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PRODUCTION OF SYNTHETIC STRUCTURES

John B. Miles, Greenville, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to synthetic linear polymers, and particularly to a process for improving the properties of shaped articles prepared from fiber-forming synthetic linear polyamides.

This invention is concerned in particular with the new class of filament-forming materials known as synthetic linear polymers described in U. S. Patents Nos. 2,071,250; 2,071,251; 2,071,252 and 2,071,253. As indicated in these patents, a characteristic property of these polymers is their crystallinity and the fact that filaments and the like prepared from them can be cold drawn, whereupon they show molecular orientation along the fiber axis. The cold drawn filaments are stronger and more elastic than the undrawn filaments and are therefore more useful in the preparation of yarns and fabrics. Other articles prepared from these polymers; e. g., bristles, ribbons, sheets, and rods, are likewise improved by cold drawing, cold rolling or other processes which bring about molecular orientation of the molecules.

A particularly useful subclass of filament-forming linear polymers is that of the polyamides. These are of two types: those obtainable from polymerizable monoaminomonocarboxylic acids and their amide-forming derivatives, including caprolactam, and those obtainable from the reaction of suitable diamines with suitable dibasic carboxylic acids or their amide-forming derivatives. The latter type is more fully described in U. S. Patent No. 2,130,948. In these polyamides the amide groups form an integral part of the main chain of atoms. The present invention will be described with particular reference to the polyamides, although it is to be understood that it is not so limited.

In my applications, Serial Nos. 125,941 and 227,014 filed February 15, 1937 and August 26, 1938, respectively, and in application Serial No. 183,922 filed by V. R. Hardy and myself January 7, 1938, there is disclosed the unusual setting effect of steam and hot water, and of hot liquids or vapors of organic non-solvent swelling agents for the polyamide or polyamide articles, that is, permanently setting the articles in a specially imposed form or shape to which they tend to recover after deformation.

Such setting of articles comprising synthetic linear polymers, even when held under a slight tension, results in shrinkage.

Textile yarns (including oriented polyamide yarns) may be shrunk (residual shrinkage removed) by a treatment of the yarns in the relaxed condition with hot water. Such treatments are usually accomplished by subjecting the yarn in skeins to the action of hot water whereupon the yarn decreases in length with an accompanying decrease in residual shrinkage and increase in denier. This decrease in length of a textile yarn upon being subjected to a shrinkage treatment will be referred to as "process shrinkage." This skein process is expensive as it must necessarily be discontinuous; likewise, the necessary handling tends to degrade the yarn. Such a process is particularly objectionable in the case of polyamide yarns since they are spun directly from melt at very high spinning speeds making possible efficient and rapid continuous production. Another disadvantage in such a process is the decrease in length and increase in denier after shrinkage. This decrease in length and increase in denier may be non-uniform and is not easily controlled.

It is known to stretch textile filaments such as cellulosic rayon and to subject them while in a stretched condition to the action of hot water followed by drying, whereupon the dried yarn is obtained in substantially the same dimensions. Such a condition is, however, unstable, for upon being subsequently subjected to shrinking conditions the yarn shrinks and shows no permanent effect of this intervening treatment under tension. In fact, such processes are used to produce yarns of abnormally high shrinkage for special purposes.

It has now been found that oriented synthetic linear polyamide filaments, sheets, and ribbons, as well as synthetic linear polyamide articles such as yarns and woven fabrics constructed from such oriented filaments, and in which construction the linear dimensions of the filaments can be restrained from shrinkage (in knitted goods, for example, the linear dimensions of the filaments cannot be restrained from shrinkage), can be set in their preshrunk dimensions by subjecting them to setting conditions while restraining the filaments, ribbons or yarns from any reduction in linear dimensions, and in the case of ribbons and sheets, planar dimensions. These structures, when so treated, tend always to retain their set dimensions even though they are subsequently exposed in a relaxed state to conditions which would result in shrinkage of previously unset structures. That is to say, the "residual shrinkage" of such structures is materially reduced, if not substantially eliminated, without subjecting them to process shrinkage. Although of less importance, it has been found that a polyamide structure can actually be stretched to

a material extent, for example, 10% or more, and set in such a stretched condition with a substantial reduction in residual shrinkage.

