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TREATMENT OF POLYAMIDES

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This invention relates to synthetic linear polyamides, and more particularly to improvements in the properties of articles comprising these polyamides.

This invention has as an object the improvement of the properties of filaments, yarns, fabrics, and other articles derived from synthetic linear polyamides. A further object is the alteration of the surface characteristics of polyamide articles. A still further object is the transformation of the normally smooth cylindrical surface of spun polyamide fibers to a rough surface exhibiting increased surface friction. Other objects, such as delustering, improving the ability of fibers to recover from elastic stretch, and increasing fiber elongation, will become apparent in the description of the invention.

The polyamides used in the practice of this invention are those described in United States Patents 2,071,250, 2,071,253 and 2,130,948. These polyamides are linear polymers containing amide groups as an integral part of the main chain of atoms in the polymer molecule. They are obtained either from polyamide-forming reactants only or from reaction mixtures containing in addition other reactants yielding linear polymers. These polyamides may be spun into filaments which can in turn be cold drawn to produce filaments exhibiting orientation along the fiber axis. From these polyamides are obtained valuable synthetic filaments, fibers, yarns, fabrics and the like. The polyamides are of two types: those derived from polymerizable monoamino-monocarboxylic acids or their amide-forming derivatives, and those derived from suitable diamines by reaction with suitable dibasic carboxylic acids or their amide-forming derivatives. On hydrolysis with hydrochloric acid the polyamides yield monomeric polyamide-forming reactants.

I have found that valuable improvements in properties are obtained when filaments or pellicles comprising the above mentioned polyamides are treated with acids or acid halides and the action of the acidic material stopped before the tenacity of the filaments or pellicles is reduced to a harmful degree.

In carrying out the invention the polyamide in a form presenting a large surface area, such as filaments, fibers, pellicles, fabrics, or the like, is immersed in a fluid medium containing the acidic material (acid or acid halide), said acidic material being removed, preferably by washing, after it has acted on the polyamide for a sufficient time. This time will vary considerably in

different instances since it is a function of the concentration, temperature, and particularly the nature of the acidic material. The required duration of the treatment can, however, be expressed in terms of the reduction of the tenacity in the article, since the tenacity becomes progressively less as treatment with acidic material continues. For the purpose of this invention the treatment is continued until the tenacity is reduced to at least 2% and not more than 40%. By this means important modifications in the properties of the polyamide article are obtained, among the more important of which are increased coefficient of friction of the fibers and crease resistance of the fabrics.

The concentration of the acidic material, which should provide at least 0.1 gram of reagent for each square meter of polyamide surface to be modified, is usually between 65% and 0.5% by weight of the fluid medium containing the acidic material. The time required will accordingly vary from about 2 seconds to 20 minutes. The action may be stopped by washing or by neutralization of the acidic material.

The following examples are illustrative of methods for carrying out the invention:

Example I

A sample of bright yarn (114 denier, 46 filament, twisted one turn per inch) spun from molten polyhexamethylene adipamide (i. e., the polymer derived from hexamethylenediamine and adipic acid) and subsequently fully oriented by cold drawing, is passed at the rate of 60 ft. per min. through a solution containing 200 cc. of sulfuryl chloride and 300 cc. of petroleum ether. Since the length of yarn immersed in the solution at any instant is 2 ft., the duration of the treatment is 2 sec. The yarn emerging from the solution is led over a guide pulley and into a bath comprising 5 cc. of concentrated aqueous ammonia (28 per cent) and 495 cc. of methanol. In the operation a segment of yarn travels 3 ft. in the air between the treating bath and the neutralizing bath, and 2 ft. in the neutralizing bath before it emerges and is wound up. All the operations are carried out at a temperature of 25° C. Residual traces of ammonia evaporate from the treated material in a few minutes, leaving it neutral in reaction. The treated yarn is noticeably delustered and possesses a rougher handle. It is evident by microscopic examination that the chemical treatment produces discontinuous corroded areas along the filaments. The surface properties of the modified yarn dif-

fer, however, from solution spun polyhexamethylene adipamide yarns in that the filaments possess no microscopically visible longitudinal striations or crevices, and in that cross-sections of the filaments display no peripheral notches or indentations which can be detected microscopically. This indicates that the alteration of the polyamide occurred only in a very thin surface layer and in this respect the modified filaments differ markedly from the perfectly smooth filaments obtained by melt spinning and from the rough crenulated fiber obtained by a wet spinning method. The chemically treated filaments are opacified only on the surface. In quantitatively measuring the static friction between perpendicular threads held in contact with forces of 0.1 to 0.3 g., the yarn treated as described above possesses a much higher coefficient of friction (0.46) than melt- or solution-spun yarn not subjected to the treatment (0.32). The above treatment with sulfuryl chloride caused a 9.5% reduction in the tenacity of the yarn.

