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MONO-COMPONENT SELF-CRIMPING ACRYLIC FIBERS
AND PROCESS FOR MAKING THE SAME
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FIG. 1.

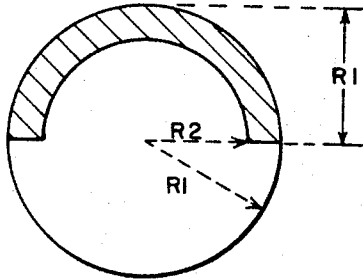


FIG. 2.

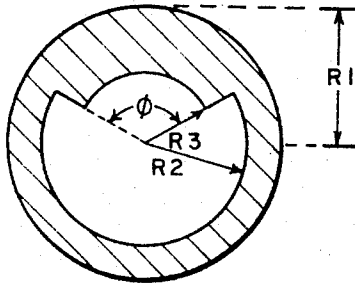
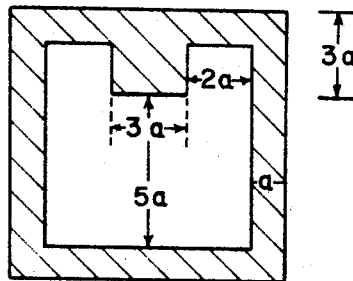


FIG. 3.



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MONO-COMPONENT SELF-CRIMPING ACRYLIC FIBERS AND PROCESS FOR MAKING THE SAME

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ABSTRACT OF THE DISCLOSURE

Mono-component, self-crimping acrylic fibers are prepared by spinning acrylonitrile polymers into a non-diffusion coagulating bath to form fibers having skin properties sufficiently different from core properties to create the eccentric distribution of skin and core necessary for permanent crimp development.

This invention relates to self-crimping, monocomponent, acrylic fibers. More particularly, the invention relates to the provision of monocomponent, acrylic fibers with a permanent self-crimp and to a process for their preparation involving extrusion of an acrylonitrile polymer spinning solution into a special coagulation medium which causes a sufficient contrast between the skin and core of the fiber to result in a permanent crimp.

It is well known in the art that acrylic fibers with a permanent self-crimp have many distinct advantages over those which must have crimp imparted by other means and normally show a lesser degree of permanence of crimp. Fibers with permanent self-crimp are normally prepared by bicomponent spinning.

Bicomponent fibers with a bilateral or asymmetric skin-core relation of two or more different components can develop self-crimp. The differential properties of the two components such as shrinkage or swelling are utilized to develop self-crimp; however, the co-spinning of two different components doubles the amount of equipment required for polymerization and dope preparation and also causes rather elaborate blending devices of conjugate jets to be used.

Crimp can also be imparted by thermo-mechanical means. A mechanical deformation is applied to the fiber and then it is heat set. This deformation may be applied by scraping the fiber over a hot acute knife-edge, or by the use of stuffing box crimpers or gear crimpers or similar devices. Various false-twist methods may also be used. The deformation may also be applied to the fiber in a gelled or swollen state. In all these methods the deformation must be set into the fiber which is normally accomplished by heat setting. Acrylic fibers respond only poorly to heat setting techniques, the heat set deformation in acrylic fibers achieves only a limited permanence by comparison to fibers of more thermoplastic polymers, such as polyamides and polyesters.

Self-crimping skin-core fibers with non-uniform skins can be prepared. However, these are mostly confined at present to rayon fibers. The non-uniform skin is produced by adjusting the acid concentration of the coagulant and the flow pattern of coagulant around the filaments so that the skin is thicker on one side of the fiber than on the other. The different shrinkage properties of the skin and core give rise to the self-crimp. Polyvinyl alcohol

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fibers with a non-uniform skin have been produced by incomplete coagulation. At present incomplete coagulation of acrylic fibers is not easily achieved; the coagulation of acrylonitrile polymer spinning solutions in conventional coagulants, whether skin forming or penetrating, is much too fast to allow for incomplete coagulation.

