

1

2,869,975

PROCESS FOR SHRINKING AND SETTING POLY-ACRYLONITRILE TEXTILE FILAMENTS WITH SPECIFIC CHEMICAL SHRINKING AGENTS

Weston Andrew Hare, Staunton, Va., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application March 28, 1955
Serial No. 497,439

10 Claims. (Cl. 8—130.1)

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

This is a continuation-in-part of my application Serial No. 462,630, filed October 15, 1954 now abandoned.

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 super-atmospheric pressures. Another object of this invention is to provide an improved process for shrinking yarns, filaments and fibers without resorting to super-atmospheric 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 75° C. and containing about 10% to about 40% of a compound selected from the group consisting of ethyl-

2

ene carbonate, propylene carbonate, trimethylene carbonate, nitromethane, delta-valerolactone and gamma-butyrolactone. 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 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

$$1.0 - \frac{C_i S_i}{C_t S_t}$$

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 are by weight unless otherwise indicated.

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 4X to produce a final yarn of about 85 denier and collected on suitable cores. The yarn was knitted from the wet packages to a loose structure 11 x 14 courses x stitches per 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

3

results obtained following the test practice previously described and using a large excess of bath to swatch are also set forth in Table A.

Table A

Adjuvant	Conc., Percent	Shrinkage Factor	Retained Crimp/cm.
Water		0.46	6.7
Water (at 120° C.)		0.49	7.0
Ethylene Carbonate	10	0.63	7.2
Nitromethane	10	0.58	8.0

Similarly, using the knit structures of Example I, i. e., a medium type structure having 16.5 x 14.5 courses x stitches per square centimeter but otherwise the same as in the first part of this example, the following results were obtained as set forth in Table B.

Table B

Adjuvant	Conc., Percent	Shrinkage Factor	Retained Crimp/cm.
Water (at 98° C.)		0.51	7.8
Water (at 120° C.)		0.57	10.5
Butyrolactone	10	0.53	9.5

Thus, it is seen that 10% ethylene carbonate or 10% nitromethane at 98° C. are as effective in setting the crimp as is water at 120° C. while butyrolactone at 10% concentration shows substantial improvement in crimp setting over water at the same temperature (98° C.). In subsequent tests, it was found that 15% concentration of butyrolactone in water was at least as effective as water at 120° C. Similarly, about 15% and 20% aqueous solutions of trimethylene cyclic carbonate and delta-valerolactone, respectively, are effective in setting the crimp in similar swatches of knit fabric. Other solvents and near solvents for acrylonitrile polymers were relatively ineffective even at much higher concentrations than shown above. For example, 10% solutions of sulfuric acid, calcium chloride, zinc chloride, N-acetylmorpholine, maleic anhydride, calcium thiocyanate, tetramethylene sulfone, acetonitrile and N,N-dimethyl formamide were ineffective. Even aqueous N, N-dimethylformamide in concentrations as high as 60% and at 100° C. failed to give as high a retained crimp as did water at 120° C. or as did the treating media of this invention.

EXAMPLE II

A knit fabric of 4x drawn yarn of acrylonitrile/methyl acrylate copolymer (94/6) was boiled off and cut into swatches which were subjected to tests as previously described with the results recorded below in Table C. In this case, the shrinkage factor recorded is the extra shrinkage above that obtained by boiling off the fabric. The first three samples in the table were treated by padding the solution on to the fabric samples and heating in atmospheric steam, while the other samples were treated by boiling in a large excess of solution.