Example II

A sample of bright oriented yarn (113 denier, 46 filament, 0.8 turn per inch twist) spun from polyhexamethylene adipamide, is passed continuously through a solution comprising 60 cc. of chloroacetyl chloride and 440 cc. of carbon tetrachloride at 25° C. at a rate of 21 ft. per minute. As the yarn emerges from this solution, it is immediately passed over a rotating "sizing" roll, wet with neutralizing bath whose composition is similar to that used in Example I. The duration of the immersion in the treating bath is 6 sec. and in the washing bath approximately 3 sec. The properties of the treated yarn in general are similar to those of the yarn treated in Example I, but they differ chiefly in the following respects: (1) The coefficient of friction of this yarn is 0.52 as compared to 0.46 for that of Example I. (2) The delustering effect is evident but is somewhat less pronounced, and this seems to be associated with the formation on the filament surfaces of irregularities of greater magnitude than the reagent of Example I produced. (3) The rapidity of the recovery of this yarn from elastic stretch is vastly increased; viz., against zero load it recovers completely from elastic stretch in less than 10 sec., whereas the yarn treated in Example I recovers 80 per cent of the stretched length in 10 sec., and untreated yarn recovers 90 per cent in 10 sec. (4) The tenacity of the yarn is reduced by 11.5%.

Example III

Bright polyhexamethylene adipamide yarn of the same sample employed in Example II is treated by passing it through a bath consisting of 25 cc. of phosphorus trichloride and 475 cc. of carbon tetrachloride at 25° C. at a rate of 62 ft. per min. The duration of treatment is 2 sec., and the time of immersion in the washing bath is 1 sec. The properties of the treated yarn are similar to those of the product of Example I, with the following exceptions: (1) The coefficient of friction of the yarn is 0.35. (2) The visible surface alteration consists of relatively larger irregularities than in Example I, and the filaments are delustered less. (3) The tenacity of the yarn is reduced 10.5%.

Example IV

A 100 g. skein of bright yarn (119 denier, 46 filament, untwisted, elongation 17 per cent) spun

from molten polyhexamethylene adipamide, is immersed in a solution comprising 100 g. of sulfamic acid and 400 g. of water at 25° C. for 2.5 hrs. The yarn is then washed in running water for 15 hrs. and allowed to dry in air. The properties of this treated yarn are substantially the same as those of Examples I and III, but it exhibits the following specific characteristics: (1) The denier is increased to 124. (2) The residual elongation is increased to 19 per cent. Taken together, these changes indicate that shrinkage or felting of the yarn occurred. (3) The coefficient of friction of the yarn is increased to a value of about 0.35. (4) The surface irregularities of the filaments are quite minute. (5) The tenacity of the yarn is reduced by 8%.

Example V

A square of transparent polyhexamethylene adipamide film 5.5 mills in thickness is immersed in a solution of petroleum ether containing 1 per cent by volume sulfuryl chloride for 20 min. at 25° C. It is then removed, washed with absolute ethanol, soaked in absolute ethanol for 10 min., and is thoroughly washed with water. The product is white, opaque, and appears to be minutely roughened. A strip of it draws readily without change in appearance. By cold-rolling the film the surface is increased by 100 per cent, and the film becomes almost transparent. When the rolled film is further oriented by cold drawing, the opacity observed immediately after treatment reappears. Under high magnification the source of the opacity is seen to be a multitude of minute circular spots.

Example VI

Dyed fabric knit from oriented polyhexamethylene adipamide yarns of two sizes (69 denier, 23 filament, and 45 denier, 15 filament) declustered with titanium oxide, is immersed in a solution comprising 200 cc. of sulfuryl chloride and 800 cc. of petroleum ether at 25° C. After 60 sec. the fabric is removed, allowed to drain momentarily, is then immersed in a solution of 400 cc. of concentrated aqueous ammonia (28 per cent) in 3,600 cc. of methanol for 2 min., and finally is rinsed with water and allowed to dry in the air. The treatment effects the following alterations in the fabrics: (1) The material is obviously roughened to the touch. (2) The color shade is somewhat lighter. (3) The fabric is less readily snagged. (4) The fabric elasticity is altered, as for example, by a decrease in the rate of recovery from stretching.

