

UNITED STATES PATENT OFFICE

2,441,085

PROCESS OF MAKING NYLON FABRICS
ELASTIC BY TREATMENT WITH FORM-
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mington, Del., a corporation of DelawareNo Drawing. Application February 20, 1945,
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11 Claims. (Cl. 8—115.5)

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This invention relates to textile fabrics, and more particularly to elastic fabrics and methods for their preparation.

Elastic fabrics constructed from covered rubber monofilaments and cut rubber strips are well known. These fabrics, which may have a one-way or two-way stretch depending upon the construction are usually heavy and stiff. This results from the inability to spin a fine denier rubber thread and the need for a relatively heavy covering of a non-elastic wrapper to provide strength, a dyeable surface, and a more pleasant feel. This special fabric, moreover, is expensive to produce due to the cost of wrapping the individual strips, the difficulty of weaving and to the complicated machinery involved.

Valuable elastic fabrics can also be obtained from yarns spun from a modified nylon known as N-alkoxymethyl polyamide. The N-alkoxymethyl polyamide is made by reacting the initial nylon (high molecular weight or fiber-forming synthetic linear polyamides of the kind described in Patents 2,071,250, 2,071,253 and 2,130,948) with alcohol, formaldehyde and acid catalyst. The yarns of N-alkoxymethyl polyamide have a fine denier with exceptional elasticity, and can be woven or knit into highly elastic fabrics without the need for a heavy nonelastic wrapping on the fibers. The manufacture of such fabrics, however, involves the difficulties incident to weaving elastic yarns, and the weaving must be controlled by special procedures in the same manner as with covered rubber fibers.

This invention has as an object a method for obtaining elastic fabrics of the kind just mentioned and from similar polyamide material, but without either wrapping or weaving of an elastic material. A further object is the manufacture of fabrics having a one way or two way stretch by a method wherein a fabric is prepared from inelastic fiber and the fabric then rendered elastic by a simple after-treatment. Other objects will appear hereinafter.

The above objects are accomplished by a method which comprises preparing a fabric with a substantial proportion of filaments which are composed of the synthetic linear polyamides described in said patents but which are undrawn or but partially drawn (and hence unoriented molecularly along the filament axis or oriented to but a minor degree), and then treating the fabric with a reaction mixture which comprises alcohol, formaldehyde, and an acid catalyst, and which produces an elastic fabric through the reaction of said composition with the undrawn filaments

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to form N-alkoxymethyl polyamide in substantial amount.

The accomplishment of the objects of this invention through the reaction involved in the formation of N-alkoxymethyl groups upon a substantial number of the amide groups in the undrawn (i. e., unoriented) portion of the polyamide fabric, is based upon my observation that whereas the drawn polyamide fiber, which contains well ordered oriented hydrogen bonded polyamide chains, is essentially unaffected by the above mentioned reaction mixture, the undrawn fiber containing polyamide chains in a disordered grouping readily react with the formaldehyde and alcohol. By this means elasticity is produced within a fabric woven from nonelastic fibers, and the problems of windup, sizes, twisting and plying, which are involved in spinning elastic yarns, is avoided by carrying out all the handling and weaving steps on a nonelastic yarn, and then contributing elasticity as a final step after preparation of the fabric.

The undrawn filaments in the filling (or warp) can be converted to an elastic state without sensibly affecting the drawn fibers in the warp (or filling) which serve to maintain the form and strength of the fabric during the treatment, thus permitting a successful handling of the fabric. Instead of using drawn nylon as the non-reactive fibers in the warp or filling it is possible to use various other nonreactive fibers, for instance, cotton, rayon, silk, wool or linen in either the warp or filling. The fabric treated to give the elastic properties should have a preponderant amount, e. g., 90%, of undrawn nylon in at least one of either the warp or filling. A two way stretch fabric can be obtained by applying the present process to a fabric in which undrawn nylon is used in both the filling and warp. More care, however, must be taken in handling and control since there is no supporting material to help maintain strength and form during the treatment.

It is to be observed that synthetic linear polyamide or nylon filaments are inherently capable of being cold drawn, that is drawn in the solid state under tension, to a permanent elongation up to 600% or more of their initial length. The undrawn polyamide filaments used in the practice of this invention includes those which are drawn, and hence oriented, in minor amount of the above mentioned elongation possible. More particularly, the filaments can be used which have not been drawn more than 2:1 or 200%, since the reaction still takes place although slowly.

