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PROCESS OF PRODUCING SYNTHETIC LINEAR POLYAMIDE FILAMENTS

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This invention relates to the processing of shaped articles, particularly large filaments prepared from synthetic linear polyamides.

The most suitable string for tennis and squash rackets and the like has heretofore been prepared from the natural gut of sheep and hogs. Such material has several inherent disadvantages. Conditions of high humidity may cause softening or breaking. The filaments are not true monofils and consequently tend to shred upon being sharply bent or when subject to abrasion. Filaments prepared from synthetic linear polymers have been suggested for the above uses, and their properties of tensile strength and resiliency recommend them for this purpose. However, filaments which have been prepared and conditioned in the conventional manner have not been entirely satisfactory because of their poor resistance to the shock of sudden impacts. Furthermore, it is desired to develop a material that can be used as a tire cord. Such a product must have low thermo-extensibility factor; that is, while in service it should not tend to elongate permanently. Cords made from synthetic linear polyamides without additional treatment have been found to have a thermo-extensibility factor which renders them undesirable for this use.

This invention has as its object the development of a new and improved process for the treatment of synthetic linear polyamides which are in filament form. Another object is to develop a process by which synthetic linear polyamide filaments may be treated so as to improve their resistance to sudden impact. Still another object is to develop a process for the treatment of filaments of synthetic linear polyamides whereby said filaments are greatly improved as to their resistance to the fatigue of repeated impacts applied in a direction transverse to the length of the filaments. Still another object is to provide a new and improved process for the treatment of filaments of synthetic linear polyamides so as to improve the thermo-extensibility factor of said filaments. Another object is to provide a new and improved process for the treatment of large monofilaments of polyhexamethylene sebacamide. Other objects will be apparent from the following description of the invention.

These objects are accomplished by the following invention which comprises soaking an oriented filament of the synthetic linear polyamide in a solution of a phenol in a solvent that is a non-solvent for said filament and subsequently heating said filament in water. The concentration of the phenol solution and the time of soaking of the filament in the phenol solution are so regulated that the filament (water saturated) absorbs at least 4% of its weight of the solution but does not absorb enough to become sticky or to dissolve. In general, the filament does not become sticky unless the concentration of the phenol is so high that the filament undergoes more than a 30% increase in weight. The optimum conditions of concentration and time are those which result in a 5 to 25% increase in weight of the filament.

The exact manner of practicing this invention may vary depending upon the particular filaments processed and upon the results to be desired; however, the following will illustrate its application.

Filaments of polyhexamethylene sebacamide having a viscosity in excess of 600 poises at 285° C. (preferably at least 1000 poises) are soaked in water for a day or more prior to cold drawing and for a day or more after cold drawing, following which they are soaked in a 3 to 9% phenol solution in water for approximately 10 minutes at a temperature of 75° to 80° C. Following the soaking in phenol the filament is boiled in water for approximately two hours and then dried in air at an elevated temperature, preferably between about 55° and 65° C. When it is primarily desired to increase the impact strength of this filament the process is applied to the filament while the filament is in the relaxed state, whereas when it is primarily desired to decrease the tendency to undergo permanent elongation or growth then the process is applied to the filament while the filament is under tension.

The synthetic polymeric materials used in the practice of this invention are synthetic linear polyamides of the general type described in U. S. Patents 2,051,250, 2,071,251, 2,071,253, and 2,130,948. The polyamides of this kind, generally speaking, comprise the reaction product of a linear polymer-forming composition, for example, one consisting essentially of bi-functional reacting material which comprises in substantial amount molecules containing two amide-forming groups, each of which is complementary to an amide-forming group in other molecules in said composition. The synthetic linear polyamide can be obtained, for example, by self-polymerization of monoaminocarboxylic acids or by reacting a

diamine with a dibasic carboxylic acid in substantially equimolecular amounts, it being understood that reference herein to amino acids, diamines, and dibasic carboxylic acids is intended to include the equivalent amide-forming derivatives of these reactants. On hydrolysis with hydrochloric acid, the polyamides revert to the amino acid or diamine and dibasic carboxylic acid from which they are derived, the amino acid and diamine being obtained in the form of their hydrochlorides.

