

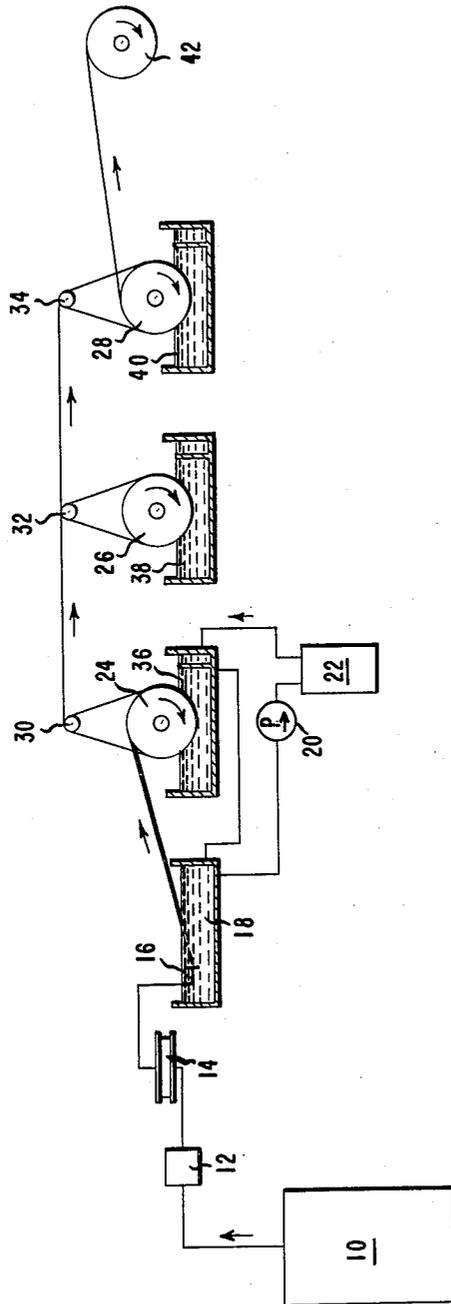
Feb. 26, 1963

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3,079,219

PROCESS FOR WET SPINNING AROMATIC POLYAMIDES

Filed Dec. 6, 1960



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PROCESS FOR WET SPINNING AROMATIC POLYAMIDES

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 Filed Dec. 6, 1960, Ser. No. 74,143
 8 Claims. (Cl. 18-54)

This invention relates to novel attenuated structures such as synthetic fibers, filaments, yarns and films of wholly aromatic polyamides and to a novel process for producing the same.

Wholly aromatic polyamides and shaped structures thereof exhibiting a valuable combination of properties are described in Hill et al. U.S. Patent No. 3,006,899, issued October 31, 1961, and Beste et al. U.S. Patent No. 3,068,188, issued December 11, 1962, including the production of high melting, highly crystalline shaped structures with high tenacity. However, attenuated structures with even higher tenacities than heretofore thought possible are provided by the present invention.

It is an object of this invention to provide attenuated structures of wholly aromatic polyamides that are capable of withstanding a greater load than heretofore when stretched in contact with a surface heated to at least 300° C. Another object of this invention is to provide highly crystalline drawn structures of wholly aromatic polyamides that have higher tenacities at moderate temperatures than any produced heretofore. A further object of this invention is to provide a novel wet extrusion process that enables solvent to be readily extracted from the formed structure and permits drawing of the structure to be immediately and continuously carried out before, during or after solvent extraction. Still another object of the invention is to provide a novel coagulating bath for wet spinning aromatic polyamides. Other objects will be apparent from the description that follows.

In accordance with this invention, an outstanding improvement in the wet spinning of wholly aromatic linear polyamides is provided by the use of an aqueous coagulating bath containing at least about 40% of calcium thiocyanate. The bath very quickly coagulates solutions of these polyamides in a manner which not only facilitates the spinning operation itself, but also makes possible the production of filaments of greatly increased strength. Minor amounts of the polyamide solvent used in the spinning solution do not interfere with the efficiency of this coagulating bath and may be allowed to accumulate in the bath up to a concentration of 25%.

