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PROCESS OF SETTING THE CRIMP IN ACRYLONITRILE POLYMER FIBERS WITH CHEMICAL SHRINKING AND SETTING AGENTS

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This invention relates to setting the crimp in acrylonitrile polymer yarns and fibers. The invention also applies to shrinking acrylonitrile polymer yarn and fibers.

Crimp is added to filaments and fibers of acrylonitrile polymers and copolymers to improve bulk and processability. Unless the crimp is "set" in a permanent manner, much of the advantage may be lost during processing. Knit wear produced from crimped filament or fiber yarns of acrylonitrile polymers and copolymers wherein the acrylonitrile content is not less than about 85% has a very desirable handle. However and especially in the case of copolymers, the loft, bulk or covering power is generally greatly diminished by hot-wet processing (such as boil-off and dyeing) of the knit structure so that the fabric acquires an open, hungry appearance. This reduction in bulk during fabric finishing is believed to be caused primarily by crimp loss occurring in the boil-off and dyeing of the knit goods. Yarns prepared from acrylonitrile homopolymer retain crimp under these hot-wet treatments much better than do yarns from copolymers of acrylonitrile prepared using up to about 15% of one or more ethylenically unsaturated compounds copolymerizable with acrylonitrile. In fact, comparison of results between knit wear of acrylonitrile homopolymer yarn and of acrylonitrile/methyl acrylate (94/6) copolymer yarn shows bulk loss in the copolymer fabric to be about 25% more than in the homopolymer fabric. Thus, while acrylonitrile homopolymer yarn knit wear is readily acceptable when properly fabricated from the right denier yarn for a given construction, 25% more yarn is needed when using only a copolymer yarn in order to produce a similar article with equal acceptability.

It has been shown that the desired loft or bulk can be retained by setting the crimp under conditions that will substantially resist removal during the hot-wet treatment used in the finishing of the knitted goods by pressure treatment of the crimped staple in a confined space with water in liquid form at 120° C. However, pressure treatment is costly and a more expedient method of crimp setting with at least as good results is desired.

Accordingly, an object of this invention is to provide an improved process for setting the crimp, crinkle or curl in acrylonitrile polymer and copolymer filaments, fibers and yarns, without involving superatmospheric pressures. Another object of this invention is to provide an improved process for shrinking yarns, filaments and fibers without resorting to superatmospheric pressure conditions. These and other objects will be apparent from the description that follows.

The objects of this invention are accomplished by impregnating the crimped fibers, filaments, yarns or the like comprised of acrylonitrile polymers or copolymers wherein the acrylonitrile content is not less than about 85% with a dilute aqueous solution heated to at least about 95° C. and containing about 0.5% to about 40.0% of a hydroxyl or amine substituted benzene or naphthalene compound soluble at least to the exent of 1% in water

at the boil and containing only the groups defined by the following generic formula

$$R(OH)_m(NH_2)_nA_p$$

wherein R represents a benzene or a naphthalene ring which is substituted as shown by —OH, —NH_2 or —A groups, m, n and p being 0, 1 or 2, $(m+n)$ being equal to 1 or 2 and A representing methyl or ethyl. The concentration of the solution will vary with the time of treatment and the efficacy of the specific compound used. When excessive shrinkage of the fiber structure is desired, the concentration should be substantially higher than for crimp setting, e. g. two or three times as much, and with acrylonitrile homopolymer as much as 30% or even 40% adjuvant may be contained in the treating bath which may be three or four times as much as needed for a copolymer fiber. For crimp setting of an acrylonitrile copolymer, as little as 0.5% of beta-naphthol is effective and, generally, concentrations in the range of from about 0.5% to about 20% are effective, depending on the specific adjuvant and time of treatment. For shrinkage, amounts of about 1% to about 40% are used. The processes are carried out at atmospheric pressure. The polymers that are used in the manufacture of the fibers used in this invention are well-known, having been described in the art in such patents as U. S. Nos. 2,404,714–2,404,727 and 2,486,241. Thus, the polymers contain 85% to 100% acrylonitrile and copolymers may be derived from the polymerization of acrylonitrile with monoethylenically or diethylenically unsaturated compounds as vinyl acetate, vinyl chloride, vinylidene chloride, methyl vinyl ketone, styrene, vinylpyridines, acrylic acid and methacrylic acid or their derivatives such as their esters, ethylenesulfonates, 1-propenylsulfonates, styrenesulfonates and the like. The copolymers may be comprised of two or three or more copolymerizing compounds.

