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PROCESS FOR SPINNING AN AQUEOUS NITRIC ACID SOLUTION OF POLY(HEXAMETHYLENE) TEREPHTHALAMIDE

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ABSTRACT OF THE DISCLOSURE

The present invention relates to a process for spinning an aqueous nitric acid solution of poly(hexamethylene) terephthalamide containing less than 0.05% of nitrous acid into an aqueous coagulation bath containing nitric acid.

The present invention relates to a process of spinning fibers which comprises extruding a spinning solution into a coagulation bath of a 60% or less aqueous solution of nitric acid, said spinning solution being prepared by dissolving a polymer having 80% or more recurring units of poly(hexamethylene)terephthalamide (said polymer is hereinafter abbreviated to poly(hexamethylene)terephthalamide) in a 65% or more aqueous solution of nitric acid at a temperature less than 30° C., said latter nitric acid being as pure as not more than 0.05% of nitrous acid. (Percent hereinafter refers to that by weight unless specified otherwise.)

Hitherto, molded products of polyamide have been usually produced by a melt-molding process. It is an advantageous point for this melt-molding process that a solvent is not necessary and the molded product has a high filling grade. However, molding of the material is limited by its melting point. In other words, the molding becomes difficult in conformity to the higher melting point and it becomes impossible in case of a material having a very high melting point or a material having a melting point higher than a decomposition point.

Of course, the melt-molding can be easily exercised for a material having a low melting point. However, it is a drawback that the degree of heat resistance for the molded product is below the melting point.

A melt-molding process is not suitable to produce a molded product having high degree of heat resistance. On the contrary, it is one of the important advantages of the solvent molding process that, as a principle, said process is not limited by the melting point. But, a process of producing molded products from poly(hexamethylene)terephthalamide is not yet known in view of industrial and economical advantages. In other words, according to the researches hitherto, trichloroacetic acid, trifluoroacetic acid, antimony trichloride, boron trifluoride and concentrated phosphoric acid or the like are cited as having the solvent ability for poly(hexamethylene)terephthalamide. But any of them has a controversial point economically, and concentrated sulphuric acid alone is cited as usable for a spinning solvent. A process of spinning fibers by the use of concentrated sulphuric acid is described in French Patent No. 1,300,756. But, when said process is industrialized, the recovery of the acid depends on the concentration process, because sulphuric acid is of non-volatile property, and it is difficult to remove the impurities from the recovered sulphuric acid. Moreover when sulphuric acid is employed on an industrial scale, there arises also a problem on the material of the process equipment.

The present inventors have exercised researches from the aforesaid viewpoint and discovered an advantageous solvent for industrial use and invented a process for producing industrially the molded product advantageously from the spinning solution prepared by the use of said solvent. Hitherto, nitric acid has been regarded as a strong oxidant substance and a process for producing the spinning solution by using nitric acid for a solvent of the said poly(hexamethylene)terephthalamide has not yet been suggested.

However, according to the research results of the inventors, it was discovered that a spinning solution stabilized sufficiently for producing the molded products can be obtained if poly(hexamethylene)terephthalamide is dissolved in an aqueous solution of 65% or more of purified nitric acid, whence nitrous acid is removed, and the resultant solution is retained below the specified temperature. The required concentration of nitric acid which is variable by the average molecular weight of the aforesaid polymer and the compositions of the copolymer and is at least, 65% or more, preferably 70% or more. When the concentration of nitric acid is in the range of 65% to 70%, poly(hexamethylene)terephthalamide is once dissolved in it, and the resultant spinning solution is liable to be separated into two layers in a long period of storage. When the concentration is 70% or more, the spinning solution which is not separated in two layers for storage in the long period can be obtained. Nitrous acid in the aqueous solution of nitric acid is liable to color the spinning solution in yellowish orange and, in this case, the polymer regenerated from said spinning solution is also liable to be colored slightly yellowish. Moreover, nitrous acid acts to depress the molecular weight of polymer in the spinning solution, so that the aqueous solution of nitric acid used in the present invention shall be beforehand purified so as to suppress the concentration of nitrous acid below 0.05%, preferably 0.02%. Furthermore, in the case of storing the spinning solution, its temperature is also important. When it is stored at a high temperature, the velocity of deteriorating the viscosity is more accelerated. In this viewpoint, a temperature of storing the spinning solution shall be below 30° C., preferably 15° C. Various kinds of nitrates such as ammonium nitrate, sodium nitrate, calcium nitrate, magnesium nitrate or the like may be appropriately added in the spinning solution of the present invention.

