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PROCESS FOR IMPROVING THE PROPERTIES OF POLYAMIDE FIBERS

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This invention relates to artificial fibers and more particularly to synthetic linear polyamide fibers.

The new class of fibers produced from synthetic superpolyamides of the kind described in U. S. Patents 2,071,250, 2,071,253 and 2,130,948, and known as nylons possess very attractive properties, including high strength, low solubility in organic solvents, and a high melting point. For most purposes, these properties are sufficient to make the nylons exceptionally valuable textile materials. However, in a few utilizations, it would be desirable for the yarns to be even more high melting and still less affected by organic solvents. Moreover, nylon fabrics are often stiff, and possess a heavy hand caused by an inferior degreee of resilience or crease proofness as compared to wool and certain other textile materials. It would accordingly be useful to the art to give these nylon yarns a softer hand, better drape, and in addition, a higher melting point, better dye receptivity and an increased resistance to solvents. Several methods for overcoming these objections have been recorded. For instance, U. S. Patent 2,177,637, drawn nylon is treated with formaldehyde and baked to increase the melting point, dye receptivity and recovery from deformation. The resulting changes, however, are insufficient to fully accomplish the objects of the present invention, and the formaldehyde pickup is limited to a very small amount. Another suggestion to overcome the above mentioned disadvantages, has been to subject the nylon fabric to a heat treatment often in the presence of an alcohol or other partial solvent, this treatment consisting of heating the fabric over its width against a heated surface to a temperature approaching the melting point. The result has been a softer hand and a better drape but there is no chemical change so that the solubility, melting point, and dye receptivity are unchanged. I have now found a new process whereby the advantages of these two improvements are obtained but to an enhanced degree.

This invention has as an object synthetic linear polyamide fibers of high melting point and of increased resistance to the action of organic solvents. A further object is fibers of this kind which are characterized by improved softness, drape and resilience. Further objects reside in methods for obtaining polyamide fibers having the above mentioned properties. Other objects will appear hereinafter.

The above objects are accomplished by a method comprising the following three steps:

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(1) Undrawn polyamide yarn, that is polyamide yarn in which the filaments are essentially unoriented molecularly along the filament axis, are reacted with a solution having a pH below 3 of formaldehyde and an oxygen-containing acid catalyst in alcohol until at least 1% but not more that 20% of the hydrogen-bearing amide linkages are substituted by N-alkoxymethyl groups;

(2) The treated yarn is cold-drawn;

(3) The filaments or yarn are crosslinked, e. g., insolubilized.

The conversion of synthetic linear polyamides to the more soluble polymers known as alkoxymethyl polyamides has been described in application Serial No. 539,195, filed June 7, 1944, by T. L. Cairns. The reaction comprises treating the initial polyamide with formaldehyde and alcohol in the presence of acid catalyst whereby the hydrogen of the amide groups—CONH—is replaced with the group CH_2OR in which R is an alcohol radical. The present invention, although it involves such treatment, is different in purpose and in procedure from the above-mentioned production of the soluble polyamides.

The present invention is based on my discovery involving the two factors, namely, (*a*) that a degree of alkoxymethyl substitution lower than that previously used to obtain the best results with regard to increased solubility in alcohols, dye receptivity, plasticity, lowered melting point, etc., confers to the polyamide properties differing markedly from both the unmodified polyamide and polyamides of the higher alkoxymethyl substitution (above 20%), the lower substituted polyamides retaining the ability to cold draw, being relatively insoluble and resembling in fiber form the initial polyamide, but yet having increased softness, pliability and dye receptivity together with ability to cross link adjacent chains by splitting out alcohol or water between substituted and unsubstituted amide groups; and (*b*) that the low degree of substitution required for the present purpose can be introduced into the polyamide fiber without destroying its form by reason of the fact that undrawn, and consequently unoriented, polyamide filament is much more chemically reactive toward the reaction solution mentioned above than is the drawn and oriented fiber, the latter fiber being substantially unreactive to formaldehyde, whereas the undrawn filament is readily reactive, particularly with a strong acid catalyst at a pH level below 3.

Referring more particularly to the three previously enumerated essential steps of the pres-

ent process, the filaments treated should be essentially unoriented, that is, they should not have been cold drawn, e. g., drawn in the solid state, more than 100% beyond their initial length. In the present reaction, the time, concentration, temperature and other reaction conditions are controlled as illustrated hereinafter to yield polyamides of the required low alkoxymethyl substitution.