By the term "residual shrinkage" is meant the percentage decrease in length which the filament or yarn undergoes when it is subjected in a relaxed condition to a hot aqueous treatment with or without detergents at temperatures of 95°–100° C. for five minutes. In determining residual shrinkage a measured sample is subjected to the shrinkage treatment described above and dried in a relaxed condition, whereupon its length is determined at the same humidity and temperature as the initial measurements and the percentage shrinkage calculated.

It is therefore an object of this invention to set structures comprising oriented synthetic linear polyamide filaments, yarns, ribbons, sheets or the like while restraining the filaments, yarns, ribbons, sheets or the like from any substantial reduction in linear dimensions, and in the case of ribbons and sheets, planar dimensions.

It is a further object of this invention to provide a process for reducing the residual shrinkage of oriented polyamide articles without allowing them to shrink.

A further object of this invention is the reduction of the residual shrinkage of oriented polyamide filaments, yarns and the like while they are maintained in such a manner that they cannot freely change their linear dimensions.

Another object of this invention is the provision of a continuous method for removing the residual shrinkage of oriented polyamide filaments without accompanying shrinkage.

Other objects of this invention will hereinafter become apparent.

The objects of this invention are accomplished, in general, by setting structures comprising oriented synthetic linear polyamide filaments, yarns, ribbons, sheets or the like by a treatment at elevated temperatures with hydroxylated or non-hydroxylated, non-solvent swelling agents for the polyamide while restraining the filaments, yarns, ribbons, sheets or the like from any substantial reduction in linear dimensions, and in the case of ribbons and sheets, planar dimensions.

The following specific examples are illustrative of the details of the invention. It is to be understood that the invention is not limited to the details set forth therein.

Example I

A 45-denier, 15-filament polyhexamethylene adipamide yarn, cold drawn 410% with a Z twist of 20 turns per inch, was wound under a tension of 10 grams, on an aluminum bobbin having a four-inch diameter. The bobbin was then placed in a steam chamber, subjected to saturated steam at 120° C. for 20 minutes and the yarn then removed from the bobbin. This steam treatment of the wound yarn set the yarn without noticeably shrinking the same. The residual shrinkage of the treated yarn was determined and found to be 1% as compared with a residual shrinkage of the untreated yarn of 7%.

Example II

A 45-denier, 15-filament polyhexamethylene adipamide yarn, drawn 376% having a twist of 4.5 turns per inch, was wound on a bobbin in the same manner as described in Example I, and was set by submerging the same in boiling water for five minutes. The residual shrinkage of the resultant yarn was 4% as compared with a residual shrinkage of the untreated yarn of 10.2%.

Example III

A woven fabric was constructed using 140 threads per inch of 100-denier, 10-filament, 10-turn S twist dull yarn of oriented polyhexamethylene adipamide as the warp, and 120 threads per inch of 35-denier, 10-filament, 10-turn S twist dull yarn of oriented polyhexamethylene adipamide in the filling. A portion of this fabric was tightly stretched on a tentering frame and held against substantial shrinkage while subjecting the same to the action of saturated steam at 105° C. for 15 minutes. A sample of this fabric when subjected to the conditions used in determining residual shrinkage of a yarn and measured in the warp and filling direction will be found to shrink approximately 1%. A sample of a similar untreated fabric when tested in the same manner will be found to shrink approximately 5%.

Example IV

An oriented polyhexamethylene sebacamide monofil having a diameter of approximately 50 mils had the following properties: denier, 13,800; tenacity (grams per denier) 3.3; tensile strength (pounds to break), 100; and an elongation (to break), 17%. This monofil had a residual shrinkage of 6%. A sample was wrapped sufficiently tightly on an aluminum bobbin to restrain against reduction in linear dimension and placed in an autoclave and subjected to saturated steam at a pressure of 70 pounds per square inch for 30 minutes. The properties of the treated monofil were determined and found to be: denier, 13,800; tenacity (grams per denier) 3.7; tensile strength (pounds to break) 110; elongation (to break) 20%. The residual shrinkage was less than 0.5%.

