

Aug. 17, 1971

KEITARO SHIMODA ET AL

3,600,491

PRODUCTION OF HOLLOW ACRYLIC FIBERS

Filed Jan. 28, 1969

2 Sheets-Sheet 1

FIG. 1

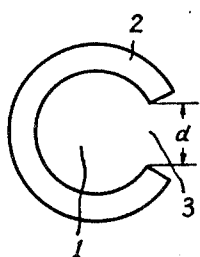


FIG. 2

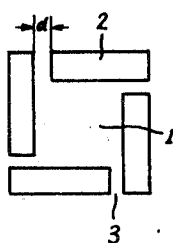


FIG. 3

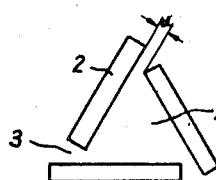


FIG. 4

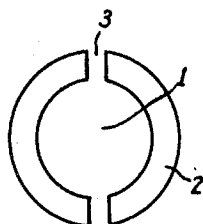


FIG. 5

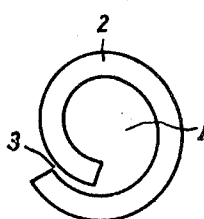


FIG. 6

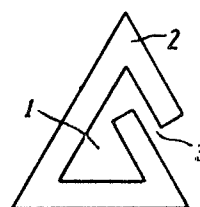
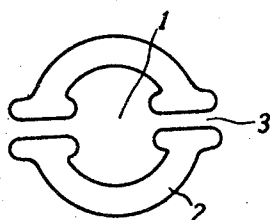


FIG. 7



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FIG. 8

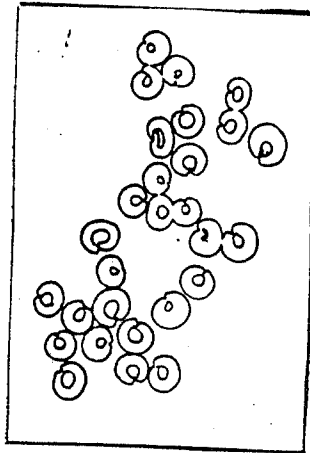


FIG. 9

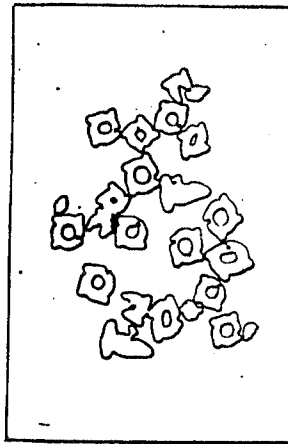
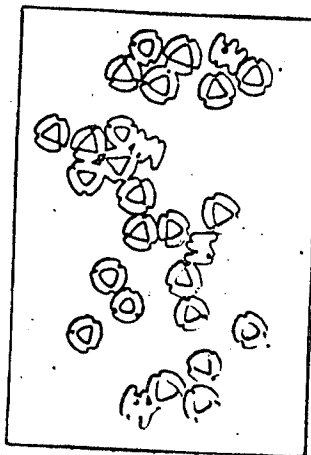


FIG. 10



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3,600,491

PRODUCTION OF HOLLOW ACRYLIC FIBERS
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43/9,527

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U.S. Cl. 264—177F

5 Claims

ABSTRACT OF THE DISCLOSURE

Process for producing hollow acrylic synthetic fibers by extruding a spinning solution of an acrylic polymer and a concentrated aqueous solution of an inorganic salt through spinning orifices into an inert gaseous medium which is incapable of coagulating the spinning solution, each spinning orifice having a continuous central portion substantially enclosed by a slit (see figures) and coagulating the thus-formed hollow current of the spinning solution within which is enclosed the inert gas.

This invention relates to a process for producing hollow acrylic fibers.

More particularly the present invention relates to a process for producing hollow acrylic synthetic fibers characterized by extruding a spinning solution prepared by dissolving an acrylic polymer in a concentrated aqueous solution of an inorganic salt into an inert gaseous medium which does not coagulate the spinning solution through spinning orifices each having a continuous central part substantially enclosed by slit having at least one narrow cut-out so that, during the passage through the inert gaseous medium, there is formed a hollow current of the spinning solution within which is enclosed the inert gas, and then leading the same into an aqueous coagulating bath so as to form coagulated hollow filaments.

