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[54] METHOD OF MANUFACTURING FIBERS AND FILMS FROM AN ACRYLONITRILE COPOLYMER

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[51] **Int. Cl.** **D01f 7/00**
[58] **Field of Search** .... 264/182, 210 F; 260/85.5 A

[56] **References Cited**

UNITED STATES PATENTS

3,089,748	5/1963	Mogensen et al.	8/130.1
3,402,234	9/1968	Borie et al.	264/182
3,499,024	3/1970	Morita et al.	260/85.5 A
3,551,547	12/1970	Knudsen	264/182
3,632,798	1/1972	Morita et al.	260/88.7 A

FOREIGN PATENTS OR APPLICATIONS

45/30346	10/1970	Japan	260/85.5 A

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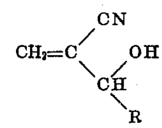
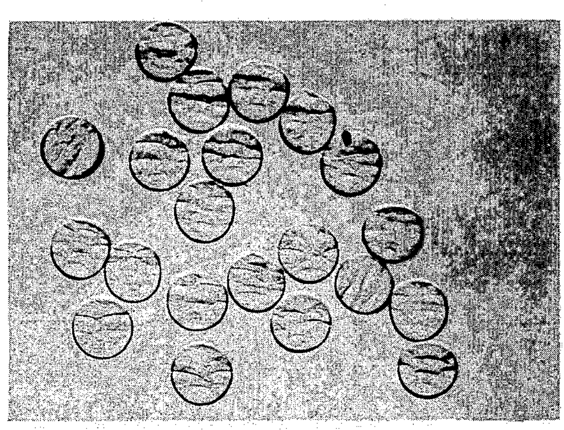
[57] **ABSTRACT**

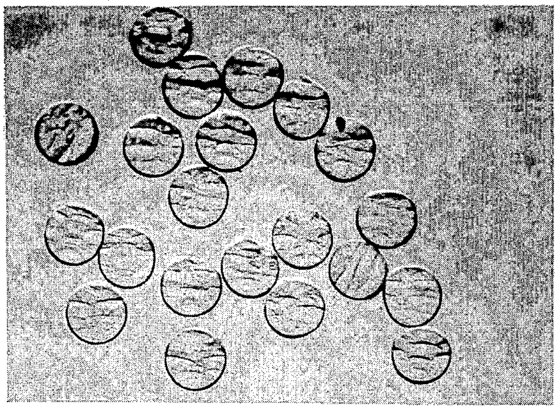
A method is provided for manufacturing shaped articles especially fibers and films from a solvent solution of copolymer comprised of at least 85 mol % of acrylonitrile and at least one other compound of the formula



wherein R is hydrogen, an alkyl group, an aryl group or alkylaryl group. In the method of this invention the solvent solution is shaped and thereafter coagulated in a bath comprised of at least 60 percent by weight of methanol. The shaped articles, for example, filaments, because of their superior properties, are especially useful as textile fibers.

7 Claims, 1 Drawing Figure





METHOD OF MANUFACTURING FIBERS AND FILMS FROM AN ACRYLONITRILE COPOLYMER

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a novel method for producing acrylonitrile copolymer shaped articles.

2. Description of the Prior Art

Heretofore, acrylic fibers from a polyacrylonitrile or an acrylonitrile copolymer have been produced commercially in substantial amounts by wet spinning processes and dry spinning processes. However, in prior art wet spinning processes coagulation is ordinarly accomplished by extruding the polymer solution into an aqueous bath which can contain solvents or dissolved salt. As used herein, an aqueous or water bath refers to a composition having water as one of its main components. When the solvent is extracted from the extruded stream of spinning solution in a coagulating bath during wet spinning, solidification of the polymer in filamentary form occurs. Noramlly, during coagulation there is an inward diffusion of the coagulating bath into the filaments undergoing coagulation, as well as a corresponding outward movement of solvent into the coagulating bath. As is well known, the solvent and bath liquid may interchange in such a manner that the resulting filaments contain microvoids or cavities (see British Patent No. 917,290 and British Patent No. 950,661 and British Patent 977,943). The filaments containing these microvoids are opaque or dull (hereinafter referred to as devitrificated), and exhibit a delustered appearance, lower tenacity, and lower abrasion resistance as compared with filaments which do not contain microvoids.