The filaments after the formaldehyde and alcohol treatment are cold drawn to an elongation at least 300% of the length of the initially formed and unoriented filament.

The step of crosslinking the polyamide of the filament in order to insolubilize it can be effected by heat alone but is best carried out by impregnating with an acid followed by baking. In this step the acid need not be an oxygen-containing one and any acid having an ionization constant greater than 1×10^{-6} can be used. The acid used in the formaldehyde and alcohol treatment of the first step, however, is usually used in the crosslinking step. Polyamide filaments in which the alkoxy group of the N-alkoxymethyl substituent is unsaturated, e. g., has ethylenic unsaturation, can be crosslinked by impregnating the filaments with a solution of benzoyl peroxide or other organic peroxy compound followed by either baking or exposure to ultra violet light.

The invention is further illustrated by the following example, in which the parts are expressed as parts by weight.

In the first step, a skein of one part undrawn polyhyexamethylene adipamide 142 denier, 13 filament yarn of a polymer of intrinsic viscosity of 0.8 was placed in 40 parts of a solution consisting of 10 parts of paraformaldehyde, 10 parts of methanol, and one part anhydrous oxalic acid and held there for 8 minutes at a temperature of 64° C. The skein was then removed, rinsed for 5 hours in 1% aqueous ammonium hydroxide solution and dried at 25° C. Analysis showed that 6% of the amide groups were substituted with a mixture of N-methylol and N-methoxymethyl groups.

In the second step the skein of yarn was back wound onto a spool and cold drawn to a ratio of 3.51:1 on commercial textile machinery.

In the third step, the yarn was soaked in a 1% aqueous oxalic acid solution for 30 minutes at 25° C., dried at 25° C. in air and baked 5 minutes at 110° C. The baked yarn was thereafter washed in pure water to remove all residual acid. The resulting yarn was greatly different in properties from a sample of yarn treated similarly in all respects except for the treatment with formaldehyde and alcohol, as will be seen in the following table:

	Solubility in m-Cresol	Temp. of Zero Strength	Tenacity, g./d.	Elong. at Break, Per Cent	Dye Receptivity
		Degrees			
Untreated Yarn	Soluble	230	4.2	41	Fair.
Treated Yarn	Insoluble	280	3.8	24	Excellent.

The yarn was woven into a plain weave fabric and found to be softer, more resilient, and less easily creased than a similar fabric from the untreated yarn.

The polyamides used in the practice of this invention contain hydrogen-bearing amide groups and are of the general type described in the previously mentioned patents. They are high molecular weight or fiber-forming polyamides characterized by an intrinsic viscosity of at least 0.4 as defined in Patent 2,130,948. The polyamides of this kind comprise the reaction product of a linear polymer-forming composition containing amide-forming groups, and can be obtained by several methods including polymerization of a monoaminomonocarboxylic acid, by reacting a diamine with a dibasic carboxylic acid in substantially equimolecular amounts, or by reaction of a monoaminomonohydric alcohol with a dibasic carboxylic acid in substantially equimolecular amounts, it being understood that reference herein to the amino acids, diamines and dibasic carboxylic acids and amino alcohols is intended to include the equivalent amide-forming derivatives of these reactants. On hydrolysis with hydrochloric acid the amino acid polymers yield the amino acid hydrochloride, and the diamine-dibasic acid polymers yield the diamine hydrochloride and the dibasic carboxylic acid, and the amino alcohol-dibasic acid polymers yield the amino alcohol hydrochloride and the dibasic carboxylic acid. The preferred polyamides obtained from these reactants have a unit length of at least 7, where "unit length" is defined as in United States Patents 2,071,253 and 2,130,948. The average number of carbon atoms separating the amide groups in these polyamides is at least two. For use in the process of this invention, I prefer that the number of carbons separating amide groups is at least two.

Examples of particular reactants that can be used in preparing the polyamides comprise basic carboxylic acids such as glutaric, adipic, pimelic, suberic, azelaic, sebacic, diglycolic, phthalic, terephthalic, isophthalic and p-phenylene diacetic acids; diamines, such as ethylenediamine, tetramethylenediamine, pentamethylene diamine, hexamethylene diamine, m-phenylene diamine, p-xylylene diamine, and triglycol diamine; and primary monoaminomonocarboxylic acids such as 6-aminocaproic and 12-aminostearic. Interpolyamides can be used in the practice of this invention, that is, those obtained from a mixture of polyamide-forming compositions. The polyamides previously indicated include also polymers obtained by reaction of a polyamide-forming composition with another polymer-forming composition such as a polyester-forming composition. Polyamides that are operable in addition to those already defined are the fiber forming polyureas, e. g., polydecamethylene urea; polysulfonamides, e. g., the polysulfonamide prepared from decamethylene diamine and m-benzenedisulfonyl chloride; polyurethanes, polythioureathanes, and polyhydrazides.