There are already known many processes for producing hollow fibers. For example, according to Japanese patent publication No. 2,928/1967, there is mentioned a process for producing hollow fibers by inserting an extremely fine tube into an orifice so that the delivery orifice is of a concentric double tube type and feeding a gas through the said fine tube when a spinning solution is extruded through the annular orifice slit. However, the structure is very complicated and further, in the case of a wet spinning process, the diameter of the orifice is so small that it will be almost impossible to make such device as is mentioned above.

Further, according to U.S. Pat. No. 3,323,168, U.S. Pat. No. 3,340,571 or British Pat. No. 853,062, there is mentioned a process for producing hollow fibers by a melt-spinning process or dry spinning process by using a spinnerette having spinning orifices each consisting of an arcuate or spiral slit. However, this method is not applicable to conventional wet spinning process and hollow fibers are not obtainable thereby.

We have made extensive researches and experiments to effectively produce hollow acrylic fibers from a spinning solution prepared by dissolving an acrylic polymer in a solvent consisting of a concentrated aqueous solution of an inorganic salt, and have accomplished the present invention.

A principal object of the present invention is to easily and effectively obtain hollow acrylic fibers by wet spinning process.

Another object of the present invention is to obtain hollow acrylic synthetic fibers light in weight and having an excellent heat insulating property.

A further object of the present invention is to obtain hollow acrylic synthetic fibers having an excellent luster.

Other objects of the present invention will become clear from the following description of the present invention.

The objects of the present invention can be attained by extruding a spinning solution prepared by dissolving an acrylonitrile polymer in a concentrated aqueous solution of an inorganic salt into an inert gaseous medium through spinning orifices each having a continuous central part substantially enclosed by a slit having at least one cut-out so that, during the passage through the inert gaseous medium, there is formed a hollow current of the spinning solution within which is enclosed the inert gas, and then passing the same through an aqueous coagulating bath so as to form coagulated hollow filaments.

The invention will be explained in more detail by referring to the accompanying drawings wherein each of FIGS. 1-7 is an enlarged view of an example of a spinning orifice which may be used in this invention, and each of FIGS. 8-10 is an enlarged photograph of a cross-section of filaments obtained by the process of this invention.

In carrying out the process of this invention an acrylic polymer having an intrinsic viscosity (η) in dimethyl formamide at 30° C. of from 0.4 to 4.0 is used. In case the intrinsic viscosity (η) is higher than 4.0, the spinnability will be remarkably reduced and the obtained hollow acrylic synthetic fibers will be very brittle, while when the intrinsic viscosity (η) is lower than 0.4, hollow acrylic synthetic fibers having a desired strength required for clothes will not be obtained.

The viscosity of the spinning solution to be used in the process of the present invention is in the range of 4×10^4 to 10^7 centipoises, preferably 5×10^5 to 2×10^6 centipoises at 30° C. For example, in the case of using a concentrated aqueous solution of a thiocyanate as a solvent, such preferable viscosity can be attained by dissolving 17 to 35% by weight of an acrylic polymer in a concentrated aqueous solution of a thiocyanate having a concentration of 47 to 65% by weight. When the viscosity of the spinning solution at 30° C. is lower than 4×10^4 centipoises, it will be difficult to obtain hollow acrylic synthetic fibers. Further, in case the viscosity of the spinning solution at 30° C. is higher than 10^7 centipoises, the spinning solution current extruded through the spinning slit will be difficult to join longitudinally along the entire length to form a complete hollow shape before it reaches the surface of the coagulating bath and therefore no hollow acrylic synthetic fiber will be obtained.

Generally, when the viscosity of the spinning solution is low, a hollow fiber having a substantially circular cross-section will be obtained irrespective of the shape of the spinning orifice. As the viscosity of the spinning solution is increased, it will become possible to obtain a hollow fiber having a cross-section of a shape closer to that of the spinning orifice. Therefore, if the viscosity of the spinning solution is made high and if the shape of the slit forming the spinning orifice is properly selected, it will be possible to obtain a hollow fiber having a noncircular cross-section.