Therefore, to overcome the inherent physical weakness of these coagulated filaments, certain aftertreatment steps have heretofore been conducted during the processing of the filaments to fully collapse the microvoids. The filaments, for example, were dried at high temperatures. In the wet spinning acrylic filaments, the degree of collapsing of the filaments differs depending upon the copolymer composition of the acrylonitrile copolymers, the kind of the solvents, the composition of the coagulation bath and the coagulating conditions. However, unless the coagulated filaments or films are collapsed by drying or homogenization steps, the resulting fibers or films have unsatisfactory properties. In addition, in methods of producing acrylic fibers or films by such conventional wet spinning processes the drawability differed according to the collapsing conditions (drying conditions, etc.) of the coagulated filaments or films. Moreover, by secondary processing, for example, dyeing and washing of products, devitrification (the loss of the transparency) is brought about again and the dimensional stability as well as the physical properties change.

Further, when producing acrylic fibers by the conventional wet spinning process, because the fiber-forming method is different from that of melt spinning, it has been found difficult to produce filaments having a cross sectional configuration corresponding to the shape of holes of the spinneret. Because of this, it has been difficult to control the production process and commerically produce such fibers, (for example, see British Patent No. 1,191,538).

It is accordingly an object of this invention to overcome the aforementioned problems and difficulties of the prior art.

Another object of the present invention is to provide a method for a wet system for spinning fibers or forming fibers of acrylonitrile copolymers without requiring a dry collapsing step.

Another object of the present invention is to provide acrylic fibers and films which are substantially void free and transparent, having stabilized physical properties and a very high tenacity and modulus.

A further object of the present invention is to provide a method of producing acrylic fibers or film of acrylonitrile copolymers which can be made with a predetermined cross sectional configuration corresponding to the shape of holes of the spinneret or the extrusion slit.

Other objects and advantages of the present invention will become further apparent hereinafter from a further reading of the specification and subjoined claims.

SUMMARY OF THE INVENTION

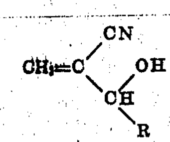
The objects of this invention have been achieved by spinning or forming an organic solvent solution of an acrylonitrile copolymer obtained by copolymerizing at least 85 mol % of acrylonitrile with at least one other compound having an alcoholic hydroxyl group, into a coagulation bath containing about 60 percent by weight of methanol.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a photomicrograph of an acrylonitrile copolymer fiber produced in accordance with the process of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the process of the present invention a method is provided for producing shaped articles such as acrylonitrile copolymers which are compact and excellent in crystallinity, tenacity and modulus. In this method of producing fibers and films of an acrylonitrile (hereinafter referred to an AN) copolymer an organic solvent solution of AN copolymer consisting of at least 85 mol % of AN and at least one compound represented of the general formula



Formula I

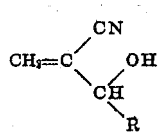
wherein R is a radical selected from the group consisting of hydrogen, alkyl, monocyclic aryl, and alkylaryl, wherein the alkyl group has up to 5 carbon atoms, is shaped and then coagulated in a coagulating bath containing not less than about 60 percent by weight of methanol.

The AN copolymers suitable for use in the present invention are known and are disclosed, for example, in U.S. Pat. No. 3,499,024. However, U.S. Pat. No. 3,499,024 only relates to the AN copolymers of the present invention, and at best, discloses that such AN copolymers show improved dyeability and absorption property. The prior art does not, however, suggest a method of producing the acrylic fibers or films of the present invention which have improved physical properties.

The use of methanol in a coagulation bath in wet spinning of acrylic fibers is known, and is shown, for example, in Japanese Patent Application Publication No. 511/1956. However, when methanol is normally used as a coagulating agent devitrification of the acrylonitrile filaments is remarkable, spinning of filament is difficult and the physical properties of the filaments obtained are quite poor. Accordingly, methanol coagulation baths have not been used commercially.

In wet spinning, the action of a coagulating agent on the spinning solution varies depending upon spinning conditions, such as the kind of the polymer and kind of solvent used in the spinning solution. Accordingly, the yarn quality of the filaments obtained varies and satisfactory filaments are not necessarily obtained. It has also been found that when wet spinning methods, previously suggested, have been employed that it was impossible to obtain transparent filaments having a cross sectional configuration corresponding to the shape of the spinneret holes.