The polymer which contains 80% or more of the recurring units of poly(hexamethylene)terephthalamide in the process of the present invention means polyamide produced from hexamethylene diamine and terephthalic acid or terephthalic derivatives by the process of solid phase polycondensation or the process of interfacial polycondensation and containing 80% at least of poly(hexamethylene)terephthalamide. Other components contain dibasic acids such as isophthalic acid, adipic acid, and sebacic acid

or dibasic derivatives, diamines such as tetramethylenediamine, pentamethylenediamine, octamethylenediamine, decamethylenediamine, p - xylenediamine, m - xylenediamine, and piperazine, lactams such as caprolactam, aminocarboxylic acids such as 6-aminocaproic acid, 9-aminononylic acid, and 11-aminoundecanoic acid, monocarboxylic acids such as benzoic acid and acetic acid, and monoamines such as benzylamine, monomethylamine, etc.

When poly(hexamethylene)terephthalamide is dissolved at a temperature of 0° C. in the aqueous solution having concentration of 75% of nitric acid purified by aeration or addition of urea so as to contain nitrous acid below 0.01% in conformity to the process of the present invention, almost colorless, transparent spinning solution is obtained. When said spinning solution is stored at the temperature, the viscosity does not change at all after the lapse of 72 hours and poly(hexamethylene)terephthalamide regenerated in the aqueous coagulation bath is purely white. This indicates that said solution has satisfactory stability as a spinning solution.

Suitable for the coagulation bath used for producing the molded products such as fibers, film, etc. from said spinning solution, is an aqueous solution of nitric acid having concentration less than that of an aqueous solution of nitric acid used for producing the spinning solution and enabling to coagulate the spinning solution. According to results of the research of the inventors, the concentration of the aqueous solution of nitric acid is found to be 60% or less and preferably 50% or less. Poly(hexamethylene)terephthalamide is not coagulated in the aqueous solution of 60% or more of nitric acid and the coagulation is generally insufficient in the concentration of 50% to 60%. In this case, various kinds of nitrates such as ammonium nitrate, sodium nitrate, calcium nitrate, magnesium nitrate, aluminium nitrate, zinc nitrate, etc. can be added in the coagulation bath to change the coagulation process.

As processes of the present invention of extruding the polyamide spinning solution into the coagulation bath consisting of aqueous solution of nitric acid, there is a process in which the solution is extruded in the horizontal direction, coagulated and wound up on a roller, a process in which the solution is extruded in the vertically or diagonally downward direction and wound up on a roller through a deviation-rod or a process in which the solution is extruded in the upward or diagonally upward direction from the bottom end of coagulation bath and wound up on a roller. All of those processes mentioned above can be used.

The molded products, coagulated in conformity to the present invention are stretched after being washed by water until nitric acid disappears substantially, but, if necessary, those may be stretched before or during the water detergence. The stretching after the water detergence is exercised by a hot water bath or a steam bath. If necessary, those products are stretched at a high temperature with heated plate or liquid bath of high boiling point.

Films, fibers and other molded products obtained by the process of the present invention are very useful on the practical use. For example, when fibers are produced by the process of the present invention, fibers having various deniers according to uses and having strengths suitable for practical uses can easily be obtained.

Then, examples are cited for explaining the process of the present invention. However, the present invention is not limited by those examples.

The reduced specific viscosity of polyamide in the examples is measured at 35° C., when the polyamide is dissolved in the concentrated sulphuric acid in the 0.5 g./100 ml. concentration.

Example I

Poly(hexamethylene)terephthalamide having 1.31 dl./g. of reduced specific viscosity is dissolved at a temperature of 0° C. in an aqueous solution of 75% of concentration of nitric acid purified so as to contain nitrous acid below 0.01% and the viscous solution was obtained. The viscosities are indicated as follows:

	No. of solution				
	I	II	III	IV	V
Concentration of polymer (g./dl.)	20	24	28	32	36
Viscosity of solution (poises)	37	82	172	298	562

The variations of the viscosities of the solutions in storage at different temperatures are shown below:

	No. of solution				
	I	II	III	IV	V
Temperature for storage (° C.)	0	0	0	15	30
Viscosity of solution (poises):					
Inst. after dissolution	37	82	172	158	155
6 hrs. after dissolution	36	82	171	150	132
24 hrs. after dissolution	37	81	172	129	87
36 hrs. after dissolution	37	82	170	114	64
96 hrs. after dissolution	37	82	173	72	16

The viscosity of solution in storage at 15° C. was deteriorated 20% or more within 24 hrs. after dissolution and the viscosity in storage at 30° C. was deteriorated 20% or more within 7 hrs. (based on the viscosity of the solution instantly after dissolution).

On the other hand, the deterioration of the viscosity of the solution stored at 0° C. was not recognized after 96 hrs.