As described in the above mentioned patents, the high molecular weight synthetic polyamides may be formed into useful filaments which, upon application of tensile stress, are permanently stretched or "cold drawn" into pliable strong fibers which show by characteristic X-ray diffraction patterns that they are microcrystalline in structure and are oriented along their fiber axes. Orientation may also be effected by the application of compressive stress such as that which takes place in the process of cold rolling as described in Miles, U. S. Patent 2,244,208, or by a combination of tensile and compressive stresses such as take place in die drawing which is described in the application of M. M. Brubaker, Serial No. 284,556, filed July 14, 1939.

The properties of filaments prepared from these polyamides depend to a large extent upon the conditions under which they are prepared. Filaments prepared by the extrusion of the molten polymer are generally rapidly cooled or "quenched" as described in the Graves U. S. Patent 2,212,772. Fibers which have been adequately quenched usually have an improved degree of toughness and pliability and can be cold drawn with less breakage.

The conditioning treatment which is given to filaments, sheets, or other shaped articles after orientation is another important factor in determining their properties.

This invention described new and useful products which are prepared by subjecting oriented filaments prepared from synthetic linear polyamides to the swelling action of aqueous phenol, following by heat treatment, preferably in boiling water, and drying to remove residual phenol. During such conditioning the filament tends to shrink, internal stresses are relieved, and the crystal structure becomes more nearly perfect (as evidenced by X-ray diffraction patterns).

This treatment results in substantial increases in the ability of the filaments to withstand sudden impacts and in resistance to the type fatigue caused by repeated impacts. Such conditioning, if too severe, also tends to lower the tensile strength and increase the elongation at break. It is thus desirable to regulate the factors of time, temperature, and concentration as well as the degree of orientation of the filaments (draw ratio) so as to obtain an optimum balance of impact strength, tensile strength, and elongation. I have found that in order to be satisfactory in regard to durability and playing characteristics, the tennis racket strings prepared from a synthetic linear polymer should have a tensile strength of at least 80 pounds and preferably above 100 pounds to avoid breaking during stringing, and elongation of less than 50% and preferably less than about 35% to facilitate stringing and avoid cold flow during storage or use, and a knot impact strength of at least about 30 in. lbs. (by the test described in Example II) and preferably about 50 in. lbs. or higher to avoid breaking during play. Although satisfactory tensile values are readily obtained with monofils or polyfils of polymers such as polyhexamethylene sebacamide, conditioning by the process described herein is the most satisfactory method which has been found by which a filament can be obtained having a practical combination of these properties. The following examples are illustrative of the invention.

EXAMPLE I

A sample of polyhexamethylene sebacamide having a viscosity of 1000 poises at 285° C. was extruded and quenched in the usual manner to form a filament having a diameter of 117 mils.; i. e., 0.117 inch. After soaking in water for several days at room temperature the filament was drawn through a two-foot column of water at 60° to 70° C. and then through a nest of Carboloy wire drawing dies at the same temperature. The minimum bearing diameters of the dies were 85, 65 and 55 mils, respectively, and the resulting drawn filament had a diameter of 54 mils.

A section of the drawn filament was immersed in a 4.8 per cent solution of phenol in water for a period of 48 hours. The increase in weight was 20.7 per cent. After removal of the phenol by heating in an oven for 20 hours at 85° to 90° C. this filament had a knot impact strength of 60 in. lbs. A sample of the same material which was not treated with phenol but was conditioned for 15 minutes in saturated steam at 152° C. as described in my application Serial No. 327,735 had an impact strength of 29 in. lbs. and the unconditioned material had an impact strength of 7 in. lbs.

EXAMPLE II

A filament of polyhexamethylene sebacamide spun from melt through a spinneret having a 127 mil orifice was fed directly into a bath of cold water in which it was guided a vertical distance of 24 inches before passing around a cylindrical guide and to the top of the bath from which it was removed by passing between rubber-faced pinch rolls. The diameter of the filament was controlled by regulating the speed of the spinning pump and that of the pinch rolls. By this means a filament was obtained which had an average diameter of 108 mils; i. e. 0.108 inch. A sample of this polymer, as extruded, had a viscosity of 870 poises at 285° C.