The formaldehyde is preferably used as paraformaldehyde, although it can be used in other forms including an aqueous solution such as formalin and the known formaldehyde-liberating materials such as polyoxymethylene.

Methanol, due to its ready reactivity and availability, is particularly suitable in the present process. However, any aliphatic alcohol which

is at least partially miscible with formaldehyde can be used, such as ethanol and the propyl, butyl and amyl alcohols, benzyl alcohol, cyclohexanol, ethylene glycol, diethylene glycol, propylene glycol and substituted alcohols such as hydroxyacetic or lactic acids. Unsaturated alcohols such as allyl, methallyl and crotyl are useful. The most useful alcohols in the practice of this invention are those containing 1 to 5 carbon atoms and having either one or two hydroxyl groups.

The mention of oxygen-containing acid catalysts herein, which are used in the formaldehyde and alcohol treatment, refers to acids having a pH of less than 3.0 and an equivalent conductance, measured at 25° C. in 0.01 N concentration, no greater than 370 ohms^{-1} cm.^{2} (e. g., not stronger than p-toluenesulfonic acid). Examples of these acids are oxalic, maleic, mono-, di- or trichloroacetic, fumaric, formic, p-toluenesulfonic, phosphoric, phosphorus, or in general, those inorganic or organic acids which in concentrations between 3% and 20% in methanol-formaldehyde solution give a pH of below 3 and do not cause excessive degradation of the polyamide. The absence of appreciable amounts of water and the use of small percentages of acid prevents such harmful degradation in the case of the inorganic acids that in aqueous solution would be considered as harmful to polyamides. To avoid degradation, acids having an equivalent conductance greater than that mentioned above should not be present in the reaction solution.

In the treatment of the undrawn filaments with alcohol and formaldehyde, the reaction temperature can be as low as 40° C. and up to 130° C. if the time is shortened to prevent degradation of the polymer chain. The temperatures most desirably used range between 50° C. and 100° C. The quantities of alcohol, formaldehyde and acid catalyst in the reaction solution can vary widely and the desired results obtained by increasing or diminishing the temperature or time, or both, as required. Thus for one mol of alcohol the formaldehyde can be present in amount from 0.5 mols to 5.0 mols. The oxygen containing acid catalyst can be present in amount of from 3% to 20% of the reacting mixture. The time of reaction, which is also dependent on temperature, will usually vary in accordance with these concentrations from one minute to sixty minutes. The optimum conditions are found with reaction conditions containing for each part by weight of alcohol from 0.5 to 2 parts formaldehyde, and from 0.05 part to 0.30 part of oxygen containing acid catalyst, with corresponding times of reaction from two minutes to fifteen minutes, and temperatures from 60° C. to 90° C.

The reaction for any particular conditions of concentration and temperature is controlled with regard to stopping it within the time at which the alkoxymethyl substitution is between 1% and 20% (that is until hydrogen-bearing amide groups consisting of from 1% to 20% of the total amide groups are converted into N-alkoxymethyl groups) by observation of the extent of swelling shown by the fiber in the reaction solution. The degree of swelling (both lateral and longitudinal) can be related to the percentage substitution by means of an analysis for the formaldehyde contained in the polymers. This analysis is accomplished by hydrolysis of polyamide with strong concentrated mineral acid followed by neutralization of the hydrolyzate. An excess of sodium sulfite is added to the solution, and the sodium hydroxide released by reaction with the free formaldehyde is titrated with a standard acid. In this way it is possible to determine the formaldehyde contained in the polymer and consequently the percentage of the amide groups that have been substituted.

As has been previously indicated, the crosslinking or insolubilizing step can be carried out in several ways. In the preferred method, the filaments are impregnated by soaking them in a dilute aqueous or alcoholic solution, usually from about 0.01 to 5% concentration of the acid followed by drying and baking from 1 to 30 minutes at a temperature of from 60° C. to 150° C., and preferably from 80° C. to 100° C., depending on the extent of crosslinking desired. Suitable acids comprise maleic, oxalic, succinic, adipic, glutaric, p-toluenesulfonic, acetic, formic, hydroxy-acetic, or lactic acids, and also inorganic acids such as sulphuric, hydrochloric and other hydrogen halide acids.