Example II

Poly(hexamethylene)terephthalamide having 1.24 dl./g. of reduced specific viscosity was added respectively into 78.8% of nitric acid solution containing 0.0003% of nitrous acid, 78.8% of nitric acid solution containing 0.02% of nitrous acid and 78.8% of nitric acid solution containing 0.18% of nitrous acid, so as each resultant solution may keep 25 g./100 ml. of concentration; the first nitric acid solution being purified by aeration and addition of urea. Those resultant solutions were stirred up and dissolved during one night at 0° C. One part of each resultant solution was taken up and regenerated by aqueous coagulation solution and dried sufficiently after water detergence.

The reduced specific viscosities of those regenerated polymers were measured as below:

No. of Solutions	Content of nitrous acid (percent)	Reduced specific viscosity of regenerated polymers (dl./g.)
VI	0.0003	1.235
VII	0.2	1.214
VIII	0.18	0.890

Then, the variations of reduced specific viscosities in relation to hours for the regenerated polymers stored at the different temperatures are shown below:

No. of solutions	Storage temperature (° C.)	Elapsed hour (hr.)					
		0	3	6	12	24	48
VI	0	1.235	1.234	1.233	1.234	1.235	1.243
	15	1.235	1.203	1.155	1.116	1.082	1.034
	35	1.235	1.088	0.882	0.733	0.566	0.384
VII	0	1.214	1.211	1.207	1.201	1.190	1.177
	15	1.214	1.196	1.154	1.102	1.050	1.033
	35	1.214	1.034	0.852	0.729	0.563	0.382
VIII	0	0.890	0.880	0.878	0.850	0.778	0.697
	15	0.890	0.772	0.703	0.632	0.567	0.491
	35	0.890	0.580	0.530	0.451	0.372	0.272

Namely, acceleration of degrading-polymer by nitrous acid in the nitric acid solution and influence of the storage temperature are disclosed, The regenerated polymer of VIII was colored slightly yellowish green.

Example III

Sixty grams of poly(hexamethylene)terephthalamide having 1.22 dl./g. of reduced specific viscosity was added in 200 ml. of 75% of nitric acid, purified so as to contain nitrous acid below 0.01% and the resultant mixture, stirred up and dissolved for 10 hrs., at 0° C. and the spinning solution, colorless, transparent and stabilized was obtained.

Said spinning solution was extruded through fine holes into the aqueous solution of 42% of nitric acid maintained at 15° C. and coagulated and wound up on the roller. Then, the fibers were washed through the water bath until the acid of the fibers disappears substantially, and filaments in favorable whiteness were obtained through drying process and heat stretching process. The obtained fiber had a denier per filament of 3.0, the dry tensile strength was measured as 2.7 g./den. and the dry elongation as 26%.

Example IV

Sixty grams of poly(hexamethylene)terephthalamide having 1.35 dl./g. of reduced specific viscosity was added in 200 ml. of 75% of nitric acid purified so as to contain nitrous acid below 0.01% and the resultant mixture was dissolved at 0° C. during 10 hrs., by being stirred up, and the spinning solution, colorless, transparent and stabilized was obtained. Said spinning solution was extruded through fine holes into the aqueous solution of 44% of nitric acid kept at 0° C. and was coagulated, and was wound up on the roller. Then, it was washed through water bath until the acid disappeared substantially, and filaments in favorable whiteness were obtained through drying and heat stretching processes. The obtained fiber had a denier per filament of 2.9 and dry tensile strength and dry elongation were measured as 3.1 g./den. and 25% respectively.

Example V

Seventy-five grams of poly(hexamethylene)terephthalamide having 1.78 dl./g. of reduced specific viscosity was added in 300 ml. of 80% of nitric acid, purified so as to contain nitrous acid below 0.01% and the resultant mixture was dissolved at 0° C. during 10 hrs., while being stirred up, and the spinning solution, colorless, transparent and stabilized was obtained. Said spinning solution was extruded through fine holes into the aqueous solution of 40% of nitric acid kept at 30° C. and was coagulated therein and wound up on the roller. It was washed through water bath until the acid disappeared substantially, and filaments in the favorable whiteness were obtained through drying and heat stretching processes. The obtained fiber had a denier per filament of 3.0 and the dry tensile strength and the dry elongation were measured as 4.2 g./den. and 22% respectively.

