

UNITED STATES PATENT OFFICE

2,540,726

TREATMENT OF A HEAT SET, ORIENTED
NYLON FABRIC WITH FORMALDEHYDE

Boynton Graham, Claymont, and Orion Edwin
Schupp, Jr., Wilmington, Del., assignors to E. I.
du Pont de Nemours & Company, Wilmington,
Del., a corporation of Delaware

No Drawing. Application December 3, 1946,
Serial No. 713,852

3 Claims. (Cl. 8—115.5)

1

This invention relates to textile materials and more particularly to improved nylon fabrics and their manufacture.

The synthetic linear polyamides known as nylon and the production of fibers and fabrics therefrom have been described in a number of United States patents and in particular in 2,071,250, 2,071,253 and 2,130,948. These fiber-forming polycarbonamides described in the previously mentioned patents are obtained by several methods, for example, by self-polymerization of a monoaminomonocarboxylic acid, e. g., 6-aminocaproic acid or 12-aminostearic acid, by reacting in substantially equimolecular proportions a dibasic acid, e. g., adipic or sebacic acid with a diamine, e. g., hexamethylenediamine or with a monoaminomonoalcoholic alcohol, e. g., monoethanolamine, it being understood that these reactants can be replaced by their equivalent amide-forming derivatives. These linear polyamides also include polyesteramides, for example, those obtained by admixture with other linear polymer-forming reactants, such as glycol-dibasic acid mixtures, or mixtures of hydroxy acids, with the previously mentioned polyamide-forming reactants. The polyesteramides, when used in the practice of the invention described herein, should contain a ratio of amide groups to ester groups of at least 10%, and preferably 50% or more, amide groups. On hydrolysis with hydrochloric acid the amino acid polymers yield the amino acid hydrochloride, 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. In these polyamides the average number of carbon atoms separating the amide groups is at least 2 and usually less than 12. The preferred polyamides have an intrinsic viscosity of at least 0.4 (defined as in Patent 2,130,948) and a unit length (defined in Patents 2,071,253 and 2,130,948) of at least 7.

The nylons used in the practice of the present invention are those obtained from reactants of the above mentioned kind which yield polyamides having hydrogen-bearing amide groups. The fibers used are oriented to an extent given by a stretching or draw ratio of at least 3.5:1, but usually as high as possible to give high tenacity filaments.

Although the nylon fibers have wide textile use, fabrics woven therefrom are for certain uses in garments not wholly satisfactory because of poor drape, lack of softness, poor wrinkle resist-

2

ance, and absence of liveliness or resilience which renders such fabrics inferior to corresponding constructions in silk or wool. Frequently, nylons have been blended with other more resilient yarns to increase their resilience and other properties. However, such blends generally possess inferior properties such as strength, launderability, and water resistance. The heat setting of woven nylon fabrics, as described in U. S. Patent 2,365,931 brings about considerable improvement in softness and crease resistance, but the fabrics remain deficient in liveliness or resilience, and further improvement is necessary for the production of high quality garment fabrics from all-nylon constructions. Furthermore, for many textile uses, improvements in the dye receptivity, solvent resistance, and melting point of nylon fabrics are desirable.

Treatments of drawn and undrawn nylon as fiber or fabric with formaldehyde with or without other reactants have been proposed for conferring one or more of the properties of increased dye receptivity, melting point, solvent resistance, recovery from deformation and elasticity. In some instances these treatments result in relatively minor changes with but traces of formaldehyde found chemically combined with the nylon, and in other instances there has been at best noticeable improvement in but one or a few of the above mentioned properties. None of the previous processes of which we are aware have yielded products which possess to a like degree the combination of valuable properties which characterize the nylon fabrics described herein.

This invention has as an object the manufacture of improved nylon fabrics. A further object is a nylon fabric having improved liveliness, fullness, crease resistance, solvent resistance, melting point and dye receptivity. Other objects will appear hereinafter.

The above objects are accomplished by treating a heat-set fabric, composed of or containing oriented nylon fibers, with formaldehyde and an acidic catalyst by a procedure which comprises impregnating the heat-set fabric with an acidic catalyst and, while the fabric is maintained at fixed dimensions against shrinkage, heating the fabric under anhydrous conditions at a temperature of from 100° C. to 250° C. with formaldehyde in the form of a vapor until the nylon in the fabric contains at least 0.5% by weight of formaldehyde.