The coagulating bath of this invention is particularly useful in the spinning of linear polyamides, wherein the amides directly connect wholly aromatic groups, from solution in a low molecular weight dialkyl amide containing a metal chloride such as calcium, magnesium, strontium, barium, lithium or aluminum chloride. The coagulated filaments or other attenuated structure produced in this way, after removal of solvent and metal chloride by aqueous extraction, can be drawn at a tension of at least 1.5 gram per denier for at least one second in contact with a surface heated to 300° C. or higher. The resulting hot drawn filaments are highly crystalline structures having tenacities in excess of 7.5 g.p.d. (grams per denier) when prepared from polyamide having an inherent viscosity of at least 1.9 subjected to a total draw in excess of 4 times the initially formed coagulated filament length. A preferred process provides tenacities in excess of 8.0 g.p.d., measured at 65% relative humidity and 70° F. using a rate of elongation of 60% per minute.

The polymer solution of this invention is comprised of about 15 to 25% of a wholly aromatic polyamide as described in aforementioned U.S. Patents No. 3,006,899,

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and No. 3,068,188, such as poly(meta-phenylene isophthalamide) or a poly-3-benzamide more fully described hereinafter, with an inherent viscosity of about 1.0 to 2.5 (when determined in solution in concentrated sulfuric acid at 30° C. at a concentration of 0.5 gram of polymer per 100 cc. of solution), about 0.5 to 3% of magnesium, strontium, barium, lithium or aluminum chloride and a dialkyl amide such as dimethylformamide or dimethylacetamide. The solution is preferably extruded at about 15° to 30° C.

The coagulating bath of this invention is comprised of about 40% to 60% or more of calcium thiocyanate [Ca(SCN)₂], preferably at least about 50%, with from 0 to 25% of the low molecular weight dialkyl amide used as a solvent in the polymer solution, and water. Preferably the bath will be used for both coagulation and preliminary extraction of the solvent from the polymer structure and will have a temperature of about 50° to 130° C.

A preferred process for preparing these high tenacity structures comprises extruding the polymer solution into the calcium thiocyanate coagulating bath and thereafter continuously extracting the solvent from the structure while drawing at a speed of from about 1 to 4 times that of the initial draw-off speed, drying and thereafter passing the dried structure over a surface heated to at least 300° C., and preferably heated to at least 330° C., to crystallize the structure and simultaneously therewith drawing an additional amount at a tension of not less than 1.5 g.p.d. to provide a total draw of at least 4 times.

Up to the present time, aromatic polyamides have preferably been spun by the dry spinning method in order to produce better physical properties in the yarn than has been possible by any wet spinning process heretofore tried. Properties of dry spun aromatic polyamide yarns were at least about 15 or 20% better than any aromatic polyamide wet spun yarn produced prior to this invention, whereas the wet spun yarns of this invention when drawn and crystallized by hot drawing have strengths at least 25% better than have been obtained from dry spun aromatic polyamide yarns.

Aqueous solutions of calcium thiocyanate of about 50% concentration and at temperatures between 100 and 140° C. produce very strong filaments that are considerably stronger than have been obtained by wet spinning in other bath compositions. High strength is developed within an inch of the spinneret face, thus permitting the filaments to be handled easily and rapidly through the coagulation and extraction baths. Because coagulation is rapid, the spinneret orifices may be placed as close together as is practical to make them, and filaments of various shapes according to the spinneret hole shape are readily produced.

The very rapid set-up of a thin skin on the extruded filaments is believed attributable to a stable chemical complex which forms between the polymer solvent and the calcium thiocyanate. By virtue of this complex formation the dialkyl amide solvent at the surface of the filament is immediately tied up and the membrane formed together with the strong attraction of the calcium thiocyanate for water is believed to prevent water penetration into the filament until the amide solvent has diffused out from the interior to leave a dense normally-collapsed filament characterized by a finely crenulated skin surface.

