United States Patent Office 3,751,546
Patented Aug. 7, 1973

3,751,546

PROCESS FOR THE MANUFACTURE OF FILAMENTS ON THE BASIS OF HIGH-MELTING POLYAMIDES

Ernst Horoldt, Kelkheim, Taunus, Germany, assignor to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Bruning, Frankfurt am Main, Germany

No Drawing. Filed July 26, 1971, Ser. No. 164,857
Claims priority, application Germany, July 28, 1970, P 20 37 254.7
Int. Cl. D01f 7/00
U.S. Cl. 264—184 5 Claims

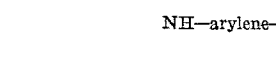
ABSTRACT OF THE DISCLOSURE

The application relates to a process for the wet spinning of preponderantly aromatic polyamides by spinning a spinning solution containing besides an aprotic solvent a dissolved metal halide into an aqueous salt-containing coagulation bath; the coagulation bath containing as salt the same metal halide as does the spinning solution. The process simplifies the manufacture of filaments made from high-melting polyamides having a high dynamic efficiency and partially a poor flammability, and it ensures an easy regeneration of the coagulation baths.

The present invention relates to a process for the manufacture of filaments on the basis of high-melting polyamides.

Polyamides having melting points above 300° C. partially possess very valuable properties apart from their good thermostability. However, those polymers can be processed from the melt only to a limited extent, especially because their melting and decomposition temperatures often are too near to each other. Shaped articles, for example filaments, fibers, films, sheets, coatings and yarns, can therefore be manufactured only from the solution in most cases. The general rule for polyamides is the following: the higher the melting point, the lesser the solubility, since hydrogen bonds and cristallinity act in the opposite direction on the melting point and the solubility. Therefore, dissolving high temperature resistant, i.e. high-melting polyamides requires the use of quite special solvents, described for example in German Auslegeschrift No. 1,107,399.

According to this Auslegeschrift, a process for the dissolution of nitrogen containing linear polycondensation products in which at least 50% of the recurring units in the chain molecule of the polymer consist of the grouping



is claimed, wherein substantially nonaqueous, acid-free, organic solvents, so-called aprotic solvents, which can dissolve at least 0.5% by weight of the polycondensation product at room temperature, are used in combination with a salt splitting off chlorine or bromine ions, which salt is soluble in these solvents. Aprotic organic solvents are for example dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone or dimethylsulfoxide. As to aprotic organic solvents, see for example the paper of A. J. Parker in Advances in Organic Chemistry, vol. 5 (1965), p. 1–46.

Thus, for example, it is known from the aforementioned Auslegeschrift that polycondensation products made from m-phenylene-diamine and isophthalic acid (chloride), m-

phenylene-diamine/4,4' - diamino-diphenyl-methane and isophthalic acid (chloride), or m-phenylene-diamine/4,4'-diamino-diphenyl ether and isophthalic acid (chloride) can be dissolved in a mixture of dimethylformamide and LiCl or dimethylacetamide and $CaCl_2$. From these polymer solutions it is possible to obtain for example filaments according to the dry spinning process described in U.S. Pat. No. 3,360,598. In this process, however, only high temperature spinning solutions containing large amounts of salt can be spun, for example a solution of 20% of polymer and 9.3% of $CaCl_2$ in dimethylacetamide. According to such a process, salt-free filaments capable of being perfectly drawn and set can only be obtained with great expenditure, since the filaments leaving the spinning chamber may contain up to 46% of $CaCl_2$.

In many cases, such as in the manufacture of fibers and filaments, it is therefore advantageous to use the wet spinning process. German Pat. No. 1,243,820 describes a process for the manufacture of filaments by wet spinning of a solution of a linear polyamide the amide bridges of which directly link purely aromatic groups into a hot aqueous coagulation bath containing at least 40% of calcium thiocyanate; the spinning solution in this case consists of a solution of the aforementioned linear polyamide in a salt solution according to German Auslegeschrift No. 1,107,399. By this process, filaments suitable for use can be obtained; however, the use of hot, concentrated calcium thiocyanate solutions as coagulation medium requires a considerable expenditure with regard to apparatuses in order to avoid a substantial decomposition of the coagulation medium during the spinning process already. Moreover, a certain discoloration of the spun filament cannot be excluded in most cases. Furthermore, the work-up of the coagulation bath containing calcium thiocyanate, metal halide (LiCl, $CaCl_2$, etc.) and, for example, aqueous dimethylacetamide is always a great problem.