The distance between the surface of the spinnerette and the surface of the solution in the coagulating bath is generally 0.2 to 5.0 cm., preferably 0.2 to 2.0 cm. If the said distance is less than 0.2 cm., the slight rocking of the coagulating bath or the spinnerette will wet the surface of the spinnerette with the coagulating solution and will adversely affect the spinnability, while if the said distance between the surface of the spinnerette and the surface of the solution is made longer than 5 cm., it will be difficult to obtain hollow fibers.

The space between the spinnerette and coagulating bath should be filled with an inert gas which does not coagulate the spinning solution. Most typically and usually, air is used as the inert gaseous medium. However, if desired any other gas which does not coagulate the spinning solution may also be used.

The spinning solution is extruded through the spinning orifices into the inert gaseous medium and then introduced into the coagulating bath.

As explained before, each of the spinning orifice or hole has a central continuous portion surrounded by a slit having at least one narrow cut-out. Some examples of the spinning orifice which may be used in the invention are shown in FIGS. 1-7 wherein the central continuous portion 1 is surrounded by a slit 2 which has at least one narrow cut-out 3. The slit may be curved or straight as shown. Of course the shape of the spinning orifice is not limited to those shown and any other shape may be employed so far as it enables the formation of an inert gas-filled hollow current of the spinning solution during the passage through the space between the spinnerette and coagulating bath.

It is preferable that the area of the continuous portion 1 surrounded by the slit 2 is at least 0.04 mm.². If the area is smaller than 0.04 mm.² it will be difficult to form satisfactory hollow fibers. The width *d* of the cutout 3 may vary depending on the particular shape of the spinning slit and also on the viscosity of the spinning solution. It is preferable however that the width *d* is from 0.03 to 0.3 mm.

When the spinning solution is extruded through a spinning orifice as mentioned above there will be initially formed a hollow current of the spinning solution with a longitudinal side slit formed due to the cut-out 3. From this longitudinal side slit the ambient inert gas flows into the hollow space. During the further flow downward but prior to reaching the coagulating bath the said longitudinal side slit is self-closed to form an inert-gas filled hollow current of the spinning solution, which is then introduced into the coagulating bath.

In this invention the acrylic polymers to be used are not only polyacrylonitrile but also acrylonitrile copolymers which contain at least 70% by weight of acrylonitrile and also include a blend of two or more of these polymers. Comonomers to be copolymerized with acrylonitrile to form the copolymers include methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, methoxyethyl acrylate, phenyl acrylate, cyclohexyl acrylate, dimethyl-aminoethyl acrylate and corresponding methacrylates; alkyl substituted products and nitrogen substituted products of acrylamides and methacrylamides; unsaturated ketones such as methyl vinyl ketone, phenyl vinyl ketone, methyl isopropenyl ketone, etc.; vinyl carboxylates such as vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate, etc.; esters of ethylene alpha and beta carboxylic acids such as fumaric acid, citraconic acid, mesaconic acid, aconic acid, etc.; N-alkylmaleimide; N-vinyl carbazole; N-vinyl succinimide; N-vinyl phthalimide; vinyl ethers; N-methylolacrylamide; vinyl pyridines such as 2-vinyl pyridine, 4-vinyl pyridine and 2-methyl-5-vinyl pyridine; styrene and its alkyl substituted products; allyl alcohol; vinyl chloride; vinylidene chloride; vinylidene cyanides; unsaturated organic sulfonic acids such as allyl sulfonic acid, methallyl sulfonic acid, allyloxyethyl sulfonic acid, methallyloxyethyl sulfonic acid, allythioethyl sulfonic acid, allylthiopropyl sulfonic acid, isopropenylbenzene sulfonic acid, vinyl bromobenzene sulfonic acid, vinyl fluorobenzene sulfonic acid, styrene sulfonic acid, methyl styrene sulfonic acid, etc. and their water soluble salts.