The invention may be practiced continuously by subjecting the yarn to hot-wet treatments while running continuously between rolls running at the same peripheral speed and gripping the yarn so that it cannot shrink. Such treatments may also be applied to ribbons, sheets, and woven fabrics in the same manner. Proper provisions may be made to prevent lateral shrinkage as by gripping belts, etc. The yarn can be treated with hot water or steam either at atmospheric or superatmospheric pressures. The speed at which the yarn or fabric may travel will depend on the length of the length of the chamber in which the treatment is applied, the temperature of the setting agents and the reduction in residual shrinkage desired. The higher the temperature of the treatment and the longer the travel of the yarn, the higher the speed of travel permissible to maintain the same reduction in residual shrinkage.

While in the foregoing examples this invention has been illustrated by hot-wet treatments involving hot water or steam it is not so limited. Organic non-solvent swelling agents for the polyamides are also useful. These may be hydroxylated compounds such as the aliphatic alcohols. Methanol, isopropanol and isobutanol are particularly useful. Other hydroxyl-containing compounds which are useful include ethyl lactate, dimethyl tartrate, ethyl glycolate, ethanolamine, diacetone alcohol and polyhydric alcohols; e. g., ethylene glycol and glycerol. Useful compounds which do not contain the hydroxyl group include organic amines such as aniline, toluidine, dibutyl amine, etc., as well as nitriles and amides. The

use of dilute aqueous solutions of alkali metal sulfites; e. g. sodium sulfite, is particularly effective. The only requirement of agents used according to this invention is that they have a swelling action on the polyamides without dissolving them; that is, they are substantially chemically inert towards polyamides. This requirement for a non-solvent, organic swelling agent may be satisfied by a mixture of a solvent and a non-solvent. Setting agents which are effective produce at least 1% increase in the length of the unoriented filament at 25° C. and preferably 10%. They should also be tested at the setting temperature to be sure they are not active solvents.

While any hot-wet treatment has a setting action on oriented polyamide articles, it is generally preferred to employ temperatures between 65° C. and 175° C. for periods of a few minutes to an hour. In order to obtain the advantages of the present invention the setting treatment should be carried out at such a temperature and for such a period of time as to reduce the residual shrinkage of the polyamide structures at least to 75% of that of the unset structure. The temperature and period of treatment depend upon the particular polyamide and its physical form and upon the setting agent employed. Generally, the higher the temperature employed the shorter the period that is necessary. The degree of setting in a given time is roughly a linear function of temperature. For example, the preferred temperature range for water and saturated steam is 95° C. to 110° C. for times ranging from one to fifteen minutes. A treatment for one minute with saturated steam is approximately equivalent to a five minute treatment with hot water at 95° C. Similarly, a five minute treatment with methanol vapor at 100° C. produces as much setting as thirty minutes liquid treatment at 65° C.

Dry heat is ineffective as an agent to substantially reduce residual shrinkage where the polyamide structure is held against shrinkage in accordance with the present invention.

While this invention has been described with particular emphasis on yarns consisting solely of oriented linear polyamide filaments, it is also applicable to mixed textile materials. Similarly, yarns comprising staple length polyamide filaments alone or in combination with other textile fibers may be treated according to this invention. Likewise, mixed fabrics may be treated according to this invention. This invention is also applicable to oriented polyamide filaments, yarns and the like comprising modifying agents, for example, luster-modifying agents, delusterants, etc.

The process of this invention may also be practiced to advantage on articles made from other synthetic linear polymers such as the polyesters, etc., described in U. S. Patent No. 2,071,251, as well as articles made from polyester-amide interpolymers.