Subject of the present invention is now a process for the wet spinning of polyamides in which at least 80% of the amide groups are directly linked by purely aromatic groups from an aprotic solvent containing a dissolved colorless metal halide as spinning solution into an aqueous salt-containing coagulation bath, wherein this aqueous salt-containing coagulation bath contains the same metal halide as does the spinning solution.

The polyamides in which at least 80% of the amide groups are directly linked by purely aromatic groups, which polyamides are to be spun according to the process of the invention, are for example described in U.S. Pat. No. 3,063,966. Especially suitable are polyamides the acid component of which is isophthalic acid and the diamine component of which is at least one of the diamines m-phenylene-diamine, 4,4'-diamino-diphenyl-methane and 4,4'-diamino-diphenyl ether. As already mentioned, all of the amide groups must not be directly linked by purely aromatic groups, but up to a maximum of 20% of the amide groups may be linked by non-aromatic groups (aliphatic, cyclo-aliphatic, araliphatic groups as known from the normal polyamides, for example from nylon-66).

The polymer viscosity of the totally or preponderantly aromatic polyamides which can be spun according to the process of the invention should be from about 1.3 to 4.0 ($=\eta_{rel}$), preferably from 2.0 to 3.5. These relative viscosity values are measured or to be measured with a solution of 0.5 g. of the polymer in 10 ml. of concentrated sulfuric acid at 25° C. The melting points of these polyamides generally are above 300° C. or at least not much below 300° C., and the decomposition point in most cases is near the melting point.

At first, the polyamide to be spun is dissolved in a spinning solution of an aprotic solvent containing a dissolved colorless metal halide. As colorless metal halides, some chlorides and bromides of the elements of the 1st, 2d and 3rd main group and of the 2d subgroup of the periodic system of the elements are suitable; however, the chlorides of lithium, magnesium, calcium, zinc and aluminum are preferred, optionally also lithium bromide.

As aprotic solvents practically all solves cited in the paper of A. J. Parker in Advances in Organic Chemistry, vol. 5 (1965), pp. 1–46 may be used; preferable in this case are the lower aliphatic alkylamides, especially dimethylforamide and dimethylacetamide, furthermore N-methyl-pyrrolidone, tetramethylene-sulfone and dimethylsulfoxide.

The viscosity of the spinning solution which should contain no more than 10% by weight of metal halide, is adjusted to a falling ball time of from 50 to 1,500 seconds, preferably of from 100 to 600 seconds, determined according to the DIN 5401 method. In this DIN method, at 20° C. the falling time of a steel ball of a diameter of 1/8 inch through 20 cm. of the solution the viscosity of which is to be measured is determined. The above mentioned falling ball time of from 50 to 1,500, preferably of from 100 to 600 seconds, is attained at a polyamide concentration of from about 15 to 25% by weight.

Since the polyamides can be prepared in such a way as to obtain solutions ready to be spun containing the dissolved polyamide in desired concentrations in a mixture of an aprotic solvent and a metal halide, for example in dimethylacetamide/calcium chloride, the isolation and work-up of the polyamide before the spinning process in many cases is no more required.

Advantageously, the spinning solution is pressed into the coagulation bath at room temperature. The filament may pass through the coagulation bath either in vertical or in horizontal direction. The coagulation bath is an aqueous solution of the same metal salt which is also present in the spinning solution. The salt concentration in the coagulation bath is from 15 to 60% by weight, preferably from about 25 to 50% by weight.

A small amount of the organic aprotic solvent entering the coagulation bath from the spinning solution does not cause any disturbance of the spinning process. In some cases, a content of from about 5 to 15% by weight of the organic aprotic solvent in the coagulation bath may even have a favourable influence on the quality of the filament. The temperature of the coagulation bath should be from about 50° to 150° C., preferably from about 70° to 110° C. The optimum coagulation bath condition necessary for the spinning process can rapidly be determined in a simple test. The coagulation filament strand generally is drawn off the coagulation bath by means of trio rollers running at constant speed, then washed and freed from salt in a suitable bath, advantageously in hot water, and drawn, pre-dried, and set with crystallisation at temperatures of from about 250° to 350° C.