When heat is used alone, the above mentioned temperatures can be used with somewhat longer time, for example, from 30 minutes to 180 minutes. In some instances, and particularly when the alcohol used in the first step of reacting the undrawn filament with formaldehyde is an unsaturated alcohol, it is advantageous to effect the crosslinking by impregnating the filaments with a solution of a peroxy compound and then curing or crosslinking by baking or exposure to a source of concentrated ultra violet light. Organic peroxy compounds useful for the present purpose include benzoyl peroxide, diacetyl peroxide, lauroyl peroxide, diethyl peroxide. Inorganic peroxy compounds, e. g., zinc peroxide and hydrogen peroxide may be used.

It is to be observed that although either the baking or irradiation with ultra violet light, which effects the crosslinking, is carried out only after the second step of cold drawing, the treatment with acid or peroxide when used can be applied before the cold drawing and immediately after the first step of treating the undrawn filaments with alcohol and formaldehyde. In fact, the acid contained in the filament can be that obtained from the acid catalyst used in the reaction solution of the first step when the filament is not washed after that step.

The filaments or yarn after the crosslinking step are characterized by an increased softening temperature and decreased solubility in organic solvents.

It is possible to weave or knit the yarn after the formaldehyde and alcohol treatment, but prior to the crosslinking step, any impregnation with acid or peroxide being done either before or after the weaving. By this means there can be obtained novelty fabric characteristics due to fiber shrinkage and realignment within the fabric construction. Staple fiber may also be prepared from this material. Fabrics constructed from such staple derive additional benefits from the resilient nature of the fiber.

The invention is useful in producing fibers with improved properties suitable for many textile uses. The increased softness, drape and resilience obtained in the fabrics made from the yarn treated by the present process is desirable in many cloth constructions, such as suiting, blankets, men's socks, etc. The increased melting point permits ironing at more elevated temperatures with consequent breadth of utility.

As many apparently widely different embodi-

ments 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 obtaining improved polyamide fibers, which comprises reacting at a temperature of from 40° C. to 130° C. a synthetic linear polyamide filament, which is essentially unoriented molecularly along the filament axis and in which the polyamide has hydrogen-bearing amide groups, with a solution having a pH below 3 of formaldehyde and oxygen-containing acid catalyst in an alcohol, stopping the reaction when from 1% to 20% of the total amide groups in the polyamide are converted into N-alkoxymethyl groups, cold drawing the filament thus treated to orient it, impregnating the oriented filament with an acid having an ionization constant greater than 1×10^{-6}, and then insolubilizing the filament by baking it.

2. A process for obtaining improved polyamide fibers which comprises the step of reacting at a temperature of from 40° C. to 130° C., a synthetic linear polyamide filament, which is essentially unoriented molecularly along the filament axis and in which the polyamide has hydrogen-bearing amide groups, with a solution having a pH below 3 of formaldehyde and oxygen-containing acid catalyst in an alcohol, stopping the reaction when from 1% to 20% of the total amide groups in the polyamide are converted into N-alkoxymethyl groups, the step of cold drawing the filament thus treated to orient it, and after one of said steps impregnating the filament with an acid having an ionization constant greater than 1×10^{-6}, and after said step of cold drawing insolubilizing the filament by baking it.

3. The process set forth in claim 1 in which said alcohol is methyl alcohol.

4. The process set forth in claim 1 in which said oxygen-containing acid catalyst is oxalic acid.

5. The process set forth in claim 1 in which said alcohol is methyl alcohol, and in which said oxygen-containing acid catalyst is oxalic acid.

6. A process for obtaining improved polyamide fibers, which comprises the step of reacting at a temperature of from 60° C. to 90° C. a synthetic linear polyamide filament, which is essentially unoriented molecularly along the filament axis and in which the polyamide has hydrogen-bearing amide groups, with a solution having a pH below 3 of formaldehyde and oxygen-containing acid catalyst in an alcohol, stopping the reaction when from 1% to 20% of the total amide groups in the polyamide are converted into N-alkoxymethyl groups, the step of cold drawing the filament thus treated to orient it, impregnating the filament after one of said steps with an acid having an ionization constant greater than 1×10^{-6}, forming the oriented filaments into a textile fabric, and then insolubilizing the filaments in the fabric by baking the fabric.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
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2,275,008	Coffman (2)	Mar. 3, 1942

FOREIGN PATENTS

Number	Country	Date
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