In the following examples, which illustrate specific embodiments of the invention, parts and percentages are by weight unless otherwise indicated:

EXAMPLE I

A wholly aromatic polyamide is prepared by reaction of meta-phenylene diamine with isophthaloyl chloride using as a solvent, dimethylacetamide. The dimethylacetamide is distilled prior to use and kept dry until it is

used. The meta-phenylene diamine, 25.92 parts, is placed in a glass vessel equipped with a paddle stirrer, a nitrogen inlet and a drying tube. To this is added 226 parts of distilled dimethylacetamide and the vessel is swept out with nitrogen to remove atmospheric oxygen from the reaction mixture. A slush of Dry Ice and acetone is placed around the vessel to chill the solution and in this process the solution is frozen to a mush. Then, 48.8 parts of isophthaloyl chloride is added all at once, and the Dry Ice bath is replaced by an ice-water bath. Stirring is continued for about 20 minutes to ½ hour. At this point, a very stirrable mass results.

There is an excess of dimethylacetamide hydrochloride above what is soluble in the dimethylacetamide in this reaction mixture, and as a result, some of this amide salt is dispersed rather than in solution. About half the calculated amount of amide salt separates. The solution contains approximately twenty percent of polymer based on dimethylacetamide and a considerable amount of hydrochloric acid resulting from the chemical interchange in the form of the acid salt of dimethylacetamide which is substantially neutralized by the addition of ammonia in an amount equal to 90% of the HCl present. This results in the immediate separation of ammonium chloride which is insoluble in dimethylacetamide and which is readily removed by filtration. The residual hydrochloride is then neutralized to a pH of about 6.0 by the addition of calcium hydroxide and this results in the formation of soluble calcium chloride, which is desirable for increasing the thermal stability of the solution. The resulting solution contains about 18.0% polymer of 1.91 inherent viscosity and 0.88% calcium chloride.

This solution is spun through a 100 hole spinneret, each hole being circular and 0.003 inch in diameter, into an aqueous bath of 50% calcium thiocyanate and 10% dimethylacetamide maintained at a temperature of 70° C. After a bath travel of 12 inches, the yarn is taken over a set of "take-up rolls" at 25 y.p.m. (yards per minute) and then is drawn 2.5× by passage onto a driven wind-up bobbin operated at 67.5 y.p.m. surface speed. The drawn yarn is washed free of bath components and residual solvent by immersion in a tank of water and is thereafter again drawn at a tension in excess of 1.5 g.p.d. over a plate heated to 330° C. between pairs of driven rolls at an additional draw ratio of 1.6× giving a total draw ratio of 4.0×. This yarn is of good appearance and luster and the physical properties of the filaments are as follows:

Denier	2.2
Tenacity	6.8 g.p.d.
Elongation	20.0 percent
Initial modulus	118.0 g.p.d.

EXAMPLE II

A solution of poly(meta-phenylene isophthalamide) in dimethylacetamide containing calcium chloride as a solution stabilizer was prepared by dissolving 540 parts of purified meta-phenylene diamine in 5430 parts of redistilled dimethylacetamide contained in a glass vessel equipped with a stirrer and maintained under an atmosphere of nitrogen. The solution was cooled to -30° C. and 964 parts of isophthaloyl chloride was added while keeping the temperature below -5° C. After thirty minutes of stirring, 153 parts of ammonia was added at -5° C. to precipitate most of the hydrochloric acid (present as dimethylacetamide hydrochloride complex) and the solution centrifuged to remove ammonium chloride crystals. The supernatant liquid of low molecular weight polymer containing about 5% of the initial primary amine groups was returned to the reaction vessel and at a temperature of about 30-45° C. successive additions of isophthaloyl chloride were made over about thirty minutes. These successive additions were in decreasing amounts (36 parts, 5.5 parts, 3.5 parts, 1.2 parts . . .),

until a suitably viscous solution resulted indicating high molecular weight of polymer. An addition of 49.0 parts of isophthaloyl chloride was thus added to the 964 parts of originally added isophthaloyl chloride making a total addition of 1013 parts. Finally, 34 parts of calcium hydroxide slurried in 212 parts of dimethylacetamide was added to complete neutralization to a pH of 6.5. The viscous solution containing about 21% polymer having 2.11 inherent viscosity also contained 0.92% calcium chloride.