The essential point of the process of the invention, i.e. the spinning solution as well as the coagulation bath containing the same metal salt though in different concentration, is at the same time its decisive advantage. For, by avoiding salt mixtures as for example required in the process of German Pat. 1,243,820, which nearly exclude their rational recovery, in the case of the spinning of polyamides according to the process of the invention an easy and trouble-free work-up of the coagulation bath is always possible. In the process of the invention as described above, transparent filaments are obtained which, after a corresponding drawing and setting, possess excellent mechanical properties, so that they may be used in fields requiring a high dynamic efficiency, for example in tire-cord or in threads for high-speed sewing machines. Furthermore, many of the polyamides spun according to the process of the invention are distinguished by their poor flammability.

Finally, it must be mentioned that additives, for example pigments or dulling agents, may be added to the spinning solution without any negative effect on the spinnability. The process of the invention is also quite suitable for the preparation of filaments dyed while being spun.

The following examples illustrate the invention; parts and percentages being always by weight. The inherent or logarithmic viscosity number is determined from the relative viscosity according to the following equation

$$\eta_{inh}=\frac{\ln \eta_{rel}}{c}$$

in which c is the polymer concentration in g./100 ml. of concentrated sulfuric acid (temperature=25° C.; c=0.5 g.).

EXAMPLE 1

120 parts of a polycondensation product of m-phenylenediamine and isophthalic acid chloride having a relative viscosity of 2.64 (η_{inh} 1.94) are dissolved in 680 parts of dimethylacetamide containing 2.17% of $CaCl_2$ and 0.1% of H_2O. The filtered and degassed solution has a viscosity of 168 falling ball seconds. The spinning solution is spun through a gold/platinum nozzle (alloy 70/30) having 140 holes of a diameter of 0.07 mm. into an aqueous coagulation bath containing 53% of calcium chloride. The portion of the coagulation bath through which the filament has to pass has a length of 30 cm. The spinning solution, under a nitrogen pressure of 1 atm. is pressed from an autoclave over a spinning arch into the coagulation bath heated at 72° C. The coagulated filament strand is drawn off the coagulation bath at a speed of 5 m./min. by means of trio rollers, subsequently washed in a bath having a length of 150 cm. and containing water heated at 85° C., and simultaneously drawn by means of a further trio roller running at a speed of 18 m./min. In a subsequent washing bath having a length of 130 cm. and a temperature of 80° C., the filament is freed from the remaining solvent and salt. The filament strand then passes through a heating channel having a length of 140 cm. and is predried by means of hot air of 250° C. With tension, it is then drawn at a speed of 20 m./min. over a contact heater line having a length of 120 cm. and a temperature of 320° C., subsequently set, optionally given a protective twist and then wound up on a bobbin.

The transparent filament so obtained has a titer of 0.6 d. tex, a tensile strength of 5.2 g./d. tex at 21% of elongation at break; the yield stress is 2.3 g./d. tex and the initial module 102 g./d. tex.

EXAMPLE 2

A spinning solution made from 150 parts of a condensation product of m-phenylene-diamine and isophthalic acid chloride having a relative viscosity of 2.64 (η_{inh} 1.94), dissolved in 850 parts of a mixture of 95 parts of dimethylformamide and 5 parts of lithium chloride, is spun under a nitrogen pressure of 1.6 atm. through a gold/platinum nozzle having 140 holes of a diameter of 0.08 mm. into a coagulation bath of 79° C. containing 31 parts of lithium chloride, 10 parts of dimethylformamide and 49 parts of water according to the conditions given in Example 1. The viscosity of the spinning solution is 176 falling ball seconds. The individual titer of the filament wound up on a bobbin is 1.5 d. tex; its tensile strength is 3.0 g./d. tex at an elongation at break of 30%.

EXAMPLE 3

The spinning solution used in Example 1 is spun through a gold/platinum nozzle having 140 holes of a

diameter of 0.07 mm. into the following coagulation baths:

Coagulation medium	Percent	Temperature, ° C.	Immersion length, cm.
$MgCl_2$	28.5	107	30
DMA [1]	18.5		
H_2O	53		
$AlCl_3$	27	94	30
DMA [1]	10		
H_2O	63		
$ZnCl_2$	47	102	10
DMA [1]	10		
H_2O	43		

[1] DMA=dimethylacetamide.

According to the method described in Example 1, also in these coagulation baths transparent filaments can be obtained.