After the filament had soaked for several days in water at room temperature it was drawn by passing through hot water for a short distance and then directly through a nest of four Carboloy wire-drawing dies having bearing diameters of 85, 65, 52 and 49 mils, respectively. The resulting filament had a diameter of 49.7 mils.

A sample of the filament, after soaking in water for several days, was conditioned in the relaxed state by immersing, first for a few seconds in boiling water to prevent precipitation of phenol on the surface, then for 10 minutes in a 7 per cent solution of phenol in water (i. e., 524 parts of 88 per cent phenol+6000 parts of water) at 75° to 80° C., and finally for two hours in boiling water, the water being changed after the first half-hour of boiling to facilitate the removal of phenol. The filament was then dryed in an oven for three days at 60° C. The resulting filament, when tested at 25° C. and 50 per cent relative humidity, had a tensile strength of 120 lbs. (4.0 g./den.), a break elongation of 33 per cent, and a knot impact strength of 87 in. lbs.

The impact strengths described herein were determined with the aid of the Olsen pendulum-type impact tester. In this test the sample is tied in a simple overhand knot and held across a 3" gap under a 26 lb. tension. The pendulum is dropped from a fixed height and the energy required to break the sample is read directly in inch pounds. This test gives a good indication of the ability of the filament to withstand blows and impacts such as are exerted on tennis and squash racket strings during play.

EXAMPLE III

A filament extruded and drawn as in Example II was boiled in water for two hours while wound tightly on a smooth metal bobbin so that no shrinkage could take place. At the end of this time it was removed from the bobbin and the loosely wound co. was immersed for 10 minutes in 7 per cent phenol at 75° to 80° C., then removed, boiled for two hours in a large volume of water, and air dried to remove residual phenol. The resulting filament had a break strength of 125 pounds (4.4 g./den.), an elongation at break of 27 per cent, and a knot impact strength of 69 in. lbs.

Comparable results were obtained by conditioning the water-saturated, preheated filament for 10 minutes in 7% phenol at 75° to 80° C. and in the relaxed state, followed by winding on a bobbin before the two-hour boiling period in water.

EXAMPLE IV

A section of the filament which was extruded and drawn as described in Example II was wound tightly on a smooth metal bobbin and conditioned for 10 minutes in 7 per cent phenol at 75° to 80° C. followed by a two-hour boil in water and air drying in a 65° oven. The resulting filament had a tensile strength of 110 lbs. (4.0 g./den.), a break elongation of 20%, and a knot impact strength of 31 in. lbs.

EXAMPLE V

A section of polyhexamethylene sebacamide filament, the extrusion and drawing of which is described in Example II, was immersed for 10 minutes in a 3 per cent aqueous solution of o-cresol at 95° to 100° C., followed by a 2-hour boil in a large volume of water, and eventual air drying. The knot impact strength of the resulting filament was above 100 in. lbs.

EXAMPLE VI

Samples of oriented, polyhexamethylene sebacamide, the extrusion and drawing of which was described in Example II, were conditioned by immersing for 10 minutes in aqueous resorcinol solutions at about 75° C., followed by boiling in water for one hour and then leaching with water at room temperature for 24 hours and air drying at 25° C. The knot impact strengths of these samples are shown below:

Per cent resorcinol in conditioning solution	Knot impact strength of sample (51 mils diameter)
5	12
15	23
18	37
21	36
25	57

EXAMPLE VII

The improvement in impact strength of a 15 mil, tension drawn, polyhexamethylene adipamide filament, upon being conditioned in a relaxed state in aqueous phenol is shown in Table I below. All samples were boiled in water and dried to remove residual phenol after treatment.

TABLE I

Treatment of polyhexamethylene adipamide with aqueous phenol for five minutes at 75° to 80° C.

Phenol concentration (per cent)	Knot impact strength in inch pounds (2 lb. tension)	Tensile (g./den.)	Break elong. (per cent)
Control (2 hr. boil in water)	3.4	3.5	35
1	4.2	3.3	33
3	5.0	3.3	48
5	>10.0	2.6	96
7	Sample softened and adhered.		