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In other words, the filaments, if they have been subjected to this degree of cold drawing, will be capable of being cold drawn to the residual amount of at least 300%. This invention, however, is most advantageously practiced with nylon filaments which are essentially wholly undrawn, that is not drawn more than about one-sixth of the total amount possible, that is with filaments that have not been drawn more than about 100%.

The fabric prepared from the undrawn polyamide fibers as described above is, in the best embodiment of the invention, reacted with the alcohol formaldehyde and acid catalyst at temperatures of from 60° C. to 80° C., although temperatures from about 50° C. to 90° C. can be used. The proportion and concentration of the reactants, referred to more particularly hereinafter, can vary considerably, and the time will depend on the temperature, concentration of the acid catalyst, and on several other factors. In general the reaction is continued until there has been some swelling of the undrawn filaments and is discontinued before there is any substantial solution of the filaments in the reaction liquid which would weaken the ultimate fibers or mat them together. An excessive period of reaction causes solution of the polymer in the treating bath with a resultant loss of material weight and eventually complete disintegration of the filling and disappearance of the fabric structure. The amount of N-alkoxymethyl substitution, which is the replacement of hydrogen of the amide groups —CONH— in the initial polyamide with the group —CH₂OR wherein R is an alcohol radical, is at least 20%, and is preferably 35%–55%. In other words in the polyamide composing the undrawn filaments after the alcohol and formaldehyde treatment, hydrogen bearing amide groups consisting of at least 20% of the total amide groups have been converted into N-alkoxymethyl groups.

The point of optimum reaction can be readily recognized as the point of maximum swelling of the reactant fiber. The swelling occurs longitudinally and laterally and it is more easily recognized as the former so that when the fabric reaches its greatest extent it is removed from the treating solution and quenched to stop the reaction. The quenching is best carried out in several steps. The swollen fabric is initially placed in an alcohol, preferably the alcohol employed in the reaction, although ethanol or methanol are satisfactory for universal use. After the reagents have been partially leached from the fabric the quenching may be stepped down towards a pure water wash in one or two steps, largely dependent upon the extent of the reaction. During quenching the swollen fabrics retract to, or slightly below, their original length. A direct quench in water tends to cause uneven retraction and to produce a rough sticky surface on the fiber due to precipitation of a small amount of dissolved N-alkoxymethyl polyamide.

The following procedure is representative of the most desirable and usually used practice of the invention:

Fabric woven from a combination of drawn and undrawn polyhexamethylene adipamide in the warp and filling, respectively, is immersed in a bath consisting of methanol, formaldehyde, and an acid catalyst in a ratio of approximately 5:5:1, and maintained at a temperature of 60–70° C. After some 15–75 minutes dependent upon the temperature and constitution of the bath, the fabric is removed and quenched in a

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wash solution. The completely quenched fabric is found to have excellent elasticity in the direction of the filling, and to be unaffected in the direction of the warp.

The practice of this invention is illustrated in more detail in the following examples in which the amounts are expressed as parts by weight.

Example I

A plain weave fabric woven on a standard ribbon loom with 47 filling ends/inch of 480 denier, 13 filament undrawn polyhexamethylene adipamide and 90 warp ends/inch of 102 denier, 13 filament polyhexamethylene adipamide, cold drawn to a ratio of 5.2:1 was placed in a solution consisting of 5 parts methanol, 5 parts paraformaldehyde, and one part anhydrous oxalic acid. The solution was maintained at 65° C. for 20 minutes, at the end of which time the fabric was carefully removed, washed in methanol for 10 minutes, then in a 50:50 methanol: water solution, and finally in water for 24 hours. The resulting fabric was slightly smaller in dimensions than originally, but otherwise had the same appearance. However, in the direction of the undrawn fiber the material was highly elastic and could be stretched to as high as 100% elongation with a 96% recovery within one minute of relaxation. There was no elasticity in the direction of the drawn fiber.