EXAMPLE 4

A solution is prepared from 160 parts of a polycondensation product of m-phenylene-diamine and isophthalic acid chloride having a relative viscosity of 1.97 (η_{inh} 1.33) in 640 parts of dimethylacetamide containing 2.0% of calcium chloride and 0.4% of water by introducing the polycondensate into the solvent mixture cooled to 2°–5° C. and dispersing it thoroughly. Subsequently, the mixture is heated, while stirring, to 60° C. and maintained at this temperature for 30 minutes. After the mixture has been allowed to cool to room temperature, pressure filtration is carried out. The viscosity of the degassed solution of 130 falling ball seconds. Under a pressure of 1.5 am., the spinning solution is spun through a nozzle having 140 holes of diameter of 0.07 mm. into a coagulation bath containing 40 parts of calcium chloride, 10 parts of dimethylacetamide and 50 parts of water. The temperature of the coagulation bath is 78° C., its length is 10 cm. The filament strand is drawn off the coagulation bath at a speed of 20 m./min. by means of trio rollers and wound up on a perforated bobbin at a speed of 60 m./min. By washing the bobbin in a suitable vessel, adhering components of the coagulation bath and the solvent are eliminated from the filament. The washed filament is then drawn for a further 100% by means of a contact heater of 330° C. A transparent, colorless filament having good physical properties is obtained: titer 2.5 d. tex; tensile strength 4.6 g./d. tex, elongation 19%.

EXAMPLE 5

48 parts of a polycondensation product made from m-phenylene-diamine and isophthalic acid chloride having a relative viscosity of 2.69 (η_{inh} 1.97) are dissolved in 252 parts of dimethylacetamide containing 2.36% of zinc chloride and 0.14% of water. The viscosity of the spinning solution is 101 falling ball seconds. The spinning solution is spun through a gold/platinum nozzle having 100 holes of a diameter of 0.15 mm. into an aqueous coagulation bath containing 40% of zinc chloride and 10% of dimethylacetamide. The portion of the coagulation bath through which the filament has to pass has a length of 60 cm., the temperature of the bath is 85° C. The filament strand is drawn off the coagulation bath at a speed of 10 m./min. The after-treatment of the coagulated spun filament, i.e. washing, drawing and setting, is carried out in analogy to the method described in Examples 1 and 2.

EXAMPLE 6

For the preparation of a spinning solution, 48 parts of the polycondensate described in Example 5 are used. The solvent consists of 252 parts of dimethylacetamide containing 1.2% of magnesium chloride and 1.39% of water. The viscosity of the spinning solution is 198 falling balls seconds. The solution is spun through a nozzle having 100 holes of a diameter of 0.1 mm. into a coagulation bath containing 16% of magnesium chloride, 10% of dimethylacetamide and 74% of water. The portion of the coagulation bath through which the filament has to pass has a length of 60 cm., the coagulation bath has a temperature of 87° C. The coagulated spun filament is drawn off the bath at a speed of 10 m./min. drawn 2.5 fold its original length, washed, dried, set under tension at 320° C. and finally wound up on a bobbin.

EXAMPLE 7

A spinning solution of 48 parts of the polycondensate cited in Example 5 is prepared. As solvent, 252 parts of dimethylacetamide containing 3.26% of aluminium chloride and 0.03% of water are used. The 16% spinning solution is spun through a nozzle having 100 holes of a diameter of 0.15 mm., into a coagulation bath containing 30% of aluminium chloride, 9% of dimethylacetamide and 61% of water. The portion of the coagulation bath through which the filament has to pass has a length of 58 cm., the temperature of the bath is 90° C. The coagulated filament strand is drawn off at a speed of 12 m./min. and washed. The filament washed free from salt is aftertreated in usual manner.

EXAMPLE 8

22.5 parts of a polycondensation product of 4,4'-diamino-diphenyl ether and isophthalic acid chloride having a relative viscosity of 5.5 (η_{inh} 3.4) are dissolved in 106.25 parts of dimethylacetamide containing 1.87% of calcium chloride and 0.9% of water. The spinning solution is spun in analogy to the method described in Example 1 in order to yield a filament.

