced to a degree not usually obtainable with acrylic yarns.

The continuous filament substrate is subjected to the heat treatment for at least about 30 seconds, and preferably about 1 minute. The duration of the heat treatment can range up to 5 minutes or longer but no appreciable benefit is realized with treatment periods over about 2 minutes. Even if amorphous polymer segments of the continuous filament substrate attain mobility instantaneously at the particular temperature employed, the substrate should still be subjected to the treatment for the minimum time period herein designated to insure that the entire yarn reaches the treatment temperature and since factors other than the relaxation of amorphous polymer regions appear to be involved which occur during the extended heat treatment. The preferred treatment time period, when the preferred temperature range hereinbefore stated for high acrylonitrile polymer yarn is used, is about 1 minute.

The acrylic filaments should be essentially solvent-free during the heat treatment. Although healing of some micropores or voids with solvent present is possible, residual solvent can interfere with the extensibility of the yarn during further processing and thereby negate one of the prime advantages and objectives of the heat treatment. Residual solvent, by evaporating during a subsequent drawing operation or even during the heat treatment, for example, can form additional internal void pockets throughout the continuous filaments, thereby lowering elongation values. Therefore, the yarn should be thoroughly dried prior to the heat treatment. This is easily achieved with the employment of low-boiling spinning solvent. As stated, the present pro-

cess has specific applicability for acrylic filaments dry spun from low-boiling solvent solutions because of their unique characteristics as compared to conventional dry spun acrylonitrile yarns. As used herein, a solvent-free acrylonitrile yarn contains less than 35 percent by weight, preferably about 5 to 25 percent, residual spinning solvent. This amount of residual solvent evaporates during subsequent processing at elevated or ambient temperatures.

During the initial heat treatment, the continuous filament substrate is under a tension required to maintain the filaments at about constant length. This tension parameter is in sharp contrast to a conventional stretching step to specifically develop enhanced tensile properties, particularly tenacity, or a controlled or free shrinkage relaxation process. Where a comparable acrylic substrate is heated at the defined temperature for the designated time during a drawing operation, elongation at the break is not increased to the extent possible with employment of the invention and, further, where additional identical processing is involved, yarn hot-wet performance properties of the yarn pre-treated in accordance with the invention are significantly superior.

Subsequent to the pretreatment process, and in accordance with the invention, the yarn can be further processed in a continuous manner to form a continuous filament product having enhanced hot-wet properties, specifically a hot-wet modulus at 95°C of at least about 6.5 gpd, and preferably above 7.8 gpd, e.g. 8.0–12.0 gpd and under the same testing conditions, an elongation at the break of at least 36 percent, preferably over 40 percent but less than 70 percent, a tenacity of at least 1.32, preferably above 1.35 gpd, e.g. 1.35–2.5 gpd, a tensile factor of at least 8.00, preferably about 8.50, and essentially 0 percent permanent set following a 10 percent extension.

The heat-treated yarn, to develop the aforementioned hot-wet properties, is first subjected to a hot draw at a draw ratio between about 2–8:1, preferably about 4.5–6.5:1. The temperature employed during drawing will be above about 105°C and, preferably will be within the preferred temperature ranges indicated for the heat treatment hereinbefore.

This fiber drawing may be accomplished in numerous manners but most often will be conducted in air or an inert atmosphere such as nitrogen or steam. The necessary heat may be supplied by one or more hot rolls, hot shoes, heated tubes, ovens and the like. Similarly, a multi-stage stretching operation with, for example, a relaxation prior to final draw, with a net draw ratio as disclosed may be used as the drawing step of the overall process.

