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SYNTHETIC POLYMER

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The present 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.

The term "synthetic" is used herein to imply that the said polymers are built up by a wholly artificial process and not by any natural process. In other words, the original reactants are monomeric or relatively low molecular weight substances.

This invention is concerned in particular with a new class of filament-forming materials known as synthetic linear condensation polymers described in U. S. Patents 2,071,250; 2,071,251; 2,071,252; 2,071,253 and 2,197,896. This application is a continuation-in-part of the last-mentioned patent, the application for which was filed on February 15, 1937. As indicated in these patents, a characteristic property of filaments prepared from these polymers is that they can be cold drawn into fibers showing molecular orientation along the fiber axis. The cold drawn filaments, i. e., the fibers, 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 orientation.

A particularly useful subclass of filament-forming linear polymers are the polyamides. These are of two types; those derived from polymerizable monoaminomonocarboxylic acids and their amide-forming derivatives, and those derived from the reaction of suitable diamines with suitable dicarboxylic acids or amide-forming derivatives of dibasic carboxylic acids. 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.

In my application Serial Number 125,941, filed February 15, 1937, now Patent No. 2,157,117, and in application Serial Number 183,922, filed by V. R. Hardy and myself January 7, 1938, there is disclosed the unusual effect of steam and hot water as agents for setting polyamide articles, that is setting the article in a permanent form or shape to which it tends to recover after deformation. In the last mentioned application, the treatment with organic swelling agents of polyamide filaments which have been oriented by cold drawing is also disclosed. The present in-

vention is directed specifically to the setting of oriented polyamide articles by means of organic compounds which have a swelling action on the polyamide without dissolving it as distinguished from the setting of these articles by water in liquid or vapor form.

An object of this invention is to improve the properties of shaped articles prepared from fiber-forming synthetic linear polymers. A further object is to improve the utility of fibers, yarns, fabrics, ribbons, films, and the like derived from synthetic linear polyamides. A still further object is to impart to said articles a more or less permanent shape to which they tend to recover after being deformed. Other objects will appear hereinafter.

These objects are accomplished by subjecting an oriented article prepared from one or more synthetic fiber-forming linear polymers, while held in a predetermined shape, to heat treatment with the liquid or vapors of an organic non-solvent swelling agent for the polyamide, and continuing the treatment until the polymer is sufficiently set in said shape that subsequent hot water treatments to which it will be subjected will not alter this shape to an undesirable extent. In the case of fibers and fabrics this will mean that the treatment with the swelling agent is continued until the article exhibits at least a 50% improvement in resistance to creasing or wrinkling.

The term "oriented" is used to indicate that the polymer molecules or crystallites in the article have been lined up in a more or less orderly arrangement by some process like cold drawing or cold rolling. For example in an oriented filament the crystallites are lined up parallel to the axis of the filament.

The term "article" or "shaped article" is used to designate an object which has been formed into a definite predetermined useful shape by some process, such as spinning, casting, molding, knitting, weaving, or the like. Typical shaped articles are fibers, bristles, fabrics, ribbons, foils, and sheets.

The term "filament" will be used herein to refer to both the unoriented and oriented filaments long or short, prepared from the polymer, while the term "fiber" will be used more specifically to designate the oriented or cold drawn filaments, whether long or short.

In carrying out my invention an oriented polyamide article, such as filaments, yarns, fabrics, ribbons, and the like, is subjected to the action of a hot (usually 65°-175° C.) organic non-sol-

vent swelling agent for the polyamide. The agent, which is preferably an alcohol, may be in the form of a liquid or a vapor. The agent may be used under pressure. If the setting agent is to be used in the form of vapor, the best results are obtained by using saturated vapors. The time of treatment is dependent upon the nature of the swelling agent and the temperature employed. For example, five minutes' treatment with methanol at 100° C. produces as much setting as 30 minutes at 65° C. In most cases the optimum time of treatment will range from a few minutes to an hour.

This invention contemplates the treatment only of polyamide articles after they are oriented. Thus, in the case of fibers, the treatment is applied after substantially complete cold drawing. However, the treatment of unoriented filaments furnishes a preliminary test for selection of the organic liquids which have a swelling action on the polyamide without dissolving it and which therefore will function as a setting agent. In this test an unoriented filament of the polymer, that is one that has not been cold drawn, is immersed in the non-solvent organic liquid to be examined. The swelling action of the liquid is determined by the resulting increase in length of the filament. The organic liquids which are effective as swelling agents produce at least 1% increase in the length of the filament, the most desirable agents producing up to 10% or more swelling. The test can be applied at ordinary temperature, i. e. 25° C., although it is advisable to repeat the test at the temperature to be used in the setting operation to make certain that the agent is a non-solvent swelling agent at this temperature and not an active solvent.