Example II

A plain weave fabric was constructed from 175 denier cotton with 60 warp ends/inch and 143 denier, 13 filament undrawn nylon with 50 filling ends/inch. The fabric was immersed in a large excess of solution of 5 parts methanol, 5 parts paraformaldehyde, and 1 part anhydrous oxalic acid at 62–64° C. for 30 minutes. At the end of this period the fabric had extended approximately 100% in width. It was removed and placed successively in methanol, a mixture of equal parts methanol-water, and in water. The fabric had now shrunk to roughly 75% of its initial width but had the same warp length as originally. The fabric was highly elastic, stretching to as high as 200% its original width with greater than a 95% recovery of this stretch after relaxation. Examination of the individual fibers revealed that the cotton was unaffected while the nylon was soft and pliable and highly elastic. In fact, the separated nylon fibers could be stretched as high as 400% with recovery of 95% of the stretch on relaxation.

Example III

A plain weave fabric was prepared from undrawn polyhexamethylene adipamide of intrinsic viscosity of 0.9 (intrinsic viscosity defined as in United States Patent 2,130,948). The fabric was constructed from 110 denier, 13 filament yarn with 100 warp ends and 50 filling ends per inch. A portion of fabric was placed in an excess of solution containing 5 parts methanol, 5 parts paraformaldehyde, and 1 part oxalic acid dihydrate maintained at a temperature of 65° C. At the end of 40 minutes, the fabric was removed from the solution and was washed in water. The material was found to be slightly shrunk in size, pliable and soft. It was highly elastic, recovering completely and rapidly from a 150% elongation in the direction of both the warp and the filling. The cloth before treatment was stiff and harsh, and had no reversible elongation. The

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stretching modulus of the treated fabric was much lower than that of the untreated fabric.

The polyamides which compose the undrawn filaments which are formed into the fabrics treated by the present process contain hydrogen-bearing amide groups and are, as has been mentioned above, those of the general type described in the patents previously referred to. They are high molecular weight or fiber-forming polymers 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 Patents 2,071,253 and 2,130,948. The preferred polyamides of this kind used in the practice of the present invention are those in which the average number of carbon atoms separating the amide groups is at least two.

Examples of particular reactants that can be used in preparing the polyamides comprise dibasic carboxylic acids such as glutaric, adipic, pimelic, suberic, azelaic, sebacic, diglycolic, phthalic, terephthalic, isophthalic and p-phenylene diacetic acids; diamines, such as ethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, m-phenylenediamine, 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 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, polythiourethanes, and polyhydrazides.

With further reference to the reactants used in treating the fabrics containing the undrawn polyamide, namely, acid catalyst, alcohol, and formaldehyde, the acid catalysts are oxygen-containing acids which produce a pH below 3 in the alcohol-formaldehyde solution used and have an equivalent conductance, measured at 25° C. in 0.01 N concentration in water, no greater than 370 ohms⁻¹ cm.². Such acids do not cause excessive degradation of the polyamide. Oxalic acid in a 5% to 10% solution is particularly

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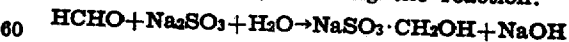
suitable. The organic acids which in methanol-formaldehyde solution produce a pH below 3 are preferred. Examples of these in addition to oxalic are maleic, fumaric, and the mono-, di-, or trichloroacetic acids, and p-toluenesulfonic acids. Certain inorganic acids and salts, such as phosphoric acid, ammonium bromide and calcium chloride can also be used, but greater care and operation within quite narrow limits is necessary to prevent excessive solution or degradation of the polymer. The useful acids are as strong as trimethylactic acid and not stronger than p-toluenesulfonic acid.

Although quantities as low as 3% and up to 20% can be used, the most desirable amount of catalyst in the reaction solution is, under most conditions, from 5% to 10% from the standpoint of readily avoiding an undesired degree of solubilization through excess of the catalyst and too slow a reaction through an insufficient amount.

Any primary or secondary aliphatic alcohol miscible with the formaldehyde used, for example those dissolving 20% or more of paraformaldehyde, can be used in the practice of this invention. The lower alcohols of four carbon atoms or less are the most advantageous for the present purpose because they produce the greatest degree of elasticity in the final product, and also react the most rapidly. Examples of suitable alcohols other than methanol are ethyl, isopropyl, n-propyl, normal, iso- and secondary butyl alcohols which may be employed as well as unsaturated alcohols such as allyl, methallyl and crotyl. Benzyl alcohol, ethylene glycol, diethylene glycol, cyclohexyl alcohol, and glycerol are also useful.