Table C

Sample	Reagent	Sol. Conc., Percent	Percent On Fabric	Heat Time, Min.	Shrinkage Factor	Retained Crimp/cm.
1	Ethylene Carbonate	10	10	5	0.08	6.0
2	do.	15	10	5	0.15	7.8
3	do.	15	15	5	0.17	8.0
4	do.	10	Boiled in Sol.	10	0.22	8.0
5	Butyrolactone	15	do.	10	0.10	8.0
6	do.	20	do.	10	0.30	9.5
7	Water		Boiled at 15 p. s. i. g. (120° C.)	10	0.11	7.0

These data show that 10% ethylene carbonate on the fabric was more effective when padded on the fabric as a 15% solution than as a 10% solution. Neither was as

4

effective as boiling in an excess of 10% solution, showing that the fabric absorbs the adjuvant from the bath. Also, 15% ethylene carbonate padded on as a 15% aqueous solution was equivalent to boiling in an excess of a 10% solution. These data also indicate that 15% butyrolactone is about equivalent to 10% ethylene cyclic carbonate as an adjuvant while 20% butyrolactone solution was a much more effective bath for shrinking and crimp setting than was 10% ethylene carbonate solution.

EXAMPLE III

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 ethylene carbonate with the shrinkage results and physical properties of the shrunk yarn as set forth in Table D below.

Table D

Treating Solution	Water	Water	10% Ethylene Carbonate	20% Ethylene Carbonate
Temperature, °C.	99	120	99	101
Percent Shrinkage	24	30	30	48
Denier	115.5	119.6	128.1	161.5
Straight:				
Tenacity, g. p. d.	2.78	2.80	2.52	1.98
Elongation, Percent	21.6	24.3	25.3	28.2
Loop:				
Tenacity, g. p. d.	2.61	2.49	2.10	2.05
Elongation, Percent	21.0	22.2	22.2	28.5

20% ethylene carbonate shrunk the yarn much more than did 120° C. water and, even at the conditions that gave high shrinkage, a fair degree of yarn tenacity was retained.

EXAMPLE IV

To study the effectiveness of short times of treatment, samples of knit tubing prepared from 4x drawn yarn of acrylonitrile/methyl acrylate copolymer (94/6) were immersed in boiling solution for five to fifteen seconds, then rinsed in water and boiled ten minutes in water to remove the treating agent. The results in terms of retained crimp per centimeter are given below in Table E.

Table E

Reagent	Percent Conc.	Retained Crimp/cm., Time in Seconds		
		5	10	15
Water (98° C.—10 min.)		(7.8)		
Water (120° C.—10 min.)		(9.0)		
Ethylene carbonate	10	7.8	7.0	6.8
Do.	15	7.3	9.0	10.0
Nitromethane	10	6.4	7.5	6.8
Do.	15	8.0	6.7	9.0

10% solutions of ethylene carbonate or nitromethane were not effective up to fifteen seconds. Increasing the concentration to 15% gives sufficient crimp setting potential to obtain rapid setting so that ten and fifteen

seconds treatment with 15% ethylene carbonate and fifteen seconds treatment with the nitromethane were as effective as the ten minute-120° C. water treatment.

5

EXAMPLE V

A 4× drawn yarn prepared from acrylonitrile homopolymer knitted into tubing and swatches thereof subjected to ten minutes treatment in the solutions and at the temperatures indicated in Table F below yielded the shrinkage and crimp setting results recorded in this table.

Table F

Adjuvant	Conc., Percent	Temp., °C.	Shrinkage Factor	Retained Crimp/cm.
Water		98	0.05	5.2
Do.		120	0.05	6.5
Ethylene Carbonate	20	100	0.15	6.9
Nitromethane	20	98	0.15	5.4
Butyrolactone	20	100	0.05	5.7

In spite of the higher than normal concentrations of adjuvant in the treating solution, only the 20% solution of ethylene carbonate produced greater retained crimp per centimeter than did the water treatment at 120° C. Nevertheless, the 20% solutions of nitromethane and of butyrolactone were somewhat effective and at still higher concentrations, equivalent crimp setting results are obtainable.

EXAMPLE VI

Yarns of the following acrylonitrile (AN) copolymers were drawn 4×, knitted into tubing, and treated with 15% aqueous ethylene carbonate at 99° C. for 10 minutes: AN/methyl vinyl ketone (92/8), AN/acrylamide (93/7), AN/methyl acrylate potassium styrenesulfonate (94/5/1), AN/vinyl acetate (90/10), AN/styrene (90/10) and AN/vinylidene chloride (96/4). After rinsing and testing as above, the retained crimp was equal to or greater than obtained in the 120° C. water controls.