EXAMPLE VIII

An 850 denier polyhexamethylene adipamide yarn was wound on a bobbin under a tension of 2.5 grams per denier and immersed in a 4% solution of phenol in water for five minutes. After removal from the phenol solution, the bobbin containing the yarn was immersed in boiling water for one hour and then dried at 65° C. for 24 hours. The resultant yarn had a thermo-extensibility factor of 0.25 as compared with 0.6 for the original yarn.

The thermo-extensibility factor is determined by loading the yarn at 135° C. to the extent of one gram per denier and measuring the unit increase in length after 30 minutes and again after 1000 minutes, the difference being expressed in per cent elongation. The thermo-extensibility factor is:

$$\frac{\left(\frac{L_{1000}-L_{30}}{L_0}\right)100}{\log. 1000-\log. 30}$$

where L_{1000} is the length of the yarn after 1000 minutes, L_{30} is the length after 30 minutes, and L_0 is the length at the time of loading.

The numerical value of the thermo-extensibility factor for a yarn or cord will depend to a considerable extent on the twist and cord construction. In general, a highly twisted yarn or cord will have a higher thermo-extensibility factor than a similar untwisted yarn or cord. To eliminate the effects of twist, therefore, comparative tests on yarns or cords should be made on untwisted products.

EXAMPLE IX

Two samples were prepared by winding plied polyhexamethylene adipamide yarn on a bobbin under a tension of 2.5 grams per denier. These were immersed in 4 per cent phenol solution for 5 minutes and then extracted with water at room temperature for 24 hours. The yarn was then allowed to return to equilibrium at 75% relative humidity and the physicals obtained. The thermo-extensibility factor for this yarn was .22.

By comparison a yarn treated in the same manner in which the phenol was extracted with hot water had a thermo-extensibility factor of .17. These results may be compared to the yarn which has not received the phenol treatment. This yarn in both instances prior to treatment

had a thermo-extensibility factor of .52. This experiment indicates that it is possible to reduce the plied growth to less than half its original value with the room temperature treatment.

Oriented filaments or ribbons prepared from synthetic linear polyamides and interpolyamides other than those described above may be conditioned by this process. Among the polyamides which have been found to be particularly useful for the purposes of this invention are the interpolymers prepared from sebacic acid, adipic acid, and hexamethylenediamine, and polyamides or interpolyamides containing azelaic acid and/or decamethylenediamine as ingredients. Interpolyamides derived from a mixture of amino acids or from a mixture comprising amino acid, diamine and dibasic carboxylic acid can also be used. Interpolymers obtained by polymerization of polyamide-forming compositions in admixture with other linear polymer-forming compositions, as for instance, glycol-dibasic acid mixtures in the case of polyester-amides, are also operative in the process. It is within the scope of this invention to condition filaments prepared from polymers within the classes described herein which have been modified by the addition of plasticizing agents, resins, cellulose derivatives, antioxidants, dyes, pigments, or fillers. Resins of the type obtained by treating phenol or its alkylated derivatives, such as p-tertiary butylphenol or o-cyclohexylphenol, with formaldehyde are particularly useful. Low molecular weight nonheat-hardening phenol-formaldehyde resins obtained by using formaldehyde and the phenol, e. g., o-cyclohexylphenol, in a ratio of 0.7 or less are used to advantage since they are more compatible with the polyamides than higher molecular weight resins. Addition of phenol-aldehyde resin to the polyamides increases the water resistance and stiffness of the filaments.

Although the preferred treatment is with aqueous phenol having a concentration of greater than 3 and of not more than 9%, substituted phenols such as o-cresol or polyhydric phenols such as resorcinol have been found to be useful. With these other agents the optimum conditions of concentration and time and temperature of treatment are not identical with those established for phenol. Their behavior in this respect appears to depend upon such factors as solubility and distribution coefficients. Likewise, the optimum concentration of phenol for conditioning may be different for different polyamides.

The phenol solvent need not necessarily be water. Any solvent for the phenol which is a non-solvent for the polyamide may be used. Alcohols in general may be used unless the particular polyamide is of the alcohol-soluble type. It should be pointed out, however, that a change in solvent will bring about a change in the distribution coefficient and consequently the effective concentrations of the phenol in the solvent will change with the different solvents, used; for example, polyhexamethylene sebacamide absorbs phenol much less readily from ethanol than from water. When using solvents other than water, other phenol derivatives may be used in place of those noted above; for example, chlorophenol, nitrophenol, aminophenol or higher alkylated phenols, or monoethers of dihydroxy or trihydroxy phenols, or salicylic acid may be used.