The solution was spun through a 100-hole spinneret as in Example I into an aqueous bath of 60% calcium thiocyanate containing initially no dimethylacetamide and at a temperature of 110° to 115° C. The yarns after fifteen inches bath travel were passed over a take-up roll having a surface speed as shown in Table A below and were then passed successively into a first washing bath containing water with a contact time of thirty seconds at the temperatures shown in Table A and then through a second washing bath at 20° C. with ten seconds contact time. The yarns were drawn between the initial draw-off roll and the washing bath rolls as shown in the table and were then wound up on bobbins. The wet yarns were dried and further drawn immediately after drying to give the total draw shown in Table A, by passing them over a plate heated to 300° C. under a tension of not less than 1.5 g.p.d. The yarn properties are shown in Table A.

Table A

Take-up (y.p.m.)	6	8	30
Initial draw (X)	2	1	1
First washing bath water (° C.)	70	80	40
Contact (secs.)	30	30	30
Second washing bath water (° C.)	20	20	20
Contact (secs.)	10	10	10
Total draw (X)	3.2	4.5	2.9
Physical properties:			
Tenacity (g.p.d.)	7.7	7.8	6.0
Elongation (percent)	21	24	37
Initial modulus (g.p.d.)	115	122	99
Denier	2.4	2.2	2.8

EXAMPLE III

A solution of 2280 parts of meta-phenylene diamine dissolved in 18,100 parts of dimethylacetamide was prepared in a glass-lined jacketed vessel equipped with a propeller type mixer and in an atmosphere of nitrogen. At about room temperature 4071 parts of molten isophthaloyl chloride was added with stirring during twenty minutes and the stirring continued for one hour. At the end of this time, 646 parts of ammonia was added over a period of about one hour and the solution filtered under nitrogen in a centrifugal filter using a laid asbestos filter to remove the ammonium chloride. The filtered solution was run into a nitrogen filled vessel with a suitable spiral stirrer and additional isophthaloyl chloride was added as follows: 135 parts at the rate of 12 parts per minute followed by 62 parts at the rate of 0.4 part per minute. By the time all the isophthaloyl chloride had been added, maximum viscosity was attained and the solution was neutralized to a pH of 6.0 with calcium oxide slurried in dimethylacetamide. The solution was found to contain 19.6% polymer of 1.93 intrinsic viscosity and 1.99% calcium chloride. The solution had a viscosity of 179 poises at 100° C.

The drawing is a diagrammatic showing of the spinning, preliminary drawing, and washing arrangement. The polymer solution was forced from the hopper 10 through a Zenith gear-type metering pump 12 and then through a 6-inch diameter plate filter 14. The filter medium consisted of a one-inch depth of 150 to 200 mesh sand, seven layers of calendered cloth woven from high bulk poly(ethylene terephthalate) fiber yarn, two sheets of fine filter paper sandwiched between layers of the cloth and finally a felt of poly(ethylene terephthalate) fiber at the top or outlet side of the filter. The spinneret 16 was ½ inch in diameter, of stainless steel and

contained 100 circular holes, each 0.0024 inch diameter. A spinneret filter was provided composed of two 80-mesh platinum screens, three layers of the calendered cloth just previously described, and one layer of poly(ethylene terephthalate) fiber felt. The calcium thiocyanate coagulating and extraction bath 18 contained 55.0% calcium thiocyanate, 11.7% dimethylacetamide and 0.5% calcium chloride, the balance being water, and was maintained at a temperature of 125° C. To remove low molecular weight polymer extracted from the filaments, the bath was constantly filtered and recirculated by means of pump 20 and glass fiber filter 22.