To measure quantitatively the amount of "retained crimp" and the "shrinkage factor" which are given in several examples that follow, the test procedures set forth below were devised. The drawn yarn was knitted and the knitted sample about 5" x 5" was immersed in a treating solution of this invention, usually at or near the boil. The sample was then rinsed and reboiled in demineralized water for ten minutes and dried at 70° C. Yarn raveled from such a sample of treated knit tubing was tested for crimp stability as follows. The raveled yarn was subject to mild tension in hot water by suspending from a loop of the yarn a weight of 17 milligrams. This weighted loop was lowered into a beaker of hot water (92° to 94° C.) and held there for five minutes. The yarn was taken from the bath and the weight removed and then the loop was reimmersed in the hot water for one minute, after which the yarn was oven dried at about 70° C. The number of crimps per centimeter in the dried, looped yarn were counted and are listed in the tables that follow in the columns under the heading "retained crimp." Shrinkage of the knit tubing was measured by counting the courses and the stitches per centimeter of the original untreated knit sample and of the treated swatch. The "shrinkage factor" or "percent area shrinkage" is defined as

$$1.0-\frac{C_iS_i}{C_tS_t}$$

where C and S are courses and stitches per centimeter respectively and i and t mean "initial" and "treated," respectively.

The following examples are given to further illustrate the invention without any intention of being limited thereby, parts and percentages being by weight.

EXAMPLE I

A copolymer of acrylonitrile/methyl acrylate (94/6) was dry spun from N,N-dimethylformamide solution to produce 330 denier-30 filament "as-spun" yarn which was hot-wet drawn 4× to produce a final yarn of about 85 denier. The yarn was knitted from the wet packages to a medium tight structure having 16.5 x 14.5 courses x stitches per square centimeter and swatches of this knitted structure were subjected for ten minutes at 98° C. to the aqueous solutions listed in Table A below. The results obtained following the test practice previously described and using a large excess of bath to swatch, e. g. about 150 to 1, are also set forth in Table A.

Table A

Adjuvant	Conc., Percent	Shrinkage Factor	Retained Crimp/cm.
Water		0.47	7.5
Water (at 120° C.)		0.57	10.5
Phenol	5	0.67	(1)
Do	2	0.56	12.0
beta-Naphthol	1	0.64	(1)
Do	0.5	0.63	10.5
Do	0.25	0.56	7.5
m-cresol	4		(1)
Do	2		11.2
Do	1		8.7
Resorcinol	10		10.0
Do	5		8.2
Hydroquinol	10		10.5
Do	5		9.0
Aniline	4		12.5
Do	2		11.0
m-toluene diamine	10	0.65	(1)
Do	5		11.0

[1] Too much shrinkage to unravel.

From these data, it can be seen that the mono-hydroxyphenols are very effective as shrinkage agents and as crimp setting agents even at very low concentrations. The dihydroxyphenols are effective, but are less potent so that at least 10% solutions are required for crimp setting equivalent to water at 120° C. Other compounds containing phenyl groups which were similarly tested and found ineffective were 0.15% p-phenyl phenol (probably because of its low water solubility), 2% nitrophenyl acetic acid, 2% thymol plus 10% isopropyl alcohol to confer adequate solubility thereto, 1% acetanilide and 5% phenyl phosphoric acid.

Also, it is to be noted that the aromatic amines are very effective, being, as are the phenols, better than the water control or the 120° C. steam pressure treatment.

EXAMPLE II

A yarn similarly prepared from acrylonitrile homopolymer knitted as before and swatches of the fabric subjected for ten minutes at 98° C. to the solutions given in Table B, using a large excess of bath, yielded the results recorded in Table B.

Table B

Adjuvant	Conc., Percent	Shrinkage Factor	Retained Crimp/cm.
Water		0.05	5.2
Water (at 120° C.)		0.05	6.5
beta-Naphthol	1.0	0.20	7.3
Phenol	2.0	0.07	5.3
Do	10.0	0.20	7.1
m-Cresol	4.0	0.15	6.3

In this case, much higher concentrations of adjuvants were needed to produce as much "retained crimp" as was possible by water treatment at 120° C.