Coagulation of acrylic fibers in coagulants reported as being skin forming followed by a stretch and relaxed drying can produce a self-crimp fiber. The fiber produced by this technique has a low bulk density and is relatively uncollapsed. The uncollapsed character of the fiber creates instability problems in textile processing and end use applications in addition to causing poor hand and luster.

The process of this invention produces self-crimping acrylic fibers from single component fibers as opposed to the conjugate fiber systems. The crimp has a permanence lacking in fibers crimped by thermo-mechanical means. No loss of physical properties is involved in achieving the crimped fibers of the invention.

An object of the present invention is the provision of monocomponent acrylic fibers with a permanent self-crimp.

Another object of the invention is to provide acrylic fibers which have a skin differing in properties from the core which on collapsing will create the eccentric distribution of skin and core necessary for permanent crimp development.

A further object of the invention is the provision of a process for the preparation of permanent self-crimping mono-component acrylic fibers.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description.

In general these and other objects of the invention may be accomplished by the provision of a standard acrylonitrile polymer spin dope solution which is extruded through any suitable spinneret or other extrusion orifice. The extrudant enters a coagulating medium which is so constituted as to not appreciably penetrate the newly extruded fiber cut creates a relatively non-porous fiber skin. This is in contrast to the porous structure of fibers formed by coagulation with a coagulant that diffuses into the fiber such as is the usual result in the prior art spinning of acrylic fibers. The freshly formed fiber is then washed to remove coagulant and any remaining solvent. The washing may be preceded or followed by a hot or a hot-wet stretching operation. The fiber is then dried at a temperature greater than 100° C. and collapsed under tension, and a second stretch applied. After drying, the fiber is relaxed in a hot or a hot-wet environment substantially free of tension, which causes the fiber to develop its inherent, permanent self-crimp. The relaxation may utilize high pressure steam, hot air, boiling water or any suitable relaxing environment. Although some crimp is achieved by relaxation without hot stretching after drying and collapsing, the crimp level is enhanced substantially by the additional hot or hot-wet stretch employed on the collapsed fiber prior to relaxation. This stretch may augment, partially replace or completely replace the hot stretch applied prior to collapsing the fiber. Table I, lists examples of this invention where relaxation was accomplished in 35 p.s.i.g. steam.

The fiber produced by this process has a skin differing in properties from the core. As such, the fiber is similar

in character to a sheath-core bicomponent fiber produced by conjugate spinning techniques. However, round cross section fibers seldom have sufficient asymmetry to develop satisfactory crimp.

The present invention produces a fiber which by virtue of the collapsing step has a higher eccentricity of cross section and consequently a higher crimp potential than fibers prepared by conventional methods. In effect, the collapsing creates and/or enhances the eccentric distribution of two or more distant phases or components, a skin and a core, having different properties by virtue of the coagulation condition within the monocomponent fiber.

The eccentricity, ϵ , of a given arrangement of components in the cross section of such a filament can be calculated from the following approach.

(1) The cross section of the self-crimping monocomponent fiber can be considered as made up of k small units of area, A_k . Of these k units, there are i units made up of component 1 and j units of component 2.

(2) The contribution of any segment of area to the eccentricity is a vector which is the product of the vector

R_k connecting the centroid of area of the cross section to the area times the area, A_k , of the segment.

(3) The contribution to eccentricity for the components is opposite in sign. The contribution of component one is arbitrarily taken as positive and the contribution of component two is taken as negative. This is denoted by a scalar quantity n which is taken as +1 for component 1 and -1 for component 2.

(4) The total contribution to eccentricity, ϵ , is the vector sum of the contribution of all units of area

$$\epsilon = \sum_k n A_k \vec{R}_k$$

which may be normalized and separated into contribution of the components:

$$\epsilon = (\sum_i A_i R_i - \sum_j A_j R_j) / \sum_k |A_k R_k|$$

R_k is further separated into axial components $R_k \sin \theta_k$ and $R_k \cos \theta_k$ where θ_k is the angle that R_k makes with an arbitrary axis in the plane of the cross section and passing through the centroid of area.