As already indicated, boiling water is preferably used in treating the phenol-swollen filaments to improve their impact strength. Water at lower temperatures, e. g., as low as 70° C., is also effective but requires a longer treatment. Hot alcohols and other liquids which are solvents for the phenol but non-solvent, mild swelling agents for the filament can be used in place of water.

Although boiling in water followed by drying in air or inert gas or in vacuum is the preferred method for removing the phenol from filaments treated in accordance with the process of this invention, other methods of removing the phenol from the heat treated filament, e. g., extraction with alcohol or dilute caustic, can be used.

Although somewhat higher impact strengths are generally obtained by treatment in the relaxed state, this invention is not limited to these conditions. As already indicated, operating under tension is desirable if improvement in thermo-extensibility factor is the effect desired. Operating under tension also leads to a product of increased stiffness. Thus the modulus of elasticity, i. e., stiffness, is markedly increased when the winding tension preparatory to the treatment is about one gram per denier or greater. This effect is especially pronounced in the case of filaments which have been drawn to diameter ratios appreciably below 0.50. Likewise, if a portion or all of the conditioning operation described herein is carried out while the filament is wrapped on a bobbin or otherwise held under tension, the resulting product generally has a lower break elongation, a higher modulus of elasticity, and a lower thermo-extensibility factor than does a like filament which has been conditioned in the relaxed state. For conditioning racket string under tension a somewhat more exact control of operating conditions, including draw ratio, is required. Somewhat less extensive drawing is desirable if the complete conditioning is carried out without relaxation of the filament.

The effects of variation in the phenol concentration on the conditioning of a 16 gage oriented polyhexamethylene sebacamide filament (51 mils in diameter) which was prepared in the usual manner from polymer having a viscosity at 285° C. of 1230 poises and drawn to 0.46 of its original diameter, are illustrated in Table II below. There samples were boiled in water and dried at 60° C. after the phenol treatment.

TABLE II

Conditioning polyhexamethylene sebacamide filaments for 15 minutes in aqueous phenol at 75° to 80° C.

Phenol concentration, per cent	Tensile		Break elong. (per cent)	Knot impact (in. lbs.)
	Pounds	G./d.		
Untreated control	120		16	7
3.2	92	2.8	20	25
5.1				70
7.1	90	2.4	36	>100
8.0	90	2.5	56	97
9.0	70	1.8	40	84
11.0	Surface softened so that adhesion took place.			

Since a filament having a knot impact strength, as described in Example II, of less than 30 in. lbs. is unsatisfactory for use in tennis or squash rackets it may be inferred, from the data in Table II that satisfactory conditioning of such polyhexamethylene sebacamide filaments by the preferred process described herein is limited to treatment with aqueous phenol solutions having a concentration of more than three per cent and of not more than 9 per cent. During the brief

treatment the filaments generally absorb a quantity of phenol from aqueous solution equivalent to from 4 to 30 per cent of their weight; consequently the relative quantities of aqueous phenol and filament must be so regulated that the bath does not become exhausted below the concentration of effective treatment, especially when successive lots of filament are treated with the same solution.

The time and temperature of treatment are not highly critical. Satisfactory properties have been obtained after treatments ranging from 1 to 15 minutes or longer in aqueous phenol having an initial concentration of 7 per cent and at temperatures of about 25° C. to 100° C., however at the lower temperatures, at which the phenol solution is more nearly saturated, there is some tendency for the phenol to precipitate on the surface of the filament, causing adhesion or etching.

The presence of water or other materials in the filaments influences the rate of absorption of the phenol from the water, and in order to more easily maintain uniformity in my preferred process the filaments are stored under water prior to conditioning.

The process described herein is not limited to filaments. For example, tubing can be drawn and conditioned as described above. Such tubing can be prepared by extrusion of molten polyamide from an annular orifice, followed by removal from the quenching bath at a rate of 2 to 10 times as fast as the linear speed of the polymer through the orifice, resulting in a tubing of appreciably smaller inside and outside diameter than that of the orifice from which it is spun.