The compound or mixture of compounds which are copolymerized with the acrylonitrile to produce the acrylonitrile copolymer used in the present invention, is represented by the formula



wherein R is a radical selected from the group consisting of hydrogen, an alkyl group having up to five carbon atoms, an aryl group such as phenyl group or an alkylaryl group. Typical compounds which may be used in the present invention are, for example, 2-hydroxymethyl acrylonitrile, 2-hydroxyethyl acrylonitrile, 2-(1-hydroxypropyl) acrylonitrile, 2-(1-hydroxyethyl) acrylonitrile, 2-(1-hydroxybutyl) acrylonitrile, 2-(1-hydroxy-2-methylpropyl) acrylonitrile and 2-(1-hydrohexyl) acrylonitrile.

In addition, the AN copolymer can contain as a third component a compound which copolymerizes with AN, such as, for example, acrylic acid, methacrylic acid, and esters thereof, styrene, an α halogenated vinyl compound such as vinyl chloride, vinylidene chloride, vinyl bromide, vinylidene bromide, acrylamide, methacrylamide, an arylsulfonic acid, styrene sulfonic acid and salts thereof.

The ratio of the compound represented by Formula I in the AN copolymer must be at least about 0.01 mol %, preferably at least about 0.1 mol %, with the content of the acrylonitrile being at least 85 mol %. When the amount of the compound shown by the Formula I is less than 0.01 mol % the compact filaments of the present invention are not obtained and the ability to spin into a coagulating bath is not sufficiently developed. On the other hand, when the AN content is less than 85 mol %, the desired properties of an acrylic fiber are not obtained.

It is, of course, possible to use mixtures of different types of AN copolymers and vinyl polymers within the above noted range, and still achieve the objects of the present invention.

As a solvent for the copolymer of the AN series, it is preferable to use an organic solvent such as dimethyl sulfoxide, dimethylacetamide, dimethyl formamide or a mixed solvent consisting mainly of these organic solvents. The concentration of the AN copolymer in the solvent should be within the range normally used with, for example, 10–35 percent by weight being preferable.

The solution of AN copolymer is spun from a spinneret into a coagulating bath containing mainly methanol. The composition of the coagulating bath is not particularly critical, provided it contains at least about 60 percent by weight and preferably at least about 65 percent by weight of methanol. When the content of methanol is less than 60 percent by weight, transparent and compact filaments are not obtained unless collapsing or homogenization aftertreatments are employed. If the coagulating bath contains at least 60 percent by weight of methanol, even if said bath contains solvent extracted from the spinning solution or water produced by absorption of moisture, the objects of the present invention can be still achieved.

The temperature and other conditions of the coagulating bath are not particularly critical. However, normally a temperature within the range of 0°–35°C is commercially advantageous because the evaporation rate of methanol is low in this temperature range.

The spinning conditions which are employed, such as, for example, the discharge rate, spinning speed and other conditions, are those conventionally employed in order to obtain filaments.

When the organic solvent solution of the AN copolymer of the present invention, namely, an AN copolymer containing a compound having an alcoholic hydroxyl group is spun into a coagulating bath containing mainly methanol, a very compact coagulated filament is produced without having to be subjected to a dry collapsing or homogenization treatment. This is surprising when it is taken into account, that heretofore when methanol was used as a coagulating bath, for 100 percent acrylonitrile filament, the amount of devitrification was quite substantial. Even if the filaments were subjected to dry collapsing, filaments having satisfactory properties were not obtained. In addition, in accordance with the present invention, because dry collapsing is not required, this step can be omitted, which makes the process commercially feasible and the coagulated filaments can be directly subjected to drawing and heat treatments.

By the conventional wet spinning of acrylic fibers, unless the filaments are collapsed during the yarn making process, especially if the filaments are spun until they are dry, the filaments are devitrified and it is not possible to obtain good drawn yarn. Moreover, depending upon the coagulation and collapsing conditions, the drawing has to be conducted under specified limited conditions. However, in accordance with the present invention, because the coagulated filaments are substantially voidless, the filaments may be drawn at once. Various drawing means, which employed hot water, hot air, a hot plate, a hot pin, steam or combination thereof can be advantageously employed. Preferably, the filaments are initially drawn in hot water or steam and thereafter drawn by a hot plate. Drawing to a high magnification is possible. An additional advantage is that the methanol in the coagulating bath is removed by the hot water or steam before the filaments are drawn by the hot plate, which is commercially advantageous. When the first stage drawing is in hot water or steam, it is advisable to use a low magnification of drawing of an extent such that the methanol in the filaments is removed, namely, to draw the filaments at least about 1.5 times at a temperature of at least 10°C and preferably at least about 50°C. As conditions for second stage drawing by a hot plate, it is advisable to draw the filaments at least 5 times their length at a temperature of at least about 0°C and preferably 100°–200°C.