The final method step of the integrated process to develop good hot-wet properties involves the heat-setting of the continuous filament substrate at a temperature above that employed in previous steps of the process and preferably above the maximum temperature to which the yarn will be exposed during subsequent operation, i.e., dyeing and finishing or during use in converted form. Either moist or dry heat may be employed with a temperature generally below about 250°C, preferably in the range of about 175°–225°C. Time of treatment is somewhat temperature dependent but for good heat-setting will be at least about 5 minutes, preferably about 10–15 minutes. Longer time periods may be used but the improvement in properties does not warrant the economic disadvantages. Of critical importance to the purposes of the invention is that the continuous filaments be heat set while held at constant length. Alternatively, a slight stretch, i.e., up to about 10 percent, may be employed. It is believed that in this manner that stresses developed during drawing are dissipated which appears to contribute markedly to the thermal stability of the molecularly oriented yarn. Additionally, microvoids formed as a result of the stretching operation are healed similar to that occurring during the initial heat treatment phase of the process. The heat setting also improves the lateral order of the polymer chains as revealed by x-ray diffraction patterns.

The following examples are presented to illustrate the invention and not to limit it in any manner. All percentages are by weight unless otherwise stated.

EXAMPLE I

This Example illustrates the improved tensile properties, particularly elongation at the break, of as-spun fibers following the heat treatment of the invention. The substrate, 60 dpf, filament yarn, formed from a high acrylonitrile polymer of about 1.4 intrinsic viscosity composed of about 95 percent acrylonitrile, about 4.5 percent methylacrylate and about 0.5 percent sodium methallyl sulfonate, by weight, is dry spun using a low boiling acetonitrile/water solvent as disclosed in the hereinbefore stated copending, commonly assigned application of Champ and Bohrer. The yarn is heated in accordance with TABLE I with the results shown and compared with an as-spun sample.

TABLE I

SAMPLE	Heat Treatment Conditions	Elongation at the Break (%)	Modulus (gpd)	Tenacity (gpd)
A	115°C for 1 minute, free to shrink	75	56	1.1
B	115°C for 1 minute, constant length	123	60	1.1
C	130°C for 1 minute, free to shrink	19	50	1.1
D	130°C for 1 minute, constant length	145	55	1.2
E	150°C for 1 minute, free to shrink	8	53	1.2
F	150°C for 1 minute, constant length	110	58	1.3
G	None (As-spun)	7	50	1.2

The above results also indicate certain preferred temperature and tension ranges as discussed above.

EXAMPLE II

This Example illustrates the superior hot-wet performance properties developed in acrylonitrile polymer continuous filament yarn by the integrated process of

the invention as compared to yarns treated in a conventional manner without either the heat pretreatment or heat setting steps, including yarns drawn and heat set but not given a heat pretreatment in the undrawn state. Processing conditions of the various samples and their hot-wet properties are tabulated in Table II. All samples are dry spun from low boiling acetonitrile/water solvent as in Example I.

TABLE II

Sample	Heat pre-treatment	Hot Drawing Conditions	Modulus 23°C dry	Modulus 85°C wet	Modulus 95°C wet	Elongation at the break 23°C dry	Elongation at the break 85°C wet	Elongation at the break 95°C wet	Tenacity 23°C dry	Tenacity 85°C wet	Tenacity 95°C wet	*ER_{10} at 95°C wet (%)	Tensile factor 23°C dry	Tensile factor 85°C wet	Tensile factor 95°C wet
H	130°C, 1 minute at constant length	5.5:1 at 130°C followed by heat set at constant length at 170°C.	108.0	11.6	8.1	11.7	23.4	41.9	5.0	2.1	1.4	99.5	14.0	9.9	8.8
I	None	2:1 at 100°C	52.3	1.7	0.8	21.2	139	32.0	1.6	0.8	0.2	53.6	6.4	9.3	3.4
K	None	Sample I further drawn 3:1 at 150°C and hot relaxed 8% at 160°C.	95.9	8.3	6.5	12.8	23.1	26.1	5.2	1.5	1.1	86.9	15.7	7.0	5.5
L	None	2:1 at 85°C followed by heat set at constant length at 170°C.	84	5.8	—	16	44	—	4.5	1.2	—	—	18.0	7.9	—

*ER_{10} – Elastic recovery for 10% extension.

This example demonstrates the excellent acrylonitrile yarn hot-wet performance properties obtained by use of the present invention (Sample H) and the improvement obtained by heat setting the drawn yarn after drawing (Samples I and L). The difference in temperature of drawing between I and L is inconsequential to the results. Sample K represents an acrylonitrile polymer continuous filament yarn having acceptable properties when tested at 23°C. dry but which is inferior when compared to yarns processed in accordance with the teachings herein and tested under hot-wet conditions.