Example VII

Dyed fabric knit from oriented polyhexamethylene adipamide yarns declustered with titanium oxide, is immersed in a solution comprising 2 cc. of sulfuryl chloride and 998 cc. of petroleum ether at 25° C. After 10 min. the fabric is removed, drained, immersed for 10 min. in a neutralizing bath whose composition is the same as that employed in Example VI, and finally is rinsed with water and allowed to dry in the air. The treated fabric exhibited the following characteristics: (1) The fabric surface was perceptibly rougher to the touch than that of untreated fabric. (2) The dye was faintly lighter in shade.

Example VIII

A skein of unoriented bright yarn (92 denier, 15 filament, twisted 2.5 turns per inch) spun from the polyamide from epsilon aminocaproic

acid is immersed in a solution comprising 2 cc. of sulfonyl chloride and 1998 cc. of petroleum ether at 25° C. After 20 minutes the yarn is removed, washed in a solution comprising 1800 cc. of methanol and 200 cc. of concentrated aqueous ammonia (28%) for 20 minutes, rinsed with water, and dried in air. The treated yarn exhibits the following differences from the untreated sample: (1) The tenacity is diminished by 21%. (2) The elongation is increased from 512% to 556% (9% relative increase). (3) The fibers lack luster and are opacified. (4) Microscopically the fibers are covered with a multitude of minute spots.

The foregoing examples illustrate the application of this invention to synthetic linear condensation polyamides in the form of yarns, fabrics, and films. It will be apparent that other polyamide articles, e. g., ribbons, bristles, sheets, and even massive molded forms, can be similarly treated.

The invention is not limited to the particular polyamides cited in the foregoing examples, but is applicable broadly to synthetic linear polyamides. As examples of other polyamides of the diamine-dibasic acid type may be mentioned polytetramethylene sebacamide, polytetramethylene adipamide, polyhexamethylene sebacamide, polydecamethylene adipamide. Polyamides of the amino acid type, such as polymerized 11-aminoundecanoic acid, may also be used. Interpolyamides, i. e., polyamides derived from a mixture of polyamide-forming compositions capable of yielding more than one polyamide if reacted in suitable combination, are also successfully treated with acid halides and acids as described above. As an example of such an interpolyamide, the polymer derived from equimolecular quantities of hexamethylenediamine, decamethylenediamine, adipic acid, and sebacic acid may be cited. Synthetic linear polyamides containing other groups, e. g. ester groups, are within the scope of this invention. An example of such a polyamide may be prepared from adipic acid, hexamethylenediamine, and hexamethylene glycol. A further example of such a polyamide is that derived from adipic acid, hexamethylenediamine, and ethylene glycol.

The polyamide articles treated may when desired contain modifying agents such as plasticizers, pigments, dyes, delusterants, antioxidants, oils, and resins. The invention can also be applied to mixed yarns and fabrics, i. e., yarns and fabrics composed of filaments of more than one polyamide and yarns and fabrics containing types of filaments other than polyamides.

Representative acidic materials in addition to the acids and acid halides previously mentioned include titanium tetrachloride, phosphorus tribromide, sulfur monochloride, thionyl chloride, sulfuric acid, hydrochloric acid, and pyrosulfonyl chloride. Mixtures of two or more of these agents may be used.

Diluents for the acidic materials are not necessary but their use is desirable, particularly in the case of the more reactive acidic materials. The diluents used can be any fluid or mixture of fluids, such as chloroform, trichlorethylene, and benzene, which does not alter the identity of the reagent by chemical reaction. The reaction mixture may contain materials such as lubricants, surface-active agents, or the like, which may facilitate the operation. The reaction mixture may also contain in addition to the reagent required for the present process, other mate-

rials which simultaneously produce in the polyamide articles other desired alterations such as dyeing, sizing, and the like.

While the process is preferably conducted at about 25° C. under ordinary pressure, the effective temperatures of the reaction vary from the lowest limit at which the treating medium remains fluid, say -50° C., to an upper limit at which the polyamide article softens, e. g., 250° C., and either atmospheric, superatmospheric or subatmospheric pressure can be employed.

The polyamide articles may be subjected to any desired tension during the treatment, limited only by the tensile strength of the material; for example, the treatment of yarn as in Examples I, II, and III, may be effected under any tension from, say, 0.01 g./d. required to lead the yarn through the treating solution at the desired rate, to about 4 g./d., depending upon the tenacity of the yarn. If unoriented yarn is subjected during the treatment to a tension greater than about 0.3 g./d., the modifications may be accompanied by orientation of the filaments.