The process described herein covers the phenol conditioning of synthetic linear polyamide filaments with or without tension. From the standpoint of improving the knot impact strength, conditioning without tension is preferred whereas conditioning under tension is preferred from the standpoint of decreasing the thermo-extensibility factor. If it is desirable to increase the stiffness of the filament a tension of at least one gram per denier is desirable.

The process may also be applied to yarns, thread, cordage, woven or knitted fabrics, sheets, or ribbons. It is especially useful for the treatment of fabrics or filaments which must withstand sudden and repeated strains, as in the case of tire cord, parachute cloth, parachute shroud lines, and sewing thread.

Filaments processed in the manner described in this invention, especially those ranging from 30 to 70 mils in diameter, are useful as strings for tennis, squash, and badminton rackets. Large filaments can also be used as tire cords in place of yarns.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not to be limited to the specific embodiments shown and described.

I claim:

1. The process which comprises treating an oriented synthetic linear polyamide filament with a solution of a phenol in a non-solvent for the filament, said solution being of insufficient concentration to dissolve the filament, and subsequently removing said phenol from said filament by heating said filament in a solvent for the phenol which is a non-solvent for the filament to a temperature of at least 70° C.

2. The process in accordance with claim 1 characterized in that the filament is in the relaxed state during treatment and subsequent heating.

3. The process in accordance with claim 1 characterized in that tension is applied to the filament during treatment and subsequent heating.

4. The process in accordance with claim 1 characterized in that a tension of at least one gram per denier is applied to the filament.

5. The process in accordance with claim 1 characterized in that the polyamide is polyhexamethylene sebacamide.

6. The process which comprises treating an oriented synthetic linear polyamide filament with a solution of a phenol in a non-solvent for the filament, said solution being of insufficient concentration to dissolve the filament and subsequently removing the phenol from said filament.

7. The process in accordance with claim 6 characterized in that tension is applied to the said filament during the first treating step.

8. The process which comprises treating an oriented synthetic linear polyamide filament with a solution of a phenol in a non-solvent for the filament, said solution being of insufficient concentration to dissolve the filament and subsequently removing the phenol from said filament while applying tension to said filament.

9. The process in accordance with claim 6 characterized in that tension is applied to said filament during the treating step and during the subsequent step in which the phenol is removed.

10. The process which comprises soaking an oriented synthetic linear polyamide filament in a solution of phenol in a non-solvent for the filament, said solution being of insufficient concentration to dissolve the filaments and of such a concentration that the filament absorbs from 4 to 30% of its weight of said solution, and thereafter heating the swollen filament in water and subsequently drying.

11. The process in accordance with claim 10 characterized in that the filament is soaked in an aqueous phenol solution containing from 4 to 9% phenol.

12. The process for the production of an improved filament of oriented synthetic linear polyamide which comprises forming the polyamide filament, soaking the filament thus formed for at least a day in water, cold drawing said filament, and soaking said cold drawn filament in water for at least a day, then soaking the cold drawn filament in an aqueous phenol solution containing from 4 to 9 per cent phenol for about 10 minutes at a temperature between 75° and 80° C., thereafter heating the filament in a relaxed condition in boiling water for approximately two hours and drying in air at a temperature between 55° and 65° C.

13. The process in accordance with claim 12 characterized in that the polyamide is polyhexamethylene sebacamide.

14. The process which comprises soaking a monofil of an oriented synthetic linear polyamide, said monofil having a diameter between 25 and 70 mils, in an aqueous phenol solution containing from 4 to 9% phenol until said filament has absorbed from 4 to 30% of its weight of said solution, thereafter heating the swollen filament in boiling water and then drying same, thereby removing the phenol from the filament.

15. The process in accordance with claim 1 characterized in that the phenol is monohydroxy benzene.

16. The process for the production of an improved filament of oriented synthetic linear polyamide which comprises soaking a cold drawn filament of oriented synthetic linear polyamide in water for at least a day, then soaking the cold drawn filament in an aqueous phenol solution containing from 4 to 9% phenol for about 10 minutes at a temperature between 75 and 80° C., thereafter heating the filament in a relaxed condition in boiling water for approximately 2 hours and drying in air at a temperature between 55 and 65° C.

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