The magnitude of the normalized eccentricity is given by

$$\epsilon = [\{ (\sum_i A_i R_i \sin \theta_i - \sum_j A_j R_j \sin \theta_j) / \sum_k |A_k R_k \sin \theta_k| \}^2 + \{ (\sum_i A_i R_i \cos \theta_i - \sum_j A_j R_j \cos \theta_j) / \sum_k |A_k R_k \cos \theta_k| \}^2]^{1/2}$$

where the absolute value sums are the means of normalizing the function ϵ will have value between zero and one. The larger the value of ϵ , the more eccentric the arrangement. The fibers of this invention have an eccentricity of at least 0.01.

For example, FIGURES 1, 2 and 3 illustrate three possible variations of cross sections and the calculated values of eccentricity which can be made.

In FIGURE 1, the calculated values for eccentricity are as follows.

R_2/R_1 :	ϵ
1.0	0
.8	.355
.6	.625
.4	.833
.2	.958
0	1.00

In FIGURE 2, the calculated values, where $R_2/R_1=0.8$ and $R_3/R_1=0.6$, are:

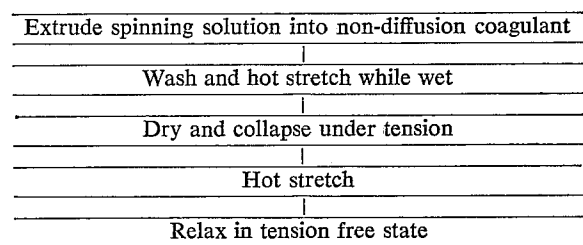
ϕ , degrees:	ϵ
180	0.2500
135	0.1875
90	0.1250
45	0.0625
0	0

And in FIGURE 3, for the relative dimensions shown the eccentricity would be 0.167.

Coagulants which produce a non-symmetric cross section increase the asymmetry and the crimp potential. In cases where the cross section of the freshly coagulated fiber is round, asymmetry can be developed during the collapsing steps if the fiber has a good skin, since collapsing distorts the shape to create the eccentric distribution of skin and core necessary for crimp development. However, in fibers with an already eccentric distribution, the eccentricity will usually be increased by collapsing. Collapsing the fiber is therefore necessary to get maximum eccentricity and consequent crimp potential. Since collapsing is commonly accompanied by a measure of stress relaxation it usually reduces the differential shrinkage between the skin and core. The hot stretch after collapsing is therefore useful to restore the desired level of differential shrinkage necessary for good crimp development.

The following flow diagram presents the process of the invention in one preferred embodiment.

FLOW DIAGRAM



The invention is applicable not only to polyacrylonitrile but also to copolymers, interpolymers and blends thereof with other suitable copolymerizable mono-olefinic monomers well known in the prior art, particularly those polymeric materials containing at least 80 percent by weight of acrylonitrile.

For example, the polymer may be a copolymer of from about 80 to 98 percent of acrylonitrile and from about 2 to 20 percent of another copolymerizable mono-olefinic monomer.

The polymer can be a ternary interpolymer, for example, products obtained by the interpolymerization of acrylonitrile and two or more of any monomers, other than acrylonitrile, copolymerizable therewith.

The polymer can also be a blend of from about 98 to 100 percent of (A) polyacrylonitrile or a copolymer of from 80 to 99 percent acrylonitrile and from 1 to 20 percent of at least one other mono-olefinic copolymerizable monomeric substance with from 2 to 50 percent of the weight of the blend of (B) a copolymer of from 10 to 70 percent of acrylonitrile and from 30 to 90 percent of at least one other mono-olefinic copolymerizable monomer.

