

1

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POLYAMIDE FIBERS CONTAINING LUBRICANT
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ABSTRACT OF THE DISCLOSURE

The lubricity of polyhexamethylene adipamide is improved by incorporating into the polymer from 0.1 to 2.5 mole percent of either N,N'-hexamethylene bis-stearamide or 12-hydroxy stearic acid.

Fibers obtained from the homopolymer prepared from the reaction of hexamethylene diamine and adipic acid (nylon 66) have obtained commercial importance and success. Although these fibers have much to commend them, there is still need and room for new and improved properties. It is known that this conventional polyamide is very hard and crystalline and quite difficult to handle in friction producing operations. For this reason and because end-uses such as tire cord, ropes and cordages are greatly benefited by a reduced yarn-to-yarn friction, a permanent low-friction property as a characteristic of the polymer is highly desirable.

Presently, in the commercial production of nylon 66 fibers, the as-spun filaments are given a treatment to improve their lubricity and handling properties. This treatment usually consists of passing the filaments, while in a bundle, through a bath of or over a wheel coated with the treating or finishing liquid. The finished, thus received by the filaments, is nothing more than a coating, and is not of a permanent nature. Most, if not all, of the lubricating agent contained within the finish bath, is lost in subsequent processing of the filament such as by mechanical handling, heating, washing, scouring, and dyeing. If the finish does remain on the fiber until the final end-product is produced, it often becomes less effective after the end-product is used for periods of time.

Therefore, what is needed is a lubricating agent of a permanent nature; one that is incorporated directly into the polymer and the fibers produced therefrom, in lieu of being merely coated on the outside of the produced filaments. If an improvement of a permanent nature such as this could be obtained, it would lead to significant reductions in yarn processing difficulties and subsequent increased end-product quality. Such an improvement would cause large reductions in fiber-to-fiber friction and thus increase the maximum strength and life obtainable in tire cords, ropes and cordages.

Accordingly, it is an object of the present invention to provide a modified polyhexamethylene adipamide polymer and fibers produced therefrom which possess high lubricity characteristics.

This and other objects and advantages will become apparent in the course of the following detailed description of the invention and the claims appended thereto.

In general, these objects are attained in accordance with this invention, by adding a modifying agent to the polymer forming reactants during the course of polymerization. The modifying agent is a compound selected from the group consisting of stearamide, 12-hydroxy stearic acid, and N,N'-hexamethylene bis-stearamide; and is used in an amount of from 0.1 to about 2.5 mole percent (based on the number of moles of the polyamide forming monomer). The preferred concentration of the modifying agent to be used is from 0.25 to 1 mole percent.

2

The modified polyamides described herein are prepared by procedures well known in the art and commonly employed in the manufacture of unmodified nylon 66 polymers. That is, the reactants are heated at a temperature of from 180° C. to 300° C., and preferably from 200° C. to 295° C. until the product has a sufficiently high molecular weight to exhibit fiber-forming properties. This condition is reached when the polyamide has an intrinsic viscosity of at least 0.4, the intrinsic viscosity being defined as:

$$C \rightarrow O \left(\frac{\log_e N_r}{C} \right)$$

in which N_r is the relative viscosity of a dilute solution of the polymer in m-cresol in the same units and at the same temperature and C is the concentration in grams of polymer per 100 cc. of solution. The reaction can be conducted at super-atmospheric, atmospheric, or sub-atmospheric pressure. Often it is desirable, especially in the last stage of the reaction to employ a reduced pressure to aid removal of the reaction by-product. Preferably, the reaction is carried out in the absence of oxygen, e.g., in an atmosphere of nitrogen. The hexamethylene diamine and adipic acid polyamide forming reactants are normally introduced into the autoclave as a preformed salt, but may be uncombined when added. The modifying agent or additive may be added to the polymerization reaction at most any point, that is, it may be added to the autoclave with the polyamide forming reactants, it may be added during the polymerization reaction, or it may be added late in the polymerization during the final finishing stages. The resulting polymers may be formed into fibers by conventional spinning and drawing procedures.

In addition to the afore-described modifying agents, delustrants, anti-oxidants, plasticizers, viscosity stabilizers, chain terminators, and other like materials may be used in the preparation of the polyamides of this invention.

In order to illustrate the invention and advantages thereof with greater particularity the following specific examples are given. It should be understood that they are intended to be only illustrative are not intended to limit the invention in any way. Parts and percentages are given by weight unless otherwise indicated.