EXAMPLE 9

A polycondensation solution prepared according to known methods from m-phenylene-diamine and isophthalic acid chloride dissolved in dimethylacetamide is directly spun. The reaction solution contains 20% of polycondensate having a relative viscosity of 3.7 (η_{inh} 2.6) and 0.75% of calcium chloride. The falling ball viscosity of the solution is 1,400 seconds. The solution is spun through a nozzle having 100 holes of a diameter of 0.15 mm. into a coagulation bath containing 40% of calcium chloride, 50% of water and 10% of dimethylacetamide. The portion of the coagulation bath through which the filament has to pass has a length of 58 cm., the temperature of the bath is 87° C. The coagulated filament strand is drawn off the bath at a speed of 10 m./min. The filament washed in hot water having a temperature of 80° C. is drawn 3.5 fold its original length, dried, set with slight afterstretching at 325° C. by means of a contact heater, and wound up on a bobbin. A filament having good technological properties is obtained.

EXAMPLE 10

For the preparation of a spinning solution, 48 parts of a polycondensation product of m-phenylene-diamine and isophthalic acid chloride having a relative viscosity of 2.63 (η_{inh} 1.93) are dissolved in 252 parts of dimethylacetamide containing 5% of lithium bromide and 0.12% of water. At about 5° C., the polycondensate is introduced into the solvent mixture within 10 minutes and well dispersed. Subsequently, the mixture is heated to 60° C., while stirring, and maintained at this temperature for 30 minutes. After the mixture has been allowed to cool to room temperature, pressure filtration is carried out. The viscosity of the solution free from gas bubbles is 118 falling ball seconds. The spinning solution is then spun under a nitrogen pressure of 0.8 atm. from a boiler via a spinning pipe through a nozzle having 100 holes of a diameter of 0.1 mm. into a coagulation bath containing 40 parts of lithium bromide and 60 parts of water. The temperature of the coagulation bath is 70° C. The bath has a length of 60 cm. The filament strand is drawn off the coagulation bath at a speed of 20 m./min. by means of trio rollers. It is washed in a subsequent bath having a length of 120 cm. and containing hot water of 80° C., and simultaneously it is drawn by means of a further trio roller running at a speed of 46 m./min. In a subsequent second bath contain-

ing hot water, the filament is freed from traces of solvent and salt. The filament strand is then dried with tension, after-drawn over a contact heater having a temperature of 320° C., and set. The final winding-up on a bobbin is carried out at a speed of 60 m./min. The filament obtained is transparent and has a tensile strength of 3.2 g./d. tex at an elongation of 25%.

What is claimed is:

1. In a process for the wet spinning of polyamides in which at least 80% of the amide groups are directly linked by purely aromatic groups and up to 20% may be linked by aliphatic, cycloaliphatic, or araliphatic groups from an aprotic solvent, the aprotic solvent being dimethylformamide, dimethylacetamide, N-methylpyrrolidone, tetramethylenesulfone or dimethylsulfoxide, containing a dissolved colorless metal halide of the elements of the first, second, third main group and of the second subgroup of the periodic system of elements as spinning solution into an aqueous salt-containing coagulation bath, the improvement which comprises using as salt for the coagulation bath the same metal halide as for the spinning solution and wherein the salt concentration of the spinning solution does not exceed 10% by weight, and the salt concentration of the coagulation bath is from 15 to 60% by weight.

2. The process as defined in claim 1 and wherein the salt concentration of the coagulation bath is from 25 to 50% by weight.

3. Process as claimed in claim 1, wherein the polyamides to be spun contain isophathalic acid as acid component and at least one diamine selected from the group of m-phenylene-diamine, 4,4'-diamino-diphenyl-methane and 4,4'-diamino-diphenyl ether as diamine component.

4. Process as claimed in claim 1, wherein as colorless metal halide one of the chlorides of lithium, magnesium, calcium, zinc or aluminium, or lithium bromide, is used.

5. Process as claimed in claim 1, wherein the viscosity of the spinning solution has a falling ball time of from 50 to 1,500 seconds, determined according to the DIN 5401 method.

References Cited

UNITED STATES PATENTS

3,414,645	12/1968	Morgan	264—210 F
3,417,163	12/1968	Beermann et al.	260—78 L
3,445,557	5/1969	Horoldt	264—210 F
3,492,390	1/1970	Borner	264—184
3,549,580	12/1970	Schmidt et al.	260—78 L
3,595,951	7/1971	Logullo	264—211
3,622,545	11/1971	Foldi	260—78 A
2,451,420	10/1948	Watkins	264—162
3,642,706	2/1972	Morgan	260—78 S

JAY H. WOO, Primary Examiner

U.S. Cl. X.R.

260— 78 S; 264—210 F