EXAMPLE VII

A batt was made from 3-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 Co. plate-type

6

from a polymer mixture containing about 92% acrylonitrile, 4% vinyl acetate and 4% methyl vinylpyridine by carding the fibers on to a crosser-lapper. The batt was needle-punched 30 times on a standard Hunter Machine Co. 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 9.1 ounces per square yard. The batt was immersed in a boiling solution of 25% ethylene carbonate in water. Instantaneous shrinkage took place to the extent of 32% in area. The shrunken batt was boiled off in water for fifteen minutes to remove the excess ethylene carbonate, after which it was dried and pressed. The finished felt had a weight of 13.4 ounces per square yard and is useful as a wicking material.

EXAMPLE IX

A batt of 3-denier, 2-inch fiber made from acrylonitrile/methyl acrylate (94/6) copolymer was needle-punched 25 times with 7-hour etched 15 x 18 x 25 x 3½ needles. Samples were then immersed in 20% by volume mixtures of propylene carbonate and water under the following conditions with the listed resultant shrinkages.

Table G

Temp.	Percent Area Shrinkage	Remarks
Boil.	71	Shrinkage instantaneous.
82° C	67	Shrinkage requires 15-30 seconds.
64° C	10	Shrinkage requires several minutes.

EXAMPLE X

As shown in Example IX, effective shrinkage can be attained at 82° C., 67% area shrinkage resulting in that experiment. The influence of temperature on the efficiency of ethylene carbonate and propylene carbonate may be seen in the following table:

Table H

Ethylene Carbonate Solution				Propylene Carbonate Solution			
26% Conc. (by weight)		28% Conc. (by weight)		22% Conc. (by weight)		24% Conc. (by weight)	
° C.	Area Shrinkage, percent	° C.	Area Shrinkage, percent	° C.	Area Shrinkage, percent	° C.	Area Shrinkage, percent
60	0	60	0	70	0	75	50
70	8	70	0	77	40.5	80	60.6
75	30	75	44	80	50	85	64
80	42	80	52.6	85	53	90	68.4
85	52.5	85	60.8	90	62	95	70
90	64	90	70.5	95	63.6	100	72.6
95	68	95	75.0	100	68		
98	73	100	79				
100	74.8						

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 4.0 ounces per square yard. The batt was immersed in a boiling solution of 25.9% ethylene cyclic carbonate in water. Instantaneous shrinkage of the batt took place to the extent of 74% in area. The shrunken batt was then boiled off in water for fifteen minutes to remove the excess ethylene carbonate, after which it was dried and pressed. The finished felt had a weight of 15.4 ounces per square yard and would be useful as a filtration fabric.

EXAMPLE VIII

A batt was made from 3-denier, 2-inch fiber prepared

The effect of concentration is noted in Table I below:

Table I

EFFICACY OF SOLUTION VS. CONCENTRATION AT 100° C.

Ethylene Carbonate		Propylene Carbonate	
Concentration (by weight) Percent	Percent Area Shrinkage	Concentration (by weight) Percent	Percent Area Shrinkage
20	50	18	58.5
24	63.5	20	62
26	68	22	67.5
28	73	24	71.5
30	74	26	77.5

As can be seen from Tables J and K relating to propylene carbonate and ethylene carbonate, respectively, the efficacy of the shrinking agent drops off with increasing length of time the solution is held at this elevated temperature. In all cases, the shrinkage indicated occurred within a few seconds.