The following examples illustrate the invention more specifically:

Example I

A 20-filament 50-denier yarn consisting of substantially completely cold drawn polyhexamethylene adipamide fibers was cut into two pieces. One piece was subjected, while held straight, to benzyl alcohol at 100° C. for 30 minutes. The second sample was not given any setting treatment. Each sample of yarn was then wound around a wedge having an angle of 23 degrees so that the yarn was bent through an angle of 157 degrees. The wedge carrying the yarn was immersed in boiling water for ten minutes. The yarn was then removed from the wedge and dried in the relaxed condition. The crease produced in the two yarns by this treatment was determined by measuring the angle of crease introduced by the wedge, the greater the angle produced the smaller the crease-resistance of the yarn. The angle introduced in the first yarn, i. e., the yarn which was preset with benzyl alcohol was 65° (out of a possible 157°), as compared with 105° for the second yarn (unset); in other words, the unset yarn underwent about 60% more creasing than the preset yarn. Expressed in different terms, the preset yarn exhibited a 58.5% recovery from deformation (92° out of 157°), whereas the unset yarn exhibited a 33.1% (52° out of 157°) recovery from deformation, which means that the alcohol setting treatment brought about a 76.7% improvement in recovery from deformation. In accordance with the process of this invention the setting treatment is preferably applied until the product exhibits at least a 50% improvement in recovery from deformation.

Example II

A stocking knitted from 15-filament 40-denier oriented polyhexamethylene adipamide yarn was positioned on a stocking form and subjected in an autoclave to saturated methanol at 110° C. for 10 minutes. After this boarding (setting) operation the stocking was successfully subjected to hot scouring, hot dyeing, and reboarding. The resultant stocking had good appearance, being smooth and free from wrinkles. A stocking which was not boarded before hot scouring and dyeing, developed persistent wrinkles during these operations.

In the treatment of the oriented polyamides in accordance with this invention, the more active swelling agents can be used quite effectively at temperatures of 65°-100° C., whereas the less active swelling agents are preferably used at temperatures of 100-175° C. The aliphatic alcohols are particularly useful setting agents, and of these methanol, isopropanol, propanol, and isobutanol are preferred. In many instances these organic agents are more effective than water. Methanol, for example, shows by the above mentioned test on the unoriented fibers about 6.5% swelling at 25° C. as compared to about 2.5% for water. Other hydroxyl containing compounds useful as setting agents are ethyl lactate, dimethyl tartrate, ethyl glycolate, ethanol amine, and diacetone alcohol, polyhydric alcohols, e. g., ethylene glycol and glycerol.

The useful organic swelling agents are not, however, limited to the hydroxyl containing compounds. Thus the organic amines, as for instance aniline, toluidine, and dibutyl amine, may be used at elevated temperatures. Nitriles and amides may likewise be used. As pointed out above, the only requirement for the setting agent is that the liquid have a swelling action on the polyamide without dissolving the polyamide, and that it be substantially chemically inert toward the polyamide. This requirement for an organic non-solvent swelling agent is satisfied in many instances by mixtures of a solvent and a non-solvent. Thus the phenols and most carboxylic acids cannot be used alone because they tend to dissolve the polymer, but these liquids can be used when diluted with water. In the preferred practice of my invention, however, I use those organic liquids, preferably aliphatic monohydric alcohol, which without admixture with water are non-solvent swelling agents.

The setting action of the organic swelling agents described above is many-fold more rapid than the action of dry heat, e. g., hot air, at the same temperature. The cause for the remarkable setting effect of organic mild swelling agents on polyamide fibers and fabrics is not understood. It is surprising that these agents should have such a marked effect on polyamide fibers at temperatures much below the melting point of the polyamide. This indicates that setting is not a molding phenomenon. Furthermore, merely softening or swelling the polyamide with the swelling agent followed by its immediate removal is not sufficient; the setting is accomplished by heating the polyamide while it contains the swelling agent. Generally from five minutes' to an hour's heating is required depending upon the temperature. Setting does not destroy the orientation of the polyamide; X-ray examination of the set polyamide fibers indicates a high degree of orientation, although the fiber diagram is slightly different than that

of the unset fibers. Another remarkable feature of the setting operation is its permanency. As indicated below, it is not reversible as in the case of silk and cellulosic fibers. For this reason the set fibers or fabrics can be dyed and laundered without materially destroying the effect of setting.

The present invention is particularly useful in connection with fabrics made from polyamide fibers. Fabrics which have been given a setting treatment show little tendency to develop wrinkles in subsequent use. In other words, setting is useful in making crease-resistant fabrics. Since polyamide fabrics become more or less permanently set in the form or shape in which they are first subjected to a setting treatment, it is necessary that this first treatment be applied while the fabrics are held in the shape it is desired to impart thereto. In this respect, polyamide fabrics differ radically from silk or rayon fabrics. Silk and cellulosic fabrics can be set in a given shape by wetting followed by drying while held in the desired shape. One such treatment does not change the manner in which a different shape can be imparted by a second similar treatment. For these fabrics setting is reversible and depends principally on drying out. With the synthetic polyamide fabrics, on the other hand, setting seems to be accomplished by contact with a hot swelling agent for the polyamide and setting is not reversible in a simple manner. In other words, a polyamide fabric which is set in a given shape by one treatment cannot be made to conform to a different shape by an equal second treatment. However, if the second treatment is made more severe, i. e., either by means of a higher temperature wet treatment or by a much more prolonged treatment at the same temperature, the fabric can be set in another form with some success. Nevertheless, it is generally desirable to prepare polyamide fabrics from fibers which have not been given any material setting treatment in order that the setting of the fabric itself can be more effectively accomplished.