Example I

A solution of 0.748 moles of hexamethylenediammonium adipate (nylon 66 salt) dissolved in 5.78 moles of water was added to a stainless steel evaporator into which had previously been placed 0.25 mole percent (based on the number of moles of the polyamide forming monomer) of stearamide. The evaporator had previously been purged of air with purified nitrogen and was so positioned that the contents thereof could be piped into a high pressure autoclave when desired. The solution was then heated under a nitrogen blanket at a pressure at 13 p.s.i.g. with the continuous removal of steam condensate until the solution reached the temperature at 137° C. At this point, the salt solution was charged to a stainless-steel high-pressure autoclave which had previously been purged of air by the use of purified nitrogen. The temperature and pressure were slowly raised until values of 220° C. and 250° p.s.i.g., respectively, were reached. The temperature was then further increased to 243° C. with the pressure being maintained at 250 p.s.i.g. by the removal of steam as condensate. At this point the pressure reduction cycle began. The pressure was gradually reduced to atmospheric over a 25 minute period and the polymer melt was allowed to equilibrate for 30 minutes at 278° C.

Upon completion of the reaction the finished polymer, which had a relative viscosity of 31.9, was melt spun directly from the autoclave through a 10-hole spinneret to

yield a white multi-filament yarn. Upon being drawn at a draw ratio of 5.65:1, this yarn of 9.4 denier per filament exhibited a tenacity of 7.8 grams per denier at an elongation of 27 percent.

Example II

A batch of polymer was prepared following the technique and procedures set forth in Example I with the exception that 0.75 mole percent (based on the moles of polyamide forming monomer) of stearamide was used in lieu of 0.25 as in Example I.

The finished polymer thus obtained had a relative viscosity of 26.4. The molten polymer was extruded directly from the autoclave through a 10-hole spinneret yielding a white, multi-filament yarn. This yarn was subsequently drawn at a draw ratio of 5.85:1 and had a measured elongation of 22 percent, a tenacity of 8.1 grams per denier, and a denier of 10.9 denier per filament.

Example III

The following materials were added to a stainless-steel evaporator which had previously been purged of air with purified nitrogen: 0.748 moles of hexamethylenediammonium adipate, 0.25 mole percent of N,N'-hexamethylene bis-stearamide, and 5.78 moles of water. This evaporator was so positioned that the contents thereof could be piped into a high-pressure autoclave when desired. The solution in the evaporator was then heated under a nitrogen blanket at a pressure of 13 p.s.i.g. with the continuous removal of steam condensate until the solution reached the temperature of 137° C. At this point the salt solution was charged to a stainless-steel high-pressure autoclave which had previously been purged of air by the use of purified nitrogen. The temperature and pressure were slowly raised until values of 220° C. and 250 p.s.i.g., respectively, were reached. The temperature was further increased to 240° C. with the pressure being maintained at 250 p.s.i.g. by the removal of steam as condensate. At this point the pressure reduction cycle began. The pressure was gradually reduced to atmospheric over a 25 minute period and a polymer melt was allowed to equilibrate for 30 minutes at 278° C.

Upon completion of this polymerization reaction, the resulting polymer, which had a relative viscosity of 28.0, was extruded directly from the bottom of the autoclave through a 10-hole spinneret to yield a white multi-filament yarn. When drawn at a draw ratio of 5.8:1 this yarn of 10.2 denier per filament exhibited an elongation of 22.4 percent.

Example IV

A batch of polymer was prepared in the manner identical to that employed in Example III except that 0.35 mole percent of N,N'-hexamethylene bis-stearamide was used. The finished polymer thus obtained had a relative viscosity of 24.8.

This polymer was then melt extruded directly from the bottom of the autoclave through a 10-hole spinneret to yield white multi-filament yarn. This yarn was then drawn at a draw ratio of 6.05:1. The drawn yarn had a denier of approximately 8.3 denier per filament and exhibited an elongation of 20.4 percent.

Example V

A solution of 0.748 moles of hexamethylenediammonium adipate dissolved in 5.78 moles of water was added to a stainless-steel evaporator into which had previously been placed 0.50 mole percent of 12-hydroxy stearic acid. This evaporator which had previously been purged of air with purified nitrogen was so positioned that the contents thereof could be piped into a high-pressure autoclave when desired. The contents of the evaporator were then heated under a nitrogen blanket at a pressure of 13 p.s.i.g. with the continuous removal of steam condensate until the solution reached a temperature of 137° C. At this point, the salt solution was charged to a stainless-

steel high-pressure autoclave which had previously been purged of air by the use of purified nitrogen. The temperature and pressure within the autoclave were slowly raised until values of 220° C. and 250 p.s.i.g., respectively, were reached. The temperature was then further increased to 243° C. while the pressure was maintained at 250 p.s.i.g. by the removal of steam as condensate. At this point the pressure reduction cycle was begun. The pressure was gradually reduced to atmospheric over a 25 minute period and the polymer melt was allowed to equilibrate for 30 minutes at 278° C.