While the preferred polymers employed in the instant invention are those containing at least 80 percent acrylonitrile, generally recognized as the fiber-forming acrylonitrile polymer, it will be understood that the invention is likewise applicable to polymers containing less than 80 percent of acrylonitrile when such polymers are useful in forming fibers.

The polymers useful in the practice of the present invention may be prepared by any conventional polymerization procedures, such as mass polymerization methods, solution polymerization methods or aqueous emulsion procedures. If it is desired to produce shaped articles from the acrylonitrile polymer solutions of the present invention which have a modified appearance, enhanced dye receptivity or other modified properties, various agents may be added to the spinning solution or to the fiber to accomplish these effects. Such added agents might be pigments, dyes, anti-static agents, flame-retarding agents, and the like. Solutions containing from 8 to 30 percent by weight of acrylonitrile polymers may be employed, with the preferred concentration range being from 15 to 25

percent. Dye receptive agents such as sodium vinylbenzene sulfonate and sodium methallyloxybenzenesulfonate may be copolymerized with the polymers of the invention.

Any of the suitable and well-known acrylonitrile polymer solvents may be used in the preparation of the spinning solutions used in practicing the invention. Among the solvents preferably, suitable are dimethylformamide, dimethylacetamide and other N,N-dialkylamides, dimethylsulfoxide, nitromethane, gamma-butyro lactone, aqueous zinc chloride, aqueous solutions of sodium thiocyanates and the like.

The spinning solution may be prepared according to any of the well-known prior art methods.

The composition of the coagulation bath is an important feature of the invention since the spinning solution must be extruded into a coagulant which does not appreciably penetrate the extruded solution of fiber but creates a relatively non-porous fiber skin. Most of the commonly used coagulation systems produce an opposite effect, that is, they result in a porous structure formed by precipitation under conditions which permit diffusion of coagulant into the fiber. It will be recognized that subtle interrelationships between solvent and coagulant exist such that the same coagulant cannot be indiscriminately used with all the suitable solvents mentioned. For a given solvent, selection of suitable coagulants for the practice of this invention can be made by reference to the following general rules.

(1) The coagulant must produce a well defined skin/core structure with skin thickness sufficient to prevent random crenulation, but not so thick as to resist buckling during drying.

(2) The density of the uncollapsed fiber when washed free of solvent and freeze-dried to prevent distorting in drying must be at least $\frac{1}{2}$ the density of a disc of compressed polymer of the same composition as the fiber ($\rho_f \geq \frac{1}{2} \rho_p$).

(3) Penetration of the coagulant into the fiber must be minimized (low penetration of coagulant is usually indicated by a non-round cross section at the coagulation bath exit).

Coagulants which meet these requirements and which may be used with dimethylformamide and dimethylacetamide include polyethylene glycols, particularly polyethylene glycol of 1000 molecular weight, the preferred coagulant. Other suitable coagulants can be determined using the above rules by one skilled in the art.

After coagulation of the fiber it is washed to remove the residual coagulant and solvent. This washing step may be preceded or followed by a hot or hot-wet stretching step to orient the polymer molecules in a manner well known in the art. This orientation stretch generally involves stretching the fiber from about 1.0 to 6.0 times its length.

After washing and stretching, the fiber is dried and collapsed under sufficient tension to prevent shrinkage. The drying is conducted by maintaining the fiber in contact with one or more heated surfaces at a temperature of 100 to 300° C. or by other suitable means such as hot air drying on perforated belts or rolls. During drying and collapsing the fiber is maintained at constant length.

The fiber is then relaxed to permit development of its inherent crimped configuration in a hot or hot-wet environment substantially while free of tension. Such an environment includes temperature of from 100 to 300° C. and may include the application of moisture in the form of steam or water sprayed on the fiber while relaxing. The fiber develops its crimp at this time and the relaxation may utilize high pressure steam, hot air, boiling water or any suitable relaxing environment.