The rollers 24, 26 and 28 were so arranged, each with an auxiliary guide roll, 30, 32 and 34 respectively, to enable a plurality of passes of yarn to be made around each of the rollers. With the surface speed of the draw-off roll 24 at 8 y.p.m., and with a relative short bath travel, the initial contact time of the freshly-formed filaments with the coagulating bath was about 1 to 2 seconds. The yarn made 15 passes around the roll 24 and its auxiliary guide roll 30 in the initial extraction step and the contact time of the yarn with this bath 36 was about 2 minutes. In the first water extraction at 20° C. in bath 38 the yarn made 15 passes around roll 26 and its auxiliary roll 32 for a contact time of about two minutes. In the second water wash at 95° C. in bath 40 the yarn made six passes around roll 28 and its auxiliary roll 34 so that the contact time of the yarn with this bath was about 1/2 minute. The wind-up bobbin 42 was maintained at a surface speed of 28 y.p.m. thereby giving a draw ratio between roller 24 and the wind-up bobbin of 3.5×.

Several samples of yarn collected on the wind-up bobbins were subsequently dried by unwinding and passing the yarn over a heated surface at a temperature somewhat in excess of 100° C. Subsequently, the yarns were further drawn to a total draw ratio as indicated below in Table B while the yarns were passing over a surface heated to 330° C. to crystallize the filament structures. In each case the draw ratio and conditions of drawing were so selected that the yarn tension during this passage was never less than 1.5 g.p.d., being in all cases above about 1.8 or 1.9 g.p.d. Also in Table B are given tenacities, elongations, initial moduli and deniers of these several yarn samples. The tenacity is measured at 65% relative humidity and 70° F. on an "Instron" tester at 60% per minute elongation. From this test is obtained the tensile strength in grams per denier, the elongation in percentage and the initial modulus in grams per denier. It will be noted that the denier of the 100 filament structure varies quite widely due primarily to changes in pump delivery and to minor differences in total draw ratios.

Table B

DRAWING AND PHYSICAL PROPERTIES

Total draw ratio	Tenacity	Elongation	Initial modulus	Denier
5.33	8.15	12.0	167	187
5.49	8.50	12.5	173	186
5.55	8.37	10.2	176	177
5.10	8.62	10.3	172	178
5.00	8.25	13.7	164	375
5.55	8.40	13.5	152	375
5.55	8.42	10.7	160	183

EXAMPLE IV

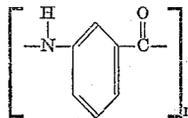
Drawing during spinning can be varied widely without affecting physical properties substantially. This is illustrated by the following table of results which indicates variations in draw between 1.0× and 3.0× during spinning have a relatively small effect on the yarn properties when the total amount of draw is of the same order.

Table C

Draw during spinning	Total draw	Tenacity	Elongation	Initial modulus	Denier
3.0	4.2	7.6	17	120	2.5
2.0	3.6	6.4	22	104	2.7
1.0	3.8	6.8	22	98	3.0

From the examples it will be noted that the best results are obtained when the concentration of calcium thiocyanate in the spinning is high, i.e., above 50% and even as high as 55% or 60%. Spinning bath concentrations of calcium thiocyanate of at least about 50% are therefore preferred. The amount of amide solvent in the coagulating and extraction baths may be varied widely and starting with a fresh bath it may be zero initially. Practically, however, it is better to operate so that a small relatively constant value is maintained, such as 10 to 15%, although as much as 25% may be tolerated without any ill effects. For the production of very high tenacity yarns in excess of 8 g.p.d., it is essential that the polymer solution used be prepared so as to minimize the formation of gels due to very high molecular weight material. To obtain such solutions, the final isophthaloyl chloride additions must be made slowly with adequate stirring as indicated above in Example III. When such polymer solutions are spun into yarns, the filaments are more uniform and are capable of withstanding higher tensions at the time of crystallization and final hot drawing. In order to attain the very high tenacities frequently desired, the yarn should be capable of withstanding for at least one second a tension of at least 1.5 g.p.d. while it is being drawn in contact with a surface heated to 300° C. and preferably to at least 330° C.