As for the concentrated aqueous solution of an inorganic salt to be used as solvent for the polymers, there can be enumerated concentrated aqueous solutions of such thiocyanates as sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate and calcium thiocyanate,

such perchlorates as sodium perchlorate and calcium perchlorate and such inorganic salts as zinc chloride and lithium chloride.

For the coagulating bath may be used water or an aqueous solution of such inorganic salt as is mentioned above having a concentration of less than 20%. Since these polymer solvents and coagulants are well known in the art of wet spinning of acrylic polymers no further detailed explanation will be necessary.

The fibers spun by the process of the present invention may be washed with water, stretched, dried and heat-treated in the same usual manner as in the case of producing acrylic synthetic fibers by an ordinary and well known wet spinning process.

According to the process of the present invention, hollow acrylic synthetic fibers can be easily obtained. Further, different from an ordinary wet spinning process, the fiber is at once extruded into air or other inert gaseous medium and is then coagulated in an aqueous coagulating bath and the filament is drawn, and therefore the spinning velocity can be increased to be remarkably higher than in the case of producing synthetic fibers by a conventional wet spinning process and a more compact fiber structure can be obtained.

Examples for working the present invention are shown in the following. But the present invention is not limited to these particular examples. In the examples, the parts and percentages are all by weight.

EXAMPLE 1

A copolymer (η)=1.4 in dimethyl formamide at 30° C.) consisting of 91.4 parts of acrylonitrile, 8.6 parts of methyl acrylate and 0.4 part of sodium allylsulfonate was dissolved in an aqueous solution of 60% sodium thiocyanate to prepare spinning solutions having copolymer concentrations of 23.75 and 26.12% respectively. The viscosities at 30° C. of these spinning solutions were respectively 96×10^4 and 125×10^4 centipoises. Each spinning solution was heated to 70° C., was extruded into air through spinnerettes at a rate of 6.45 g./min. for the spinning solution having the copolymer concentration of 23.75% and at a rate of 5.86 g./min. for the spinning solution having the copolymer concentration of 26.12%. As for the spinnerettes there were used a spinnerette having 7 spinning orifices of such shape as is shown in FIG. 1 of an outside diameter of 0.605 mm., an inside diameter of 0.345 mm. and a distance *d* of 0.123 mm., a spinnerette having 7 spinning orifices of such shape as is shown in FIG. 2 of a short side of 0.094 mm., a long side of 0.754 mm. and a distance *d* of 0.230 mm. and a spinnerette having 7 spinning orifices of such shape as is shown in FIG. 3 of a short side of 0.091 mm., a long side of 0.649 mm. and a distance *d* of 0.200 mm. In each case the distance between the under surface of the spinnerette and the surface of the solution in the coagulating bath was 0.3 cm. The extruded spinning solution current was then passed through an aqueous solution of 12% sodium thiocyanate kept at -3° C. Then the coagulated filaments were drawn at a godet speed of 41.3 m./min., then washed with water, stretched 8 times the length in steam at 120° C., then dried for 1 minute on a roller heated to 115° C. and were heat-treated to be relaxed for 4 minutes in steam at 115° C. to obtain hollow acrylic synthetic fibers of a monofilament fineness of 7 deniers. For example, microscopic photographs of the cross-sections of hollow acrylic synthetic fibers obtained from the spinning solution of the acrylonitrile copolymer concentration of 26.12% by using spinnerettes of shapes shown in FIGS. 1 to 3 are respectively shown in FIGS. 8 to 10.

For comparison, the same acrylic polymer as was used above was dissolved in an aqueous solution of 60% sodium thiocyanate to obtain a spinning solution having a copolymer concentration of 11.3%. The spinning solution was heated to 70° C. and extruded into an aqueous solution of 12% sodium thiocyanate kept at -3° C.

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through a spinnerette having 7 circular spinning orifices of a diameter of 0.10 mm. The coagulated filaments were washed with water, stretched 8 times the length in steam at 120° C., then dried for 1 minute on a roller heated to 115° C. and were heat-treated to be relaxed for 4 minutes in steam at 115° C. to obtain 7 denier acrylic synthetic fibers.

The properties and lusters of the respectively obtained fibers are as indicated in Table 1.