Example VI

Sixty grams of poly(hexamethylene)terephthalamide having 1.56 dl./g. of reduced specific viscosity was added in 200 ml. of 75% of nitric acid, purified so as to contain nitrous acid below 0.01% and the resultant mixture, while being agitated, was dissolved at 0° C. for 10 hrs., and the spinning solution colorless, transparent and stabilized was obtained. The spinning solution was extruded through fine holes into the aqueous solution of 47% of nitric acid, kept at −5° C., coagulated, and wound up on the roller. Then, those fibers were washed through the water bath until the acid disappeared substantially and filaments in the favorable whiteness were obtained through drying and heat stretching processes. The obtained fiber had a denier per filament of 3.1, dry tensile strength and dry elongation were measured as 3.9 g./den. and 25% respectively.

Example VII

Seventy-five grams of poly(hexamethylene)terephthalamide having 1.92 dl./g. of reduced specific viscosity was added in 300 ml. of 80% of nitric acid, purified so as to contain nitrous acid below 0.01% and the resultant mixture, while being agitated, was dissolved at −5° C. for 15 hrs., and the spinning solution, colorless, transparent and stabilized was obtained. The spinning solution was extruded through the fine holes into the aqueous solution of 42% of nitric acid kept at 15° C., coagulated and wound up on the roller. Then, the fibers were washed through the water bath until the acid disappeared substantially, and filaments in the favorable whiteness were obtained through drying and heat stretching processes. The obtained fiber had a denier per filament of 1.45, dry tensile strength and dry elongation were measured as 4.6 g./den., and 11% respectively.

Example VIII

Seventy-five grams of poly(hexamethylene)terephthalamide having 2.1 dl./g. of reduced specific viscosity was added in 300 ml. of 80% of nitric acid, purified so as to contain nitrous acid below 0.01% and the resultant mixture, while being agitated, was dissolved at 15° C. for 5 hrs. The spinning solution, colorless, transparent and stabilized was obtained. The spinning solution was extruded through fine holes into the aqueous solution of 42% of nitric acid kept at 15° C., coagulated and wound up on the roller. Then, the fibers were washed through the water bath until the acid disappeared substantially. Filaments in favorable whiteness were obtained through drying and heat stretching processes. The obtained fiber had a denier per filament of 1.5, dry tensile strength and dry elongation were measured as 5.5 g./den. and 8% respectively.

Example IX

Sixty grams of copolymer, consisting of 90% component of poly(hexamethylene)terephthalamide and 10% component of poly(hexamethylene)adipamide and having 1.30 dl./g. of reduced specific viscosity was added in 200 ml. of 70% of nitric acid purified as to contain nitrous acid below 0.01%, and the resultant mixture was dissolved at 0° C. for 10 hrs. while being agitated, and the spinning solution, colorless, transparent and stabilized was obtained. The spinning solution was extruded through fine holes into the aqueous solution of 35% of nitric acid kept at 15° C., coagulated and wound up on the roller. Then, the fibers were washed through the water bath until the acid disappears substantially, filaments in favorable whiteness were obtained through drying and heat stretching processes. The obtained fiber had a denier per filament of 3.0 and dry tensile strength and dry elongation were measured as 3.2 g./den. and 23% respectively.

Example X

Sixty grams of copolymer consisting of 90% component of poly(hexamethylene)terephthalamide and 10% component of poly(m-xylene)terephthalamide and having 1.36 dl./g. of reduced specific viscosity was added in 200 ml. of 70% of nitric acid, purified as to contain nitrous acid below 0.01%. The resultant mixture was dissolved at 0° C. for 10 hrs., as it was being stirred up, and the spinning solution, colorless, transparent and stabilized was obtained. The spinning solution was extruded through fine holes into the aqueous solution of 35% nitric acid kept at 15° C., was coagulated and wound up on roller. Then, fibers were washed through the water bath until the acid disappeared substantially. The filaments in favorable whiteness were obtained through drying and heat stretching processes. The obtained fiber had a denier per filament of 3.1 and the dry tensile strength and the dry elongation were measured as 2.9 g./den. and 24% respectively.

What is claimed is:

1. A process of spinning fibers which comprises extruding a spinning solution into a coagulating bath of an aqueous solution of nitric acid in the coagulable concentration, the said spinning solution being prepared by dissolving a polymer having 80% or more recurring units of poly

(hexamethylene)terephthalamide at a temperature of 30° C. or less into an aqueous solution of nitric acid, purified so as to contain the 0.05% or less concentration of nitrous acid.

2. A process of spinning fibers which comprises extruding a spinning solution into a coagulating bath of an aqueous solution of 60% concentration or less of nitric acid, the said spinning solution being prepared by dissolving and storing a polymer having 80% or more recurring units of poly(hexamethylene)terephthalamide at a temperature of 30° C. or less in an aqueous solution of 65%

concentration or more of nitric acid, purified so as to contain 0.05% or less of nitrous acid.

References Cited

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