Hot-wet modulus or tensile modulus at elevated temperatures is determined by immersing the sample in water at the test temperature for 1.5 minutes under zero stress conditions and then stretching the fiber and plotting its stress-strain curve in accordance with conventional procedures. The modulus value corresponds to the initial slope of the stress-strain curve.

Tensile factor is calculated by the formula $te^{1/2}$ wherein "t" is tenacity (gpd) and "e" is elongation at the break (percent). The significance of the tensile factor determination is discussed in an article by Dr. Arnold J. Rosenthal, "$TE^{1/2}$, An Index for Relating Fiber Tenacity and Elongation," Proceedings of the Symposium on Polypropylene Fibers, September 17 and 18, 1964, published by the Southern Research Institute, Birmingham, Alabama.

EXAMPLE III

This example compares in Table III the improvement developed in continuous filament acrylonitrile yarn of identical polymer composition spun from low boiling and high boiling solvents subjected to constant length and free to shrink heat treatment conditions for one minute. The low boiling solvent employed is the acetonitrile/water solvent as described in the aforementioned Champ and Bohrer application. The high boiling solvent system is a conventional dimethylformamide composition dry spun, washed and dried in the usual manner.

TABLE III

HEAT TREATMENT (°C)	ELONGATION AT THE BREAK (%)		
Solvent	Low Boiling		High Boiling Solvent
	60 dpf Yarn	12.8 dpf Yarn	18 dpf Yarn
None (As-spun)	7	6	238
115—free to shrink	75	18	182
115—constant length	123	18	171
130—free to shrink	19	23	189
130—constant length	145	21	191
150—free to shrink	8	28	70
150—constant length	110	24	97
175—free to shrink	—	26	44
175—constant length	—	23	88

The results of Example III illustrate the elongation properties of a yarn dry spun from low boiling solvent systems as compared to a conventional dimethylformamide high boiling system and the relative improvements obtained therein by constant length and relaxation heat treatments. Constant length treatment yields superior results with low boiling precursor material. Free to shrink conditions are best with yarn conventionally spun from a high boiling solvent system, although below the as-spun value of such high boiling spun material.

The constant length heat treatment may be accomplished in various manners obvious to those skilled in the art. For example, during continuous operations a multi-wrap, i.e., 25 or more wraps, hot roll process may be employed or simultaneous, multiple passage through an elongated oven. Of course, with very heavy denier yarn, such as for carpet use, heat treatment may be ac-

complished by inserting wound bobbins in a suitable oven.

Various modifications will appear obvious to those skilled in the art, such as the heat treatment of acrylo nitrile yarns dry spun from other low boiling solvent systems. Further, the yarn may be of a semi-continuous nature. The low boiling solvent system of the said Champ and Bohrer application comprises acetonitrile and preferably acetonitrile/water in the proportions of about 82/18 to 73/27. By the term "low boiling solvent" is meant a solvent system for acrylonitrile fiber-formable polymers, particularly high acrylonitrile polymers, boiling below about 125°C, more particularly within the range of about 75° to 100°C, as exemplified by the acetonitrile solvent of Champ and Bohrer.

What is claimed is:

1. A high acrylonitrile continuous filament yarn of at least 90 percent acrylonitrile and from about 0.1 to 10 percent of a copolymerized monomer, said yarn characterized by a residual acetonitrile solvent content of less than 35 percent by weight and having the following properties under hot-wet conditions at 95°C., a hot-wet modulus of at least 6.5 gpd, an elongation at the break of at least 36 percent, a tenacity of at least 1.32, a tensile factor of at least 8.00 and a permanent set following 10 percent extension of about 0 percent.

2. The yarn of claim **1** wherein said hot-wet modulus is at least 8.0 gpd, said elongation at the break is at least 40 percent, said tenacity is at least 1.35 and said tensile factor is at least 8.50.

3. The yarn of claim **1** wherein the acrylonitrile yarn contains from about 5 to 25 percent acetonitrile.

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