EXAMPLE III

Since it is desirable to set the crimp in a matter of seconds on the run, for example in the crimper box or in a relatively small extension thereto, the following experiments were run with beta-naphthol. It was noted

that 1% beta-naphthol was not as effective in fifteen seconds' exposure as was desired (or as effective as 0.5% concentration for ten minutes). In order to get 2% beta-naphthol in solution, some added component was needed. For this purpose, 25% aqueous glycerol was used. This permitted clear solutions at 2% beta-naphthol concentrations at about 90° C. or above. This solution at 98° C. was effective as a crimp setting medium when in contact with a crimped fiber structure for about fifteen seconds.

EXAMPLE IV

Yarn samples prepared as described in the first part of Example I and in the form of small skeins were subjected to shrinkage tests with water and with beta-naphthol with the shrinkage results and physical properties of the shrunk yarn as set forth in Table C below.

Table C

Treating Solution	Water	Water	0.5% beta-Naphthol	1.0% beta-Naphthol
Temperature, ° C	99	120	99	99
Percent Shrinkage	24	30	31	48
Denier	115.5	119.6	126.7	160.0
Straight:				
Tenacity, G. P. D	2.78	2.80	2.39	2.02
Elongation, Percent	21.6	24.3	26.0	29.5
Loop:				
Tenacity, G. P. D	2.61	2.49	2.33	1.94
Elongation, Percent	21.0	22.2	25.5	30.1

The yarn treated with beta-naphthol shrunk more than the 120° C. water treated yarn and, even at conditions that shrunk the yarn 48%, a fair degree of yarn tenacity remained.

EXAMPLE V

A number of yarn samples were prepared by dry spinning N,N-dimethylformamide solutions of the following copolymers:

(*a*) Acrylonitrile/methyl vinyl ketone (92/8)
(*b*) Acrylonitrile/acrylamide (93/7)
(*c*) Acrylonitrile/methyl acrylate/potassium styrene sulfonate (94/5/1)
(*d*) Acrylonitrile/vinyl acetate (90/10)
(*e*) Acrylonitrile/styrene (90/10)
(*f*) Acrylonitrile/vinylidene chloride (96/4)

These samples were drawn 4× and knitted into the tubing and subjected to treatment with 2% phenol at 98° C. as described in Example I. In every case, "retained crimp" was equal to or greater than that obtained by subjecting the control samples to the 120° C. water treatment.

EXAMPLE VI

A batt was made from 2-denier, 3-inch acrylonitrile/methyl acrylate (94/6) copolymer fiber by carding the fibers on to a crosser-lapper. The batt was needle-punched 25 times on a standard Hunter Machine Company plate-type needle loom at a rotational speed of 250 R. P. M. and a linear speed of 120 yards per hour, using number 15 x 18 x 25 x 3½ regular barb felting needles which had been etched in 37% hydrochloric acid for seven hours. After needle-punching, the batt weighed 2.7 ounces per square yard. The batt was immersed in a boiling solution of 1% beta-naphthol in water. Instantaneous shrinkage of the batt took place to the extent of 66% in area. The shrunken batt was boiled off in water for fifteen minutes to remove the excess beta-naphthol, after which it was dried and pressed. The finished felt had a weight of 8.0 ounces per square yard and would be useful as a filtration fabric.

Although the invention has been largely described by reference to crimp setting yarn in the form of knitted structures, it should be understood that these illustra-

tions are in the nature of reproducible tests to assess quantitatively the efficacy of the treatment. Fibers, filaments, yarns and tows may be crimped and crimp set in much the same stage of manufacture. In some cases, a tow of filaments may be crimped and the crimp setting may not take place until the crimped filaments have been converted into staple. So, too, excessive shrinkage may be effected at any time and at the stage of manufacture where it is needed. Applications of the shrinking agents may be made early in the manufacturing process prior to winding and/or fabricating, or they may be delayed and used in the course of converting fibers, filaments, yarns or the like into fabric structures. For example, the shrinking agents may be applied during a felting process to bring about better felting properties, or they may be applied to felts or formed fabrics, woven or non-woven, to prevent laddering or to stiffen or to full them.