The setting of polyamide structures in accordance with the present invention can be definitely discerned in the set structures. The setting treatment changes the crystalline characteristics of synthetic linear polyamide structures as evidenced by X-ray investigation. The X-ray diffraction patterns which change markedly upon cold drawing become much sharper after the yarn is subjected to the setting treatments of this invention. By X-ray investigation it can therefore be definitely ascertained whether or not a structure has been subjected to the process of this invention.

By the practice of this invention it is possible to produce, continuously or discontinuously, oriented polyamide filaments, yarns, and the like having a uniformly low residual shrinkage by treatment whereby the linear dimensions of the yarn are not materially reduced. It is therefore possible to produce woven fabrics and the like which will not shrink appreciably upon subsequent treatment with hot water, steam or other non-solvent swelling agents for the polyamides and in which the structure of the fabric is not injured by shrinking treatment. Yarns treated in accordance with this invention can also be used for the production of knitted fabrics which will not shrink appreciably in hot water, steam, and the like. Furthermore, the same treatments which are used to remove the residual shrinkage when applied to fabrics impart to them substantially permanent crease resistance. Since it is possible to reduce the residual shrinkage without undergoing shrinkage, there is no loss of length so that the yarns produced can be used more efficiently and effectively than those produced by other processes.

Since it is obvious that many changes and modifications can be made in the details of the invention above set forth, it is to be understood that the invention is not to be limited except as set forth in the appended claims.

I claim:

1. In a process for reducing the residual shrinkage of oriented synthetic linear polyamide structures of filaments, yarns, ribbons, sheets and woven fabrics the construction of which will permit prevention of shrinkage of filaments and yarns of which they are made, the step which comprises setting said structures by treating the same with a non-solvent swelling agent for the polyamide at a temperature of between 65° C. and 175° C. for a sufficient period of time to reduce the residual shrinkage of the structure at least to 75% of that of a similar unset structure while preventing substantial reduction in dimension of said structures.

2. In a process for reducing the residua. shrinkage of oriented synthetic linear polyamide structures of filaments, yarns, ribbons, sheets and woven fabrics the construction of which will permit prevention of shrinkage of filaments and yarns of which they are made, the step which comprises setting said structure by treating the same with a non-solvent swelling agent for the polyamide at a temperature of between 65° C. and 175° C. for a period of 1 to 15 minutes while preventing substantial reduction in dimension of said structures.

3. In a process for reducing the residual shrinkage of woven fabric the construction of which will permit prevention of shrinkage of filaments and yarns of which it is made and in which said filaments and yarns are composed of oriented synthetic linear polyamides which comprises subjecting said yarns and filaments to a setting treatment with a non-solvent swelling agent for the polyamide at a temperature of 65° C. to 175° C. for a period of 1 to 15 minutes while preventing substantial reduction in linear dimension of said filaments and yarns.

4. In a process for reducing the residual shrinkage of filaments and yarns composed of oriented synthetic linear polyamides which comprises setting said filaments and yarns by treating the same with a non-solvent swelling agent for the polyamide at a temperature of 65° C. to 175° C. for a period of 1 to 15 minutes while pre-

venting substantial reduction in linear dimension of said filaments and yarns.

5. In a process for reducing the residual shrinkage of filaments and yarns composed of oriented synthetic linear polyamides which comprises continuously setting said filaments and yarns by treating the same with a non-solvent swelling agent for the polyamide at a temperature of 65° C. to 175° C. for a period of 1 to 15 minutes while preventing substantial reduction in linear dimension of said filaments and yarns.

6. In a process for reducing the residual shrinkage of sheets and ribbons composed of oriented synthetic linear polyamides which comprises setting said sheets and ribbons by treating the same with a non-solvent swelling agent for the polyamide at a temperature of 65° C to 175° C. for a period of 1 to 15 minutes while preventing substantial reduction in planar dimensions of said sheets and ribbons.

7. The product produced by the process of claim 1.

8. The product produced by the process of claim 2.

9. The product produced by the process of claim 3.

10. The product produced by the process of claim 4.

11. The product produced by the process of claim 5.

12. The product produced by the process of claim 6.

JOHN B. MILES.