Although the invention has been described with particular reference to synthetic linear polyamides, it is also applicable to oriented shaped articles derived from other synthetic linear polymers, e. g., polyesters, polyethers, polyacetals, mixed polyester-polyamides, e. g., those derived from diamine, dibasic acid and glycol, and other interpolymers. The procedure is in general the same although the liquids used as setting agents may be different due to the difference in solubility of the products. Examples of additional synthetic linear polyamides to which this invention is applicable are polytetramethylene sebacamide, polypentamethylene adipamide, polypentamethylene sebacamide, polyhexamethylene glutaramide, polyhexamethylene sebacamide, polyoctamethylene adipamide, polydecamethylene carbamide, and polyparaxylylene sebacamide. Polymerized 6-aminocaproic acid, 9-aminononanoic acid, and 11-aminoundecanoic acid represent polyamides of the amino acid type which can also be set by hot organic non-solvent swelling agents. The invention is also applicable to articles derived from copolyamides (interpolyamides) or from mixtures of polyamides.

The articles treated need not consist solely of synthetic linear polymer. Other materials, such as plasticizers, luster modifying agents (e. g., titanium dioxide), pigments, extenders, fillers, dyes, resins, oils, cellulose derivatives and the

like, may be present in the article in addition to the polymer. It will be evident from the foregoing that this invention describes a simple process for improving the properties of oriented shaped articles derived from synthetic linear polymers. The invention is applicable to a variety of products. It is particularly useful in connection with knitted and woven fabrics where crease-resistance and non-wrinkling are desired. It is also applied with advantage to pile fabrics, e. g. velvets, plushes and upholstery fabrics, since it markedly improves the crush resistance of the pile. Fabrics made from crimped fibers retain their wool-like character longer if subjected to the setting treatment of this invention. This invention is also useful in connection with bristles, films, foils, and the like, where improvement in recovery is desired. An advantage which the setting agents of this invention, particularly the lower boiling alcohols, have over water and steam is that they are more easily removed from the articles after treatment. Moreover, a number of the organic agents are active at lower temperatures than water. Still another advantage of the agents of this invention is that they show less tendency to corrode equipment in which they are used than do water and steam. This lessens the danger of contaminating the articles treated.

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 setting oriented synthetic linear polymer which comprises impregnating said polymer with an organic non-solvent swelling agent, heating the polymer so impregnated while maintaining it in substantially unchanging shape, at a temperature above 65° C. but below the melting point of the polymer, and maintaining the quantity of the said non-solvent swelling agent in the said polymer substantially constant during at least part of the said heating.

2. A process for setting a fiber comprising oriented synthetic linear polymer which comprises impregnating said fiber with an organic non-solvent swelling agent for the polymer and heating the impregnated fiber at a temperature of 65-175° C. for at least five minutes while maintaining it in substantially unchanging shape.

3. In the process of setting a fabric structure consisting of fibers comprising oriented synthetic linear polymer, the steps which consist of heating said structure while it is in continual contact with a non-solvent swelling agent for said polymer to a temperature of 65-175° C., and maintaining it at such temperature until the crease-resistance of said structure has increased at least 50%, while constantly maintaining said structure in a substantially unchanging shape.

4. The process set forth in claim 1 wherein the said polymer is a polyamide.

5. The process set forth in claim 1 wherein the said polymer is polyhexamethylene adipamide.

6. The process set forth in claim 1 wherein the said polymer is a polyamide obtainable by polymerization of a monoaminomonocarboxylic acid.

7. The process set forth in claim 1 wherein the said polymer is polymeric 6-aminocaproic acid.

8. The process set forth in claim 2 wherein the said polymer is a polyamide.

9. The process set forth in claim 2 wherein the said polymer is polyhexamethylene adipamide.

10. The process set forth in claim 2 wherein the said polymer is a polyamide obtainable by polymerization of a monoaminomonocarboxylic acid.

11. The process set forth in claim 2 wherein the said swelling agent is an aliphatic alcohol.

12. The process set forth in claim 2 wherein the said polymer is a polyamide obtainable by condensation polymerization from a diamine and

a dicarboxylic acid, and in which said swelling agent is an aliphatic alcohol.

13. The process set forth in claim 3 wherein the said swelling agent is an aliphatic alcohol.

14. The process set forth in claim 3 wherein the said polymer is a polyamide obtainable by condensation polymerization from a diamine and a dicarboxylic acid, and in which said swelling agent is an aliphatic alcohol.

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