The crimp level is markedly enhanced by the additional hot or hot-wet stretch employed on the collapsed fiber prior to relaxation. The use of the hot stretch at this point may supplement, partly replace, or completely replace the orientation stretch applied prior to collapsing the fiber. This stretching normally results in a lengthening of the fiber of from about 1.25 to 10.0 times its length.

The total stretch employed in all stretching operations need not exceed about 12X.

Example 1

A terpolymer containing 89 wt. percent acrylonitrile, 4 wt. percent styrene, and 7 wt. percent vinylacetate with a η_{sp} of 0.15 (wt. percent in dimethylformamide at 25° C.) was dissolved with heating and stirring into dimethylformamide to make a 25 wt. percent solution. This solution was extruded at a rate of 11 ml./min. from a spinnerette containing 100 holes of .003" diameter into a polyethylene glycol (molecular weight 1000) bath at 95° C. The immersion length was 12 inches. The fiber was removed from the bath at the rate of 33 ft./min. then continuously washed, and stretched 2X in boiling water. The stretched fiber was collapsed and dried without relaxation on hot (135° C.) rolls moving at the rate of 66 ft./min. and then drawn an additional 2X through a hot (175° C.) tube. The fiber was quenched on cold rolls and wound onto a package (132 ft./min.). A portion of the fiber was placed unrestrained in boiling water and developed about 5 crimps per inch. The crimp was developed in the first minute of exposure, prolonged exposure (2 hours) did not alter the crimp frequency or character. The fiber had the same crimp frequency when either wet or dry.

Microscopic observation of the fiber cross section revealed a skin around the filaments. From the shape of the filament cross section and a measurement of the relative thickness of the skin, the eccentricity was calculated to be 0.09.

Example 2

Another portion of the fiber prepared in Example 1 was relaxed free of tension in 30 p.s.i.g. saturated steam. The fiber developed 32 crimps per inch in this environment. The crimp of this fiber was staple to prolonged exposure to boiling water.

Example 3

Example 1 was repeated except that the polyethylene glycol coagulant was replaced with water, a penetrating coagulant, at 55° C. The resultant fiber when boiled, or exposed to high pressure steam did not crimp. A portion of the fiber which had been previously mechanically crimped (15 c.p.i.) lost its crimp slowly on exposure to boiling water. After a two hour exposure, no trace of crimp remained.

Example 4

The process of Example 1 was repeated except that the 2X boiling water stretch was replaced by a 4X boiling water stretch and the subsequent hot air stretch eliminated. About 2 crimps per inch were observed in a portion of the fiber placed in boiling water. Another portion of the fiber exposed to saturated steam at 30 p.s.i.g. did not show any crimp.

Example 5

The table below lists the crimp frequency in crimps per inch of several other self-crimping fibers. The polymers with the composition given in weight percent were made into 25 wt. percent solutions in dimethylacetamide (with the exceptions of the systems labeled Blend I and II) extruded through 3.5 mil. holes (100 holes per sample) at the rate of .11 m./min./hole. Blend I was a solution in dimethylacetamide of 2.3% by weight of a copolymer containing 50% acrylonitrile and 50% methylvinylpyridine and 16.7 by weight of a copolymer containing 94% acrylonitrile and 6% vinylacetate. Blend II was a solution in dimethylacetamide containing 2.02% by weight of a copolymer containing 50% acrylonitrile and 50% methylvinylpyridine, 14.7% by weight of a copolymer containing 94% acrylonitrile and 6% vinylacetate, and 2.3% by weight of polyvinylacetate.

In the following table examples of the invention are

presented where relaxation was accomplished in 35 p.s.i.g. steam and a spin bath temperature of 50° C. unless otherwise indicated.