The formaldehyde is preferably used as paraformaldehyde, although other forms of formaldehyde and formaldehyde-liberating substances such as polyoxymethylene can be used. Aqueous solutions, however, are not desirable since the presence of water inhibits the reaction. For this reason the reaction mixture should not contain more than 20% water. It is preferred to use reaction solutions which are essentially non-aqueous, namely those containing not more than 5% water.

The quantity of formaldehyde and alcohol present in the reaction mixture can vary over relatively wide limits. The alcohol can be present in amount of from 20% to 75% of the reaction mixture, these amounts being from 30% to 50% for optimum reaction. The reaction mixture can contain as high as 75% or as low as 15% formaldehyde although for optimum reaction there should be from 20-40% formaldehyde present, which amount may be determined by titration with sodium sulfite, following the reaction:



The procedure followed to obtain the most advantageous properties varies with a number of factors. Thus the use of a high acid concentration enables more rapid reaction and the use of lower temperatures than does a low acid concentration. A similar effect results from a high formaldehyde content. The time required is dependent upon the nature and quantity of the acid and formaldehyde, the temperature, age of the reaction solution, degree of orientation of the fiber, thickness of the fiber, and the constitution of the polyamide. In general, with the best balance of conditions between 5 and 60 minutes is the most suitable reaction period. However, at high temperatures and high acid concentra-

tions the required elasticity can be obtained within a minute's time while under certain circumstances as long as 10 hours is necessary.

A modification of this process comprises the application of the above procedure to a polyamide fabric in which the synthetic linear polyamide has previously been subjected to a cross-linking treatment in the undrawn state. This cross-linking can be carried out by reaction of the polyamide with formaldehyde and an acid catalyst under mild conditions which do not give rise to elastic fibers. The cross-linked polyamide is obtained by a baking treatment. Fabric containing such cross-linked polyamide has greater resistance to the effect of organic solvents when subsequently treated with formaldehyde, alcohol and an acid catalyst to give an elastic fabric.

The fabric used in the treatment described herein can have a variety of forms. The essential feature for a one-way stretch is an undrawn unoriented reactive polyamide fiber woven together with a nonreactive fiber such that production of elasticity in the reactive fiber permits elongation of the fabric as a whole. Thus, not only a plain weave, but a twill, satin, figure, double or gauze weave may be employed. In addition to the use of drawn, oriented nylon in the non-reactive direction of the weave, it is possible and often desirable to use other such nonreactive fibers as cotton, mercerized cotton, rayon, linen, silk, wool and casein fiber. All these fibers are essentially unaffected by the treatment involved. It is, of course, not essential that the undrawn nylon be in the filling and the drawn nylon in the warp, for the reverse is equally operable. However, in weaving it is generally most desirable to employ the drawn yarn in the warp.

The production of a two-way elastic fabric by use of undrawn nylon throughout is particularly attractive. The procedure is the same as for one-way stretch, although, as has been previously noted, somewhat more care is required in the handling of the material during reaction. Not only woven, but also knitted fabric can then be used.

The N-alkoxymethyl polyamide fibers that are formed during the treatment of the fabric with the reaction solution, and which constitute the elastic portion of the fabric are cross-linked in the process of formation, so that after isolation they are insoluble in alcohols and are essentially infusible. It is possible to obtain further cross-linking by means of certain aftertreatments. The fabric may be impregnated with a small amount of acid and then baked. For this purpose any organic or inorganic acid, such as maleic, oxalic, sulfuric, hydrochloric, having an ionization constant greater than 10^{-8} , can be used. Again, unsaturated alcohols may be included in the reaction bath, and further cross-linking obtained by impregnation with benzoyl peroxide or other organic peroxy compounds followed by baking or irradiation with ultraviolet light.

Fabrics of the type described herein having what is known as one-way or two-way stretch are useful in a number of applications. For instance, they may be incorporated into clothing such as girdles, brassières, and other undergarments, bathing suits, hat bands, stocking tops, elastic bandages, athletic supporters, trusses, etc. For these and other uses a variety of constructions and fabrics of different weights and degrees of elasticity are required. By control of the extent of treatment the elastic efficiency and

the elastic modulus may be varied over wide limits, thus meeting these requirements.