As mentioned above, in accordance with the present invention, because compact and transparent acrylic copolymer fibers or films are obtained without dry collapsing or homogenization, not only are the process steps simplified as compared with the conventional wet system, but also many of the problems in quality of the fibers or films produced by the normal collapsing step such as discoloration and deterioration are avoided. It goes without saying that in the present invention fibers or films obtained by a wet process after coagulation may also be subjected to dry collapsing or homogenization treatments. However, in this case extreme dry collapsing conditions are not required as in the case of conventional wet spinning system and it is accordingly commercially feasible.

Further, in accordance with the present invention, because collapsing of filaments or films in the coagulation bath is excellent, it is possible to obtain filaments or film having a cross sectional configuration substantially the same as the shape of holes in the spinneret or the slit. It now is possible to readily obtain filaments having any shape including a truly circular cross sectional configuration which has heretofore been technically difficult to obtain by the conventional wet system or a non-circular cross sectional configuration and also films having excellent surface smoothness and transparency. For example in accordance with the present invention, when spinning is carried out using a spinneret in which the shape of the holes is circular, it is possible to obtain filaments having a substantially circular cross sectional configuration.

The FIGURE is a photomicrograph (200 times) showing the cross sectional area of coagulated filaments obtained by one example of the present invention. As can be seen from the drawing, the cross sectional configuration of the filaments of the present invention are substantially truly circular and said filaments are very compact and void free.

With reference to compactness, when the X-ray small angle scattering intensity is measured, in case of the coagulated filaments of the present invention, it is less than 40 counts per second (C/S), which is surprising when it is taken into account that the intensity of the conventional filaments, for example, commercially available filaments of the acrylic series, such as the commercial acrylic fiber Toraylon which is produced in an organic solvent - water bath is at least 150 C/S.

The filaments obtained by the present invention may be used for clothings and because of the flexibility in the amount of drawing which can be applied, are also useful in various industrial application and other applications, as will be obvious to those skilled in the art, such as for making carbon fiber.

EXAMPLE 1

Using N, N′-azobisisobutylonitrile (hereinafter referred to as AIBN) as a catalyst and dimethyl sulfoxide (hereinafter referred to as DMSO) as a solvent, the following polymers were obtained by solution polymerization:

1. Polyacrylonitrile (hereinafter referred to as PAN).
2. An acrylonitrile (95.6 mol %) — methyl acrylate (4.0 mol %) — sodium arylsulfonate (0.4 mol %) — copolymer (hereinafter referred to as P(AN-MEA-SAS).
3. An acrylonitrile (99.6 mol %) — sodium arylsulfonate (0.4 mol %) copolymer (hereinafter referred to as P(AN-SAS).
4. An acrylonitrile (99.4 mol %) — 2-hydroxyethly acrylonitrile (0.6 mol %) copolymer (hereinafter referred to as P(AN-HEN).
5. An acrylonitrile (99.0 mol %) — 2-hydroxyethyl acrylonitrile (0.6 mol %) — sodium arylsulfonate (0.4 mol %) copolymer (hereinafter referred to as P(AN-HEN-SAS).

The values of the intrinsic viscosity[N] of these copolymers using dimethylformamide (DMF) as the solvent are shown in Table 2. In each case, the solution concentration was 20 percent by weight.

These copolymers were coagulated from a spinneret having 200 circular holes each having a diamter of 0.08 mm and spun into a methanol bath at a spinning speed of 2 m/min. The spun undrawn filaments were thereafter subjected to the four treatments listed in Table 1.

The following examples are given by way of further illustration of the present invention and are not intended to limit the scope of the invention beyond that of the subjoined claims. All parts and percentages are parts and percentages by weight, not volume, unless otherwise noted.

The degree of circular cross section and the X-ray small angle scattering intensity (abbreviated as SASI) appearing in the following examples were obtained as follows.