3. The process of claim 1 wherein the acrylonitrile polymer comprises polyacrylonitrile.
4. The process of claim 1 wherein the acrylonitrile

TABLE

Polymer composition	Spin bath	Orientation stretch	Post-collapse stretch	Denier/filament	Crimp frequency, c.p.i.	Spinning speed (approx.), ft./min.
AN-VA (95-5)	PEG (95° C.)	1.0	2.0	5.90	12	132
AN-VA (95-5)	PEG (95° C.)	1.0	1.0	5.44	None	120
AN-VA (95-5)	TBA (55° C.)	1.30	2.0	6.7	7	100
AN-VA (95-5)	Xylene (55° C.)	1.3	3.0	5.29	8	125
AN-VA (95-5)	Xylene (55° C.)	1.0	2.0	10.92	7	51
Blend II	PEG (95° C.)	3.0	1.5	4.28	11	150
AN-VA-S (91-7-2)	PEG (95° C.)	4.0	1.5	4.30	18	150
AN-VA-S (91-7-2)	PEG (95° C.)	2.0	2.5	2.66	11	250
AN-VA-S (91-7-2)	PEG (95° C.)	3.0	2.0	3.28	10	200
AN-VA-S (91-7-2)	PEG (95° C.)	4.0	1.3	5.31	11	132
AN-VA-S (91-7-2)	PEG (95° C.)	1.0	3.0	4.06	10	198
AN-VA (95-5)	CaCl ₂ (40/60) 90° C.	1.0	1.5	8.09	10	99
AN-VA (95-5)	CaCl ₂ (40/60) 75° C.	4.0	2.0	4.22	7	132
Blend I	CaCl ₂ (40/60) 75° C.	2.0	2.0	4.22	7	132

This invention produces self-crimping acrylic fiber from a single component fiber as opposed to conjugate bi- or multi-component fiber systems. The crimp has a permanence lacking in fibers crimped by thermo-mechanical means and the crimp is not achieved at a loss in physical properties as is the case when crimp is imparted mechanically. Uniform dyeing and optimum crimp levels for textile processing are obtained in the process of the invention.

We claim:

1. A process for the preparation of self-crimping, mono-component acrylonitrile polymer fibers comprising the steps of:

- (1) dissolving an acrylonitrile polymer comprising at least 80 percent acrylonitrile in a solvent to form a solution;
- (2) extruding the solution through an extrusion orifice into a coagulating medium containing a skin-forming, low-penetrating coagulant to form a fiber;
- (3) washing the fiber;
- (4) stretching the fiber from about 1.0 to 6.0 times its length;
- (5) drying the fiber at a temperature of from 100° C. to 300° C.;
- (6) stretching the fiber from about 1.0 to 10.0 times its length; and
- (7) relaxing the fiber substantially free of tension in the presence of steam to permit shrinkage and crimp development.

2. The process of claim 1 wherein the acrylonitrile polymer comprises a copolymer of from about 80 to 98 percent acrylonitrile and from about 2 to 20 percent of another copolymerizable mono-olefinic monomer.

polymer comprises a blend of from about 50 to 98 percent of (A) a copolymer of from 80 to 99 percent acrylonitrile and from 1 to 20 percent of at least one other mono-olefinic monomer with from 2 to 50 percent of (B) a copolymer of from 10 to 70 percent of acrylonitrile and from 30 to 90 percent of at least one other mono-olefinic monomer.

5. The process of claim 1 wherein the solvent is dimethylacetamide.

6. The process of claim 1 wherein the solvent is dimethylformamide.

7. The process of claim 1 wherein the solvent is dimethylsulfoxide.

8. The self-crimping monocomponent acrylonitrile polymer fiber produced by the process of claim 1.

9. The self-crimping monocomponent acrylonitrile polymer fiber containing at least 80 percent acrylonitrile produced by the process of claim 1.

10. The self-crimping monocomponent acrylonitrile polymer fiber containing at least 80 percent acrylonitrile and up to 20 percent vinyl acetate produced by the process of claim 1.

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