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 obtaining elastic fabrics which comprises treating at a temperature of from 50° C. to 90° C. a textile fabric composed of fibers comprising filaments of synthetic linear polyamide containing hydrogen-bearing amide groups and capable of being cold drawn at least 300% with a reaction solution having a pH below 3 containing not more than 20% water and comprising formaldehyde, an aliphatic alcohol and an oxygen containing acid catalyst, continuing the reaction until dwelling of said polyamide filaments takes place and until the alkoxymethyl substitution of the hydrogen of the amide groups is from 35% to 55%, and discontinuing the reaction before any substantial solution of said filaments takes place, said alcohol being selected from the group consisting of primary and secondary alcohols.

2. A process for obtaining elastic fabrics which comprises treating at a temperature of from 50° C. to 90° C. a textile fabric composed of fibers comprising filaments of synthetic linear polyamide containing hydrogen-bearing amide groups and capable of being cold drawn at least 300% with a reaction solution having a pH below 3, containing not more than 20% water and comprising formaldehyde, an aliphatic alcohol and an oxygen containing acid catalyst, continuing the reaction until swelling of said polyamide filaments takes place and until the alkoxymethyl substitution of the hydrogen of the amide groups is from 35% to 55%, and, before any substantial solution of said filaments takes place, stopping the reaction by immersing the filaments in an alcohol, and then, after partial extraction of the reactants, immersing the filaments in water.

3. A process for obtaining elastic fabrics which comprises treating, at a temperature of from 50° C. to 90° C. with a reaction solution having a pH below 3 containing not more than 20% water and comprising formaldehyde, an aliphatic alcohol and an oxygen containing acid catalyst, a textile fabric woven in one of the warp and filler directions with fibers non-reactive with said solution and woven in the other of said directions with filaments of synthetic linear polyamide containing hydrogen-bearing amide groups and capable of being cold drawn at least 300%, continuing the reaction of said solution on the polyamide filaments until swelling thereof takes place and until the alkoxymethyl substitution of the hydrogen of the amide groups is from 35% to 55%, and discontinuing the reaction before any substantial solution of said filaments takes place, said alcohol being selected from the group consisting of primary and secondary alcohols.

4. A process for obtaining elastic fabrics which comprises treating, at a temperature of from 50° C. to 90° C. with a reaction solution having a pH below 3 containing not more than 20% water and comprising formaldehyde, an aliphatic alcohol, and an oxygen containing acid catalyst, a textile fabric woven in both the warp and filler directions with filaments of synthetic linear polyamide containing hydrogen-bearing amide groups and capable of being cold drawn by at

least 300%, continuing the reaction of said solution until swelling of the polyamide filaments takes place and until the alkoxymethyl substitution of the hydrogen of the amide groups is from 35% to 55%, and discontinuing the reaction before any substantial solution of said filaments takes place, said alcohol being selected from the group consisting of primary and secondary alcohols.

5. The process set forth in claim 1 in which said filaments are essentially wholly undrawn.

6. The process set forth in claim 1 in which said alcohol is one having not more than four carbon atoms.

7. The process set forth in claim 1 in which said reaction solution is essentially non-aqueous.

8. The process set forth in claim 1 in which said polyamide is hexamethylene adipamide.

9. The process set forth in claim 1 in which said filaments are essentially wholly undrawn, in which said alcohol is one having not more than four carbon atoms, and in which said reaction solution is essentially anhydrous.

10. The process set forth in claim 1 in which

said filaments are essentially wholly undrawn polyhexamethylene adipamide filaments, in which said alcohol is one having not more than four carbon atoms, in which said reaction solution is essentially anhydrous.

11. The process set forth in claim 3 in which said first mentioned fibers are fibers which are composed of said synthetic linear polyamide but which are drawn and oriented to the extent at which they are non-reactive with said solution.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,177,637	Coffman (1)	Oct. 31, 1939
2,275,008	Coffman (2)	Mar. 3, 1942

FOREIGN PATENTS

Number	Country	Date
565,066	Great Britain	Oct. 25, 1944

Certificate of Correction

Patent No. 2,441,085.

May 4, 1948.

ALLAN K. SCHNEIDER

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Column 8, line 20, for the word "dwelling" read *swelling*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of June, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,

Assistant Commissioner of Patents.

least 300%, continuing the reaction of said solution until swelling of the polyamide filaments takes place and until the alkoxymethyl substitution of the hydrogen of the amide groups is from 35% to 55%, and discontinuing the reaction before any substantial solution of said filaments takes place, said alcohol being selected from the group consisting of primary and secondary alcohols.

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