Degree of Circular Cross Section

A photograph of the cross section area of the filaments was prepared, from which the axial ratio of the cross section of the longer axis, a, of the cross section area and the shorter axis, b, of the cross section area was of the filaments obtained. The closer a/b is to 1, the closer is the cross section to circular.

Sasi

Using an X-ray small angle scattering device (40KV — 40 mA) manufactured by Rigaku Denki Co. Ltd., a 10 mg/10 mm sample was prepared from the filaments and set in the device. Under conditions of a sample distance of 26.5 cm and a scattering angle of 50′, the small angle scattering intensity (SASI) was obtained.

TABLE 1

No.	Treating conditions
1	Dried in air at 20°C (room temperature).
2	Immediately after coagulation, washed with water at 25°C and dried in air.
3	Immediately after coagulation, washed with boiling water and dried in air.
4	After washing with boiling water, dried in air at 130°C.

After these copolymers were treated under the conditions shown in Table 1, the X-ray small angle scattering intensity (hereinafter referred to as SASI) and degree of circular cross section of each undrawn filaments was measured. The results are shown in Table 2.

TABLE 2

Number	Kind of polymer	Concentration of dope percent	[η]	SASI Treatment 1	SASI Treatment 2	SASI Treatment 3	SASI Treatment 4	Ratio of circular cross section
1	PAN	20	1.43	250	290	300	350	0.3
2	P(AN-MEA-SAS)	20	1.42	180	160	210	200	0.5
3	P(AN-SAS)	19.5	1.49	190	190	200	190	0.4
4	P(AN-HEN)	20	1.42	40	20	50	30	0.9
5	P(AN-HEN-SAS)	19.5	1.43	35	20	50	30	0.95

It can be seen from the Table 2 that filaments obtained by coagulating an AN copolymer containing a compound having an alcoholic hydroxyl group such as 2-hydroxyethyl acrylonitrile in a bath of the methanol series had no microvoid having compact and homogeneous yarn quality. In addition, it can be seen that the filaments obtained in accordance with the present invention have a remarkably large ratio of circular cross section, being substantially circular.

In Table 3, the measured results of values of the tenacity and elongation of the undrawn filaments are shown. The number of the sample in Table 3 corresponds to that in Table 2.

TABLE 3

No.	Treatment 1 Tenacity (g/d)	Treatment 1 Elongation (%)	Treatment 2 Tenacity (g/d)	Treatment 2 Elongation (%)
1	0.2	31.0	0.1	11.3
2	0.3	13.1	0.3	13.8
3	0.4	12.3	0.5	14.5
4	1.4	50.0	1.5	51.3
5	1.2	51.0	1.5	52.6

From the above Table 3, it can be seen that the filaments of the present invention are definitely superior in tenacity and elongation to the prior art material.

The five copolymer solutions described above were then coagulated in a methanol bath to prepare films having a thickness of 0.08 mm. The obtained films were subjected to the same treatments shown in Table 1 and values of the X-ray small angle scattering intensity were measured. The results are shown in Table 4. It can be seen that the films of the present invention are superior in compactness and homogeneity and excellent in transparency.

TABLE 4

No.	Treatment 1	Treatment 2	Treatment 3	Treatment 4
1	300	350	300	350
2	180	190	230	215
3	180	190	250	210
4	30	40	40	30
5	30	20	30	30

EXAMPLE 2

Into 4,045 g of DMSO were charged 4,48 g of N,N'-azobisvaleronitrile (ADVN), 1,051 g of AN, 11,5 g of SAS, 11,7 g of HEN and 1,07 g of dodecyl mercaptan. The mixture was polymerized at 50°C for 20 hours to obtain a polymer solution of P(AN-HEN-SAS) whose [N] measured at a concentration of 19 percent by weight at 25°C in DMF (dimethyl formamide) was 1,52. This solution was spun from a spinneret having 100 circular holes each having a diameter of 0.08 mm into coagulating baths of the various compositions shown in Table 5. The spinning was carried out at a take-up speed of 2.5 m/min to obtain 12 denier undrawn filaments.

TABLE 5

No.	Methanol	DMSO	Butanol	Water
	Composition of the coagulating bath			
1	95–100	0–5	0	0
2	65	35	0	0
3	55	45	0	0
4	95	0	0	5
5	0	0–5	95–100	0
6	0	55	0	45

The obtained undrawn filaments were washed with water (25°C) and dried in relaxed states at room temperature. The measured results of values of the SASI and degree of circular cross section of the undrawn filaments after being dried at room temperature are shown in Table 6. The numbers in Table 6 correspond to those in Table 5.