As is apparent from the data given above, the concentration of adjuvant in the aqueous treating solution may vary widely, depending on the form of or specific use intended for the treated fibers, filaments or yarns; i. e. whether crimp setting or excessive shrinkage is primarily desired. Also, acrylonitrile homopolymer structures require more drastic treatment than do copolymer structures containing 85% to 99% acrylonitrile. The concentration will, of course, be governed by the temperature of the treating bath, the method of its application, the relative efficacy of the specific agent and the length of time the treating solution is in contact with the polymer structure. In some cases, concentrations as high as 30% to 40% or even more may be used. Yet, as little as 0.5% or slightly less may prove entirely satisfactory, as, for example, in the case of beta-naphthol. Generally, temperatures, near the atmospheric boiling point of the solution are preferred, for instance 98° to 100° C. or higher, but frequently with the better agents, acceptable results can be secured at temperatures as low as about 95° C. Instead of placing the fibers to be treated in the liquid treating agents, a spray or vapor of the solutions at the said temperatures may be directed against the fibers. The simplest method is the immersion technique and this is preferred. The time involved may be from one second to about twenty minutes, the time being usually ten seconds or longer.

In the manufacture of felts from synthetic filaments and fibers, the key to success is a high order of retractability. The instant invention is eminently suited to the production of very high shrinking fibers and filaments. Accordingly, the invention is readily adaptable for use in the process of forming needled felt described in Lauterbach application Serial No. 312,067, filed September 29, 1952, as well as in other felting processes.

For best results, the treated material should be rinsed and preferably boiled in water to remove the adjuvant. Complete removal of the adjuvant from the fiber structure after it has effectively set the crimp or shrunk the fiber may not always be accomplished because of the selective absorption of some of these treating agents within the acrylonitrile polymer structure. Generally, very little or no adjuvant remains.

This invention enables the retention of crimp, imparted to fibers and filaments soon after drawing, through numerous processing steps, such as carding, combing, drafting, spinning, winding and various fabricating steps. Not only does the setting of the crimp greatly improve loft or bulk in the final structure, but it enhances processability, with the production of higher quality end products. Because the crimp can be set effectively at atmospheric pressure, the cost of processing is greatly reduced. Also, it is a simple matter to bring about excessive shrinkage whenever it is desired and without resorting to expensive pressure methods.

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

I claim:

1. The process of treating mechanically crimped fibrous material composed of acrylonitrile polymer of at least about 85% by weight of acrylonitrile and up to about 15% by weight of monoethylenically unsaturated monomer copolymerized with the said acrylonitrile, said fibrous material being capable of being shrunk and the crimp being set, which comprises impregnating the said crimped fibrous material with an aqueous solution heated to a temperature between about 95° C. and its boiling point under atmospheric pressure for a time up to about 20 minutes until the fibrous material is shrunk and the crimp set, said aqueous solution containing from about 0.5% to about 40% of an aromatic compound having the formula:

$$R(OH)_m(NH_2)_nA_p$$

in which R is selected from the group consisting of benzene and naphthalene nuclei, *m*, *n*, and *p*, are cardinal numbers not greater than 2, the sum of *m* and *n* being at least 1 and no more than 2, and A is selected from the group consisting of methyl and ethyl.

2. A process of claim 1 in which the said polymer is polyacrylonitrile homopolymer.

3. A process of claim 1 in which the said polymer is a copolymer.

4. A process of claim 1 in which the said polymer is a copolymer of acrylonitrile and methyl acrylate.

5. A process of claim 1 in which the said polymer is a copolymer containing styrene sulfonic acid polymerized in the polymer molecule.

6. A process of claim 1 in which the said aromatic compound is a phenol.

7. A process of claim 1 in which the said aromatic compound is an amine.

8. A process of claim 1 in which the said aromatic compound is beta-naphthol.

9. A process of claim 1 in which the said aromatic compound is phenol.

10. A process of claim 1 in which the said contacting endures from about one second to about twenty minutes.

11. A process of claim 1 in which the said aromatic compound is soluble to at least the extent of 1% in water at the boiling point.

12. A process of claim 1 in which the said contacting is done using an aqueous solution containing about 0.5% to about 20% of said aromatic compound for about ten seconds to about twenty minutes, to effect setting the crimp in said fibrous material.

13. A process of claim 1 in which the said contacting is done using an aqueous solution containing about 1% to about 40% of said aromatic compound for about one second to about twenty minutes, to effect shrinkage of said fibrous material.

14. A process of claim 12 in which the said aromatic compound is phenol.

15. A process of claim 13 in which the said aromatic compound is beta-naphthol.

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