Upon completion of this polymerization reaction the resulting polymer, which had a relative viscosity of 24.5, was melt spun directly from the bottom of the autoclave through a 10-hole spinneret to yield a white multi-filament yarn. The yarn which was subsequently drawn at a draw ratio of 5.8:1 exhibited a tenacity of 8.6 grams per denier, a denier of 10.8 denier per filament, and an elongation of 21 percent.

Example VI

Polymer was prepared by employing procedures and techniques identical to those used in Example V, except that 1.0 mole percent of 12-hydroxy stearic acid was used in lieu of 0.5 mole percent as in Example V. Also in this Example, a vacuum of 100 mm. of mercury was applied to the polymerization reaction during the final 30 minute polymer holding or finishing cycle in order to increase the relative viscosity of the final polymer.

The polymer having a relative viscosity of 25.9 was melt spun directly from the bottom of the autoclave through a 10-hole spinneret to yield a white multi-filament yarn. This yarn was drawn 5.95 times its original length to a measured tenacity of 7.4 grams per denier at an elongation of 21 percent and a denier of 10.6 denier per filament.

The filaments obtained in the above examples were closely examined and compared with filament obtained from the standard unmodified polyamide nylon 66. The filaments of this invention exhibited a much more waxy or lubrid feel to the hand than those prepared from the standard, unmodified nylon 66 polymer. Additionally, a high lubricity was evidenced by the ability of the fibers to slide freely over one another in bundles.

As previously noted, the products obtained in the practice of this invention are particularly useful in the manufacture of tire cords, ropes, and cordages where polyamide filaments having a low fiber-to-fiber friction are especially desirable. The products obtained in the practice of this invention may also be used to advantage in the manufacture of fabrics, film and the like where the ultimate end-use intended would be benefited by the employment of a polymer having high lubricity characteristics.

This improvement in lubricity has been obtained without degradation of other physical properties. This is to say, the physical properties such as tenacity and elongation, of the fibers produced in accordance with this invention have been maintained at the same desirable levels as those exhibited by the standard commercially successful polyamide nylon 66.

As many different embodiments would readily occur to those skilled in polymer chemistry, it is to be understood that the specific embodiments of the invention as presented herein are not to be construed as limiting, but that the limitations are to be determined only from the appended claims.

Having thus described my invention in detail, what I claim as new and desire to secure by Letters Patent is:

1. A fiber-forming synthetic linear polyamide, which comprises, the product obtained by reacting at a temperature of between 180° C. and 300° C., reactants comprising, (A) a polypimide forming monomer consisting of the salt formed by substantially equimolecular portions of adipic acid and hexamethylene diamine, and (B) from 0.1 to about 2.5 mole percent based on the moles of (A)

5

of an additive selected from the group consisting of N,N'-hexamethylene bis-stearamide, and 12-hydroxy stearic acid.

2. The fiber-forming synthetic linear polyamide as set forth in claim 1, wherein said additive is present in an amount of from 0.25 to 1.0 mole percent based on the moles of the polyamide forming monomer. 5

3. The fiber-forming synthetic linear polyamide as set forth in claim 2 wherein said additive is 12-hydroxy stearic acid. 10

4. The fiber-forming synthetic linear polyamide as set forth in claim 2 wherein said additive is 12-hydroxy stearic acid.

5. A textile fiber comprising the polyamide as defined in claim 2. 15

6

References Cited

UNITED STATES PATENTS

2,174,527	10/1939	Peterson	260—78
2,252,554	8/1941	Carothers	260—78
2,252,555	8/1941	Carothers	260—78
2,265,119	12/1941	Coolidge	260—31.8
3,009,900	11/1964	Hasen	260—18
3,156,750	11/1964	Cuculo	260—18

FOREIGN PATENTS

1,130,160	5/1962	Germany.
945,659	7/1956	Germany.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, lines 9 and 10, for "12-hydroxy stearic acid" read -- N,N'-hexamethylene bis-stearamide --.

Signed and sealed this 29th day of April 1969.

SEAL)

test:

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Commissioner of Patents