TABLE 6

No.	SASI (C/S)	Degree of circular cross section
1	20	0.95
2	30	0.91
3	180	0.95
4	40	0.95
5	30	0.40
6	175	0.40

From Table 6 it can be seen that the filaments obtained by using coagulating baths consisting mainly of methanol were compact and had a very good degree of circular cross section.

The undrawn filaments were drawn 2 times first in hot water (98°C) and then in steam at 110°C immediately after the filaments coagulated. The resulting drawn filaments were dried in air in a relaxed state and values of the SASI and degree of circular cross section of these filaments were measured. The results are shown in Table 7.

From Table 7, it can be seen that filaments other than the filaments obtained from the coagulating baths consisting mainly of methanol were devitrified by the drawing heat media.

TABLE 7

No.	Hot water SASI (C/S)	Hot water Degree of circular cross section	Steam SASI (C/S)	Steam Degree of circular cross section
1	40	0.95	40	0.95
2	40	0.91	35	0.91
3	200	0.95	210	0.95
4	40	0.95	35	0.95
5	150	0.41	200	0.41
6	200	0.38	180	0.38

EXAMPLE 3

As spinning solutions, No. 1 of Table 2 (PAN) and No. 5 of Table 2 (P(AN-HEN-SAS)) were used. As coagulating baths, No. 1 and No. 6 of Table 5 were used. To draw the filaments a two-stage drawing was adopted. In the first stage, drawing was carried out in hot water (98°C). In the second stage, drawing was carried out on a hot plate (165°C).

When hot water was used for first stage drawing, it was especially effective for removing methanol and the solvent retained in the filaments from the coagulation. In the first stage drawing the filaments were drawn 2 times their original length and thereafter the second stage drawing was carried out.

The properties of the obtained drawn filaments are shown in Table 8. It is apparent that by the method of the present invention, the maximum draw ratio became remarkably high and the obtained filaments had excellent compactness and homogeneity despite the fact that the prior art collapsing treatment was not carried out. Further, it should be noted, that the drawn filaments produced according to the present invention exhibited excellent yarn characteristics including a tenacity of more than 7 g/d and a Young's modulus of more than 190 g/d. These are considered to be due to the fact that a compact and homogeneous coagulated filament is obtained.

such as 2-hydroxyethyl acrylonitrile had no microvoids and had compact and homogeneous yarn qualities. Also, the degrees of circular cross section of the filaments were remarkably high and the cross sectional configurations were substantially circular.

When the copolymerization ratio of 2-hydroxyethyl acrylonitrile (HEN) exceeded 20 mol %, the stability of the filaments toward hot water tended to lower suddenly so that it is preferable to make about 20 mol % the upper limit of the copolymerization amount.

TABLE 9

No.	Treating conditions
1	Dried at 20°C (room temperature) in air.
2	Washed with water at 25°C immediately after coagulation and dried in air.
3	Washed with boiling water immediately after coagulation and dried in air.
4	Washed with boiling water immediately after coagulation and dried in air at 130°C.

TABLE 8

	No. of the coagulating bath	Maximum draw ratio, times	Drawing ratio, times	Yanr characteristics: Tenacity, g./d.	Elongation, percent	Young's modulus	SASI, C/S	Degree of circular cross section
Polymer:								
No. 1	1	6.3	5.1	3.4	15.3	52	190	0.45
No. 1	6	5.1	4.5	3.0	7.5	49	213	0.43
No. 5	1	12.5	9.3	7.3	8.9	193	41	0.98
No. 5	6	7.1	4.0	3.1	9.8	53	210	0.45

TABLE 10

	Kind of polymer	[η]	Copolymerized amount of HEN mol percent	SASI C/S: Treatment 1	Treatment 2	Treatment 3	Treatment 4	Degree of circular cross section	Boiling water shrinkage
Number:									
1	PAN	1.43	0	450	430	460	470	0.32	1.0
2	P(AN-HEN)[1]	1.42	0.00	180	140	210	250	0.53	1.3
3	P(AN-HEN)[1]	1.43	0.01	40	20	45	31	0.90	1.2
4	P(AN-HEN)[1]	1.42	0.1	38	30	38	37	0.93	1.3
5	P(AN-HEN)[1]	1.43	0.6	35	20	40	40	0.96	1.3
6	P(AN-HEN)[1]	1.21	5	35	31	40	37	0.96	1.6
7	P(AN-HEN)[1]	1.20	20	37	34	40	38	0.96	2.3
8	P(AN-HEN)[1]	1.20	25	35	36	38	38	0.96	8.0

[1] 2-hydroxyethyl acrylonitrile.