TABLE 1

	Used spinnerette				
	Circular orifice	Orifice shape of—			
		Fig. 1	Fig. 3	Fig. 2	
Polymer concentration, percent.....	11.3	23.75	26.12	26.12	26.12
Dry strength (g./d.).....	3.18	3.60	3.90	3.60	4.26
Knot strength (g./d.).....	2.00	2.30	2.80	2.57	2.34
Dry elongation (percent).....	29.6	27.4	29.2	27.4	28.0
Knot elongation (percent).....	10.4	16.9	22.0	19.1	19.0
Luster.....	30	48	46	45	56

In this example, the luster was measured by the following method:

Luster

(1) 1 g. of fibers cut to 4 to 5 cm. long was taken and the fibers were arranged and ironed.

(2) The arranged fibers were pasted at both ends to a cardboard by using a binder and were then ironed.

(3) The luster of the above mentioned fibers pasted to the cardboard was measured by using a Murakami MG5 luster meter (made by Murakami Color Technical Laboratory).

As apparent from the Table 1, the hollow fibers obtained by the process of the present invention had the same yarn properties as the fibers obtained by the ordinary wet spinning process, but had lusters better than of the solid fibers obtained by the ordinary wet spinning process.

EXAMPLE 2

The same acrylic polymer as was used in Example 1 was dissolved in an aqueous solution of 50% sodium thiocyanate to prepare spinning solutions respectively having polymer concentrations of 21.72 and 17.42%. The viscosities at 30° C. of these spinning solutions were respectively 22.4×10^4 and 4.89×10^4 centipoises. Each spinning solution was heated to 70° C., and was extruded into air through a spinnerette having 7 spinning orifices of such shape as is shown in FIG. 2 (a short side of 0.094 mm., a long side of 0.754 mm. and a distance d of 0.230 mm.) or through a spinnerette having 7 spinning orifices of such shape as is shown in FIG. 3 (a short side of 0.091 mm., a long side of 0.649 mm. and a distance d of 0.200 mm.). The distance between the under surface of the spinnerette and the surface of the solution in the coagulating bath was 0.3 mm. The extruded solution was then passed through an aqueous solution of 12% sodium thiocyanate kept at -3° C. The coagulated filaments were drawn at a godet speed of 35 m./min., then washed with water, stretched 8 times the length in steam at 120° C., dried for 1 minute on a roller heated to 115° C. and were heat-treated to be relaxed for 4 minutes in steam at 115° C. to obtain 10 denier (monofilament denier) hollow acrylic synthetic fibers.

EXAMPLE 3

The same acrylic polymer as was used in Example 1 was dissolved in an aqueous solution of 60% sodium thiocyanate to prepare a spinning solution having a copolymer concentration of 17%. The viscosity at 30° C. of the spinning solution was 5.50×10^4 centipoises. The spinning solution was heated to 70° C., and extruded into air through a spinnerette having 7 spinning orifices of such shape as is shown in FIG. 1 (an outside diameter of 0.762 mm., an inside diameter of 0.502 mm., an area of the part enclosed with the slit of 0.20 mm.² and a distance d of

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0.123 mm.). The distance between the under surface of the spinnerette and the surface of the solution in the coagulating bath was 0.2 cm. Then the extruded solution was coagulated in an aqueous solution of 12% sodium thiocyanate kept at -3° C. The coagulated filaments were drawn at a godet speed of 40 m./min., washed with water, stretched 8 times the length in steam at 120° C., dried for 1 minute on a roller heated to 115° C. and were heat-treated to be relaxed for 4 minutes in steam at 115° C. to obtain 10 denier (monofilament denier) hollow acrylic synthetic fibers.

EXAMPLE 4

The same spinning solution as in Example 3 was warmed to 70° C., and extruded into air through a spinnerette having 7 spinning orifices of the shape shown in FIG. 1 (an outside diameter of 0.908 mm., an inside diameter of 0.702 mm., an area of the part enclosed with the slit of 0.40 mm.² and a distance d of 0.146 mm.). The distance between the under surface of the spinnerette and the surface of the solution in the coagulating bath was 0.5 cm. Then the extruded solution was coagulated in an aqueous solution of 12% sodium thiocyanate kept at -3° C. The coagulated filaments were drawn at a godet speed of 35 m./min., washed with water, stretched 12 times the length in steam at 120° C., dried for 1 minute on a roller heated to 115° C. and were heat-treated to be relaxed for 4 minutes in steam at 115° C. to obtain 10 denier (monofilament denier) hollow acrylic synthetic fibers.