Wholly aromatic polyamides and polymer solution compositions other than shown in the examples may also be used in accordance with this invention with good results. The U.S. patents mentioned earlier list numerous other aromatic polyamides in other amide solvents and with other metal halides present as stabilizing agents. Poly-3-benzamide, a linear polyamide comprised of recurring aminobenzoyl units of the structural formula:



where n is a large whole number, may also serve as the fiber-forming polymer. Likewise, the invention should not be considered as limited to the spinning of filaments and yarns but is applicable also to the extrusion of other shaped structures that may be drawn only in the longitudinal direction or drawn both in the longitudinal and transverse directions, such as for instance a sheet or a wide film. Wherever high melting, highly crystalline and unusually strong films, sheets and like structures are needed, this invention may be applied with excellent results.

The yarns, filaments, fibers and the like produced in accordance with this invention have the necessary high strength and high modulus to make them especially suitable for use as cord for reinforcing rubber products, such as tires, belts, hose and the like, as a reinforcing structure in plastic goods, as a sewing thread, and for any use under high temperature conditions where high strength per unit of weight is needed.

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited by the specific illustrations except to the extent defined in the following claims.

I claim:

1. In the wet spinning process for forming shaped articles from a solution of a linear polyamide wherein the amide linkages directly connect wholly aromatic groups,

the improvement which comprises extruding said solution into an aqueous coagulating bath containing at least about 40% of calcium thiocyanate.

2. A process as defined in claim 1 wherein the aqueous coagulating bath contains about 40% to about 60% of calcium thiocyanate and 0 to 25% of a low molecular weight dialkyl amide.

3. A process as defined in claim 2 wherein the aqueous coagulating bath is at a temperature of 50° to 130° C.

4. The process for forming attenuated shaped articles from a linear polyamide wherein the amide linkages directly connect wholly aromatic groups, said polyamide having an inherent viscosity of about 1.0 to 2.5, which comprises preparing a solution of said polyamide in a low molecular weight dialkyl amide solvent to contain about 15% to 25% of the polyamide and about 0.5% to 3% of a metal chloride selected from the group consisting of calcium, magnesium, strontium, barium, lithium and aluminum chlorides, extruding said solution in the form of a continuous attenuated structure, coagulating said solution to form a self-supporting structure in an aqueous bath containing about 40% to 60% of calcium thiocyanate and up to 25% of low molecular weight dialkyl amide, removing dialkyl amide solvent and metal chloride from the polyamide by aqueous extraction, and drawing the structure over a surface heated to at least 300° C. at a tension of at least 1.5 grams per denier to produce a high melting, crystalline, drawn structure.

5. The process as defined in claim 4 wherein the polyamide solution is extruded at a temperature of about 15° to 30° C. into said bath.

6. The process as defined in claim 4 wherein the polyamide solution is extruded through a spinneret directly into said bath and the bath is maintained at a temperature of about 50° to 130° C.

7. The process for forming attenuated shaped articles from a linear polyamide wherein the amide linkages directly connect wholly aromatic groups, said polyamide having an inherent viscosity of about 1.0 to 2.5, which comprises preparing a solution of said polyamide in a low molecular weight dialkyl amide solvent to contain about

15% to 25% of the polyamide and about 0.5% to 3% of a metal chloride selected from the group consisting of calcium, magnesium, strontium, barium, lithium and aluminum chlorides, spinning said solution at a temperature of about 15° to 30° C. into an aqueous calcium thiocyanate bath at a temperature of about 50° to 130° C. containing about 40% to 60% of calcium thiocyanate and up to 25% of low molecular weight dialkyl amide to coagulate the solution into filaments, continuously withdrawing the filaments from the coagulation zone and removing remaining solvent by aqueous extraction while forwarding the filaments at a speed within the range of to about 4 times the initial draw-off speed, and drawing the filaments at a tension of at least 1.5 grams per denier over a surface heated to at least 300° C. to crystallize the polyamide structure.

8. The process as defined in claim 7 wherein said polyamide has an inherent viscosity of at least 1.9 and the length of the filaments withdrawn from the coagulation zone is subsequently increased by a total draw in excess of 4 times to provide a tenacity in excess of 7.5 grams per denier.

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