Table J

EFFICACY OF PROPYLENE CARBONATE SOLUTION VS. TIME

22% at 100° C.		22.4% at 90° C.	
Time, Minutes	Percent Area Shrinkage	Time, Minutes	Percent Area Shrinkage
0	67.8	0	63.5
30	66	30	61
60	62	60	61
90	61	90	61
130	55.5	150	60
		195	55.5
		260	53
		315	50
		370	49.7

Table K

EFFICACY OF ETHYLENE CARBONATE SOLUTION VS. TIME

26% at 100° C.		28% at 90° C.	
Time, Minutes	Percent Area Shrinkage	Time, Minutes	Percent Area Shrinkage
0	68	0	64
20	66	15	64
40	63.5	90	64
60	61	185	63.5
90	55.5	240	62
		365	56
		420	55

From the result shown above, it is noted that by increasing the temperature or the concentration an increase in shrinkage is attained. However, lengthening the time over which the hot solution is maintained leads to a loss in effectiveness. This is attributed to loss of shrinking agent through degradation and the effect is much more pronounced at 100° C. than at 90° C. In practice, it may well be desirable to operate at lower solution temperatures, such as 80°-90° C., to attain a more uniform shrinking effect in batt to batt over a period of time.

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 illustrations 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. The process may be used with blends such as acrylonitrile polymers or copolymers with wool, cotton, rayon, etc.

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 maintained at the elevated temperature. In some cases, concentrations as high as 30% to 40% or even more may be used. Let, as little as 10% or slightly less may prove entirely satisfactory, as for example in the case of ethylene carbonate. Generally, temperatures near the atmospheric boiling point of the solution are preferred, for instance 90° to 100° C. or higher, but frequently with the better agents, acceptable results can be secured at temperatures as low as about 75° 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. Generally there is no need to carry out the treatment for more than twenty minutes and long treatments especially at the higher temperatures are to be avoided, unless some other treatment is being simultaneously effected and the lower shrinkage is satisfactory.

In the manufacture of felts from synthetic filaments and fibers, the key to success is a higher 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, now abandoned, 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 structures, 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. It is possible to obtain good shrinkage using nitric or formic acid. For example, the use of a 31% by weight aqueous solution of nitric acid and 60% by weight aqueous solution of formic acid led to area shrinkages on felt of 7.3× and 7.6×, respectively. However, such materials are corrosive and difficult to handle and must be completely removed from the treated fibrous material. The agents of this invention are non-corrosive and are handled with ease in conventional apparatus and small residues of the agent in the finished articles can be tolerated.

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

I claim:

1. A process for shrinking and setting filamentary textile material inherently capable thereof made from a polymer obtained by polymerizing at least 85% acrylonitrile and up to 15% of ethylenically unsaturated monomer

copolymerizable with the acrylonitrile, which comprises contacting the said textile material without dissolving it with an aqueous solution at a temperature of from about 75° C. to its boiling point at atmospheric pressure for at least one second until shrinkage takes place, said aqueous solution containing from about 10% to about 40% of a compound selected from the group consisting of ethylene carbonate, propylene carbonate, tri-methylene carbonate, nitromethane, delta-valerolactone and gamma-butyrolactone.

2. The process of claim 1 in which the said polymer is a homopolymer of acrylonitrile.

3. The process of claim 1 in which the said compound in solution is ethylene carbonate.

4. The process of claim 1 in which the said compound in solution is propylene carbonate.

5. The process of claim 1 in which the said compound in solution is nitromethane.

6. The process of claim 1 in which the said contacting is from five seconds to twenty minutes.

7. The process of claim 1 in which the said filamentary textile material is mechanically precrimped.

8. The process of claim 1 in which the said polymer is a copolymer.

9. The process of claim 8 in which the copolymer is one of acrylonitrile and up to 15% of an ethylenically unsaturated monomer.

10. The process of claim 9 in which the copolymer is one of acrylonitrile and methyl acrylate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,217,113	Hardy	Oct. 8, 1940
2,249,756	Finzel	July 22, 1941
2,716,586	Terpay	Aug. 30, 1955
2,730,479	Gibson	Jan. 10, 1956

FOREIGN PATENTS

544,821	Great Britain	Apr. 29, 1942
883,764	France	Mar. 29, 1943
896,083	France	Apr. 17, 1944

OTHER REFERENCES

Textile Research Journal, July 1954, pp. 597 and 603.