EXAMPLE 5

The same acrylic polymer as was used in Example 1 was dissolved in an aqueous solution of 60% sodium thiocyanate to prepare a spinning solution having a copolymer concentration of 25%. The viscosity at 30° C. of the spinning solution was 110×10^4 centipoises. The spinning solution was warmed to 70° C., and extruded into air through a spinnerette having 7 spinning orifices of such shape as is shown in FIG. 1 (an outside diameter of 0.464 mm., an inside diameter of 0.224 mm., an area of the part enclosed with the slit of 0.04 mm.² and a distance d of 0.100 mm.). The distance between the under surface of the spinnerette and the surface of the solution in the coagulating bath was 0.3 cm. Then the extruded solution was coagulated in an aqueous solution of 12% sodium thiocyanate kept at 13° C. The coagulated filaments were drawn at a godet speed of 35 m./min., washed with water, stretched 8 times the length in steam at 120° C., dried for 1 minute on a roller heated to 115° C. and then were heat-treated to be relaxed for 4 minutes in steam at 115° C. to obtain 10 denier (monofilament denier) hollow acrylic synthetic fibers.

EXAMPLE 6

The same acrylic polymer as was used in Example 1 was dissolved in an aqueous solution of 60% sodium thiocyanate to prepare a spinning solution having a copolymer concentration of 26.88%. The viscosity at 30° C. of the spinning solution was 198×10^4 centipoises. The spinning solution was warmed to 70° C. and extruded into air through a spinnerette having 7 spinning orifices of the shape shown in FIG. 1 (an outside diameter of 0.605 mm., an inside diameter of 0.345 mm., an area of the part enclosed with the slit of 0.09 mm.² and a distance d of 0.123 mm.). The distance between the under surface of the spinnerette and the surface of the solution in the coagulating bath was 0.7 cm. Then the extruded solution was coagulated in an aqueous solution of 12% sodium thiocyanate kept at -3° C. The coagulated filaments were drawn at a godet speed of 50 m./min., washed with water, stretched 12 times the length in steam at 120° C., dried for 1 minute on a roller heated to 115° C. and were heat-treated to be relaxed for 4 minutes in steam at 115° C. to obtain 10 denier (monofilament denier) hollow acrylic synthetic fibers.

What we claim is:

1. A process for producing hollow acrylic synthetic fibers which comprises extruding a spinning solution prepared by dissolving an acrylic polymer in a concentrated aqueous solution of an inorganic salt selected from the group consisting of sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate, calcium thiocyanate, sodium perchlorate, calcium perchlorate, zinc chloride and lithium chloride through spinning orifices into an inert gaseous medium which is incapable of coagulating the spinning solution, each spinning orifice having a continuous central portion substantially enclosed by a slit having at least one cut-out in order that during passage through the inert gaseous medium an inert gas-filled hollow current of the spinning solution is formed, and coagulating the hollow current by means of an aqueous coagulating bath.

2. A method as claimed in claim 1 wherein the continuous central portion of the spinning orifices has an area of at least 0.04 mm.².

3. A method as claimed in claim 1 wherein the acrylic polymer is polyacrylonitrile or a copolymer of at least 70% by weight of acrylonitrile the balance being at least one ethylenically unsaturated monomer copolymerizable with acrylonitrile.

4. A method as claimed in claim 1 wherein the viscosity of the spinning solution is in the range of from 4×10^4 to 4×10^7 centipoises.

5. A method as claimed in claim 1 wherein the distance

between the under surface of the spinnerette and the surface of the solution in the coagulating bath is from 0.2 cm. to 5.0 cm.

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U.S. Cl. X.R.

264—182; 18—8SC, 8SS; 161—177, 178