EXAMPLE 4

Using N,N'-azobisisobutylonitrile (AIBN) as the catalyst and dimethyl sulfoxide (DMSO) as a solvent, polymers shown in Table 10 were prepared by solution polymerization. The concentration of each of the spinning solutions was made 20 percent by weight and the spinning solutions were spun from a platinum — gold spinneret having 200 circular holes each having a diameter of 0.08 mm into a methanol bath to obtain 15 d undrawn filaments. The spinning speed was 3 m/min.

The resulting undrawn filaments were subjected to the treatments shown in Table 9. The X-ray small angle scattering intensity (SASI) of each of the samples subjected to these four treatments was measured as well as the degree of circular cross section and boiling water shrinkage of each of the samples subjected to treatment No. 1 in Table 9. The measured results were shown in Table 10.

As can be seen from these results, the filaments obtained by coagulating in a methanol bath an AN copolymer containg at least 0.01 mol % of a compound

EXAMPLE 5

Spinning solutions were prepared using AN copolymer having an inherent viscosity of 1.58 copolymerizing 0.6 mol % of 2-hydroxyethyl acrylonitrile (HEN) and using as a solvent DMSO, dimethyl formamide (DMF), dimethyl acetamide (DMAC), ethylene carbonate (EC), propylene carbonate (PC) and nitromethane (NM). These solutions were stable and each had a concentration of 17 percent by weight.

The solutions were spun from a spinneret having 100 circular holes each having a diameter of 0.06 mm into a methanol bath to obtain 20 d. undrawn filaments. The spinning was carried out at a take-up speed of 4 m/min. The obtained undrawn filaments were treated same as in Example 4.

As shown in the results in Table 11, it can be seen that DMSO and DMF have especially excellent properties as organic solvents.

TABLE 11

Solvent	Characteristics of undrawn filaments					
	Measured results of SASI C/S				Degree of circular cross section	Boiling water shrinkage
	Treatment 1	Treatment 2	Treatment 3	Treatment 4		
DMSO	35	20	40	40	0.96	1.3
DMF	34	25	40	38	0.96	1.2
DMAc	40	30	52	50	0.87	1.2
EC	70	93	98	98	0.78	5.6
PC	80	91	95	102	0.75	5.9
NM	83	93	93	108	0.75	8.6

These undrawn filaments were drawn 2 times in hot water, thereafter values of the maximum draw ratio was measured using a hot pin and a hot plate. At the same time, filaments drawn 12 times were obtained and their yarn quality values were measured. The results were shown in Table 13. When the concentration of the spinning solution was less than 10 percent by weight, it was found that the yarn quality values were lowered.

TABLE 13

Number	Concentration of the spinning solution, percent by weight	Maximum draw ratio, times	Draw ratio of sample, times	Characteristics of drawn filaments			
				Tenacity, g./d.	Elongation, percent	Young's modulus, g./d.	SASI C/S
1	40						
2	35	19	10	7.5	9.8	181	39
3	30	22	13	9.3	9.1	193	39
4	20	20	13	8.4	9.1	195	39
5	15	21	13	8.3	9.0	190	39
6	10	19	10	7.4	9.6	175	38
7	5	7	5	3.0	14.1	43	62

EXAMPLE 6

Using N,N'-azobisvaleronitrile (ADVN) as a catalyst, dodecyl mercaptan (DM) as a molecular weight control agent and DMSO as a solvent, a copolymer consisting of 99.0 mol % of AN, 0.6 mol % of HEN and 0.4 mol % of sodium arylsulfonate (SAS) was prepared by solution polymerization. The polymer concentration in the solution was 20 percent by weight. By adding DMSO to the solution, polymer solutions having a polymer concentration of 15,10 and 5 percent by weight were prepared, and by concentration of said solution, polymer solutions having polymer concentrations of 30, 35 and 40 percent by weight were prepared. The inherent viscosity of said copolymer was 1.52.