The operation of washing the yarn after treatment with an acid or acid halide solution is intended simply to stop the action of the reagent by removing that which is adsorbed on the surface. The washing medium is consequently usually of alkaline reaction, but it may be a neutral fluid, preferably one which is miscible with the treating fluid containing the acid or acid halide. If the acidic material is very volatile the washing step can in some cases be eliminated since the acidic material will evaporate.

The procedure outlined above is capable of considerable variation. For example, the treatment with acid or acid halide may form a part of a series of operations such that the contact of the polyamide article with a medium containing acid or acid halide may be preceded or succeeded by immersion in other fluids for the purpose of washing, sizing, dyeing, drying, or the like. For example, sizes or finishes may be applied to the products which have been treated with the acidic material. In fact, the treatment of the invention improves the adhesion of sizes, finishes and the like. Films and sheets can also be treated by the process of this invention giving products to which adhesives, subcoats and other finishes show improved adhesion. Wire coated with polyamide can also be treated according to the present process.

The process of the invention described herein is useful in producing in polyamide articles alterations having intrinsic merit and in producing modifications which result in improved quality of other polyamide articles fabricated from the treated materials. For example, the transformation of characteristically smooth, lustrous polyamide surfaces to rough surfaces characterized by high frictional properties and lack of luster is generally useful in obtaining woven or knit fabrics possessing improved properties. Thus, a fabric woven from the modified polyhexamethylene adipamide yarn described in Example I was characterized by superior recovery from creasing and by better draping qualities. After firmly creasing the fabric (180° angle) for 1 min., it returned to an angle of 30° (83.3% recovery) in 30 sec., compared with an angle of 40° (77.8% recovery) for otherwise comparable but untreated fabric. The ability of this altered fabric to drape, measured in terms of the length of a strip of fabric required to bend through a

45° angle under its own weight, was 18 per cent greater than that of the similar untreated fabric.

The process may also be advantageously employed in modifying knitted articles so as to obtain a high degree of resistance to slipping, running, and snagging, and an altered hand. Other valuable effects of the process are the longitudinal contractions, or "felting," induced in oriented fibers and the unique improvement conferred by this treatment in the ability of polyamide filaments to recover rapidly from elastic stretch.

As will be apparent from the foregoing description the present process confers several unique properties on the polyamide articles. The surface alteration produced by acid or acid halide treatment may be associated with a very greatly increased coefficient of static friction. This phenomenon is not observed in polyamide articles prepared by any other process. A related modification is the concomitant opacification which is produced only on the surface of the polyamide article, without the incorporation of any heterogeneous material and, surprisingly, without the union of detectable quantities of the reagent with the polyamide substance. The physical form of the transformed polyamide surfaces responsible for the above-mentioned properties is characterized by minute irregularities which show no similarity to the surface deformations resulting from other processes of preparing polyamide articles. For example, filaments resulting from this process do not possess longitudinal striations or ridges or crenated cross-sections.

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 I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for increasing the coefficient of friction of a synthetic linear polyamide article in the form of a filament, pellicle or the like, which comprises treating said article with an acidic material of the class consisting of acids and acid halides and then removing said mate-

rial before the tenacity of the article has been reduced to a harmful degree.

2. A process for increasing the coefficient of friction of a synthetic linear polyamide article in the form of a filament, pellicle or the like, which comprises treating said article with an acidic material of the class consisting of acids and acid halides and then removing said material after the tenacity of the article has been reduced at least 2% and not more than 40%.

3. A process for increasing the coefficient of friction of a synthetic linear polyamide article in the form of a filament, pellicle or the like, which comprises treating said article with a fluid medium containing from 0.5 to 65% of material of the class consisting of acids and acid halides and then removing said material after the tenacity of the article has been reduced at least 2% and not more than 40%.

4. The process set forth in claim 2 in which said polyamide is that obtainable from a diamine and a dibasic carboxylic acid.

5. The process set forth in claim 2 in which said polyamide is that obtainable from a polymerizable amino acid.

6. The process set forth in claim 2 in which said acidic material is sulfuryl chloride.

7. In a process for increasing the coefficient of friction of synthetic linear polyamide articles, the step of treating such article with sulfuryl chloride.

8. The process set forth in claim 2 in which said acidic material is chloroacetyl chloride.

9. The process set forth in claim 2 in which said acidic material is sulfuric acid.

10. The process set forth in claim 2 in which said polyamide is polymeric hexamethylene adipamide.

11. The process set forth in claim 2 in which said polyamide is an interpolyamide.

12. A process for increasing the coefficient of friction of a synthetic linear polyamide in the form of a filament, pellicle or the like, which comprises treating said polyamide with a solution of sulfuryl chloride in an organic solvent for a period ranging from two seconds to twenty minutes.

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