Using these 7 kinds of copolymer solutions as spinning solutions, filaments were spun from a spinneret having 100 circular holes each having a diameter of 0.06 mm into a methanol bath as a coagulating bath at a take-up speed of 3.5 m/min. The denier of the resulting undrawn filaments was 10 d.

When the spinning solution had a polymer concentration which exceeded 35 percent by weight, spinning was impossible due to gelation of the solution. The resulting undrawn filaments were treated as in Example 4 and values of the X-ray small angle scattering intensity, degree of circular cross section and boiling water shrinkage of these filaments were measured. The results are shown in Table 12.

TABLE 12

Number	Concentration of the spinning solution percent by weight	Characteristics of undrawn filaments					
		Measured SASI values C/S				Degree of circular cross section	Boiling water shrinkage
		Treatment 1	Treatment 2	Treatment 3	Treatment 4		
1	40	Could not be spun due to gelation					
2	35	28	20	35	35	0.98	1.2
3	30	28	25	30	35	0.97	1.2
4	20	36	21	40	40	0.98	1.3
5	15	36	21	39	40	0.96	1.2
6	10	38	30	39	39	0.96	1.2
7	5	38	38	42	42	0.95	2.3

EXAMPLE 7

Using ADVN as the catalyst, DM as a molecular weight control agent and DMSO as a solvent, solution polymerization was carried out. The composition of the obtained copolymer contained AN 99.0 mol %, HEN 0.6 mol %, and SAS 0.4 mol % and the inherent viscosity of the obtained polymer was 1.57. The polymer concentration in the polymer solution was 21.3 percent by weight.

The polymer solution used as a spinning solution was spun from a spinneret having 200 circular holes each having a diameter of 0.06 mm into a methanol bath maintained at various temperatures. The denier of the obtained undrawn filaments was 15 d.

The spinning states in the coagulating bath at various temperatures and values of the X-ray small angle scattering intensity as scales of compactness of undrawn filaments were observed and measured. It was found that when the temperature of the coagulating bath was less than 0°C, the coagulating speed was slow and fusion of the molofilaments occured. At the same time, the yarn peeling property lowered. However, the temperature of the coagulating bath exceeded 30°C, it was found that the compactness of the undrawn filaments rapidly decreased. The results are shown in Table 14.

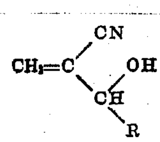
TABLE 14

Temp. of the coagulating bath °C	Maximum take-up speed m/min	SASI C/S	Spinning states
50	15	180	The monofilaments tended to be devitrified
40	15	180	Do.
35	13	120	Do.
30	13	40	
20	12	39	
10	10	40	
5	8	40	
0	2	35	
−5	0.5	35	Fusion of the monofilaments took place at the time of spinning

I claim:

1. The method for manufacturing shaped articles comprising (a) extruding an organic solvent solution of an acrylonitrile copolymer obtained by the copolymerization of a monomer mixture comprised of

1. at least about 85 mol % of acrylonitrile and
2. at least about 0.01 mol % of a compound of the formula



wherein R is a radical selected from the group consisting of hydrogen, alkyl, and alkylaryl, said alkyl group having up to five carbon atoms, and (b) coagulating the extruded acrylonitrile solution in a coagulation bath comprised of at least about 60 percent by weight of methanol.

2. The method according to claim 1 wherein said organic solvent is comprised of at least one member selected from the group consisting of dimethyl formamide, dimethyl sulfoxide, dimethyl acetamide and mixture thereof with water.

3. The method according to claim 1 wherein the concentration of said copolymer of the acrylonitrile in said solvent solution is within the range of 10 – 35 percent by weight.

4. The method according to claim 1 wherein the temperature of said coagulating bath is within the range of 0°– 35°C.

5. The method according to claim 1 wherein the shaped article is a filament and after being coagulated is immediately subjected to drawing.

6. The method according to claim 5 wherein the resulting undrawn filaments after being coagulated are subjected to two-stage drawing, first in hot water, or steam, and then on a hot plate.

7. The method according to claim 6 wherein the resulting undrawn filaments are drawn at least about 1.5 times in hot water or steam at least at about 110°C, and then drawn at least 5 times on a hot plate at 100°–200°C.

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