The heat-set nylon fabrics used in the practice of this invention are obtained by known methods which in general consist in heating the fabric at

3

a temperature within 25° C. of the softening point of the nylon in the medium in which the heating is effected. A convenient method is that described in the above mentioned Patent 2,365,931, wherein the fabric is pressed against a heated surface to a temperature of at least 190° C. and within 5° to 25° C. below the fusion point of the fibers. When the fabric is treated while impregnated with an agent which swells or softens the fabric, the fusion temperature, and hence the temperature at which heat-setting is conducted, is lower. For example, the greige or laundered fabric can be steeped in a 20% aqueous solution of ethylene glycol for 30 minutes, followed by wringing, air drying, and heating at 150° C. When glycol is the swelling agent, it is necessary to remove it since alcohols interfere with the subsequent formaldehyde reaction of the present invention. This removal can be accomplished by either a standard laundering procedure or by simple rinsing in water.

The acidic catalysts can be organic or inorganic and should be non-volatile in the usual sense that they are wholly non-volatile or only very slowly volatile at the temperature of treatment. The catalysts of this kind used in the practice of this invention are the acids and salts which yield a saturated aqueous solution of the catalyst having a pH below 3. While the concentration of the catalyst is not of particular importance, the treatment is most satisfactorily conducted in a manner that will impregnate the catalyst in the fiber, or deposit it thereon, in amount of from 0.1% to 5.0% of the weight of the nylon fiber.

In the best method of practicing the invention, a woven heat-set fabric is impregnated with a strong acid or acid-reacting salt, such as oxalic acid or ammonium chloride, by soaking several hours at room temperature in a 1% aqueous solution of the catalyst. Other catalysts include maleic acid, p-toluenesulfonic acid, phosphoric acid and calcium chloride. The concentration of catalyst in water may be as low as 0.1%. The catalysts of this invention may also be defined as acids which have ionization constants of not less than 1.0×10^{-2} at 25° C. or salts of such acids with weak bases. Briefer impregnations with more concentrated solutions or at higher temperatures may be used. The excess catalyst solution may be removed by passing the fabric through wringer rolls. Although excess catalyst does not inhibit the subsequent reaction with formaldehyde, its removal is desirable for uniformity of reaction and to avoid undue tendering of the fabric during the subsequent high temperature treatment. The impregnated fabric is then dried, either at room temperature or at an elevated temperature. A drying temperature of below 30° C. is preferable to avoid tendering of the fabric. During drying, the fabric should be held smoothly and under sufficient tension to prevent wrinkling or undue shrinkage. This may be accomplished either by wrapping the fabric smoothly on a tube or by supporting it in a suitable frame.

Final traces of moisture are then removed from the fabric by submitting it to brief heating at the temperature of the subsequent formaldehyde treatment, five minutes in a suitable oven being satisfactory. It is important that essentially all moisture be removed from the fabric prior to its treatment with formaldehyde vapor, since such moisture degrades the nylon and tends to inhibit the reaction of the nylon with the for-

4

maldehyde. The fabric is then suspended in the vapors of anhydrous formaldehyde at an elevated temperature. The time and temperature of treatment will vary with the degree of modification which is desired, 15-30 minutes at 130-150° C. being preferred. Noticeable improvement in resilience characteristics is obtained when the fabric combines with at least 0.5% of its weight of formaldehyde, and preferably with at least 1.5%. The amount of combined formaldehyde may be determined analytically by hydrolysis of the treated polyamide with a strong concentrated mineral acid, followed by neutralization, addition of excess sodium sulfite and titration of the sodium hydroxide generated.

The anhydrous formaldehyde vapor may conveniently be generated either by heating massive paraformaldehyde or by adding powdered paraformaldehyde to hot mineral oil. Alkaline catalysts accelerate this decomposition.

The acidic catalyst should finally be removed from the formaldehyde-treated fabric either by standard laundering procedures, or by simple rinsing in water.

Practice of this invention is illustrated more fully by the following examples in which amounts are given as parts by weight.

Example I

A satin fabric woven from drawn 3-denier/filament polyhexamethylenedipamide yarn was washed and ironed and then soaked for 40 minutes at room temperature in 20% aqueous ethylene glycol. The fabric was then passed through a wringer to remove excess liquid, allowed to dry at room temperature for 16 hours, ironed for 3 minutes at 150° C., and thoroughly rinsed. It was then soaked for 16 hours at room temperature in 1% aqueous ammonium chloride solution, excess solution was removed by passing through wringer rolls, and the fabric was wound smoothly on a tube. It was then dried for 5 hours at room temperature, followed by 5 minutes at 150° C. It was then immediately introduced for 15 minutes into a chamber filled with the vapors of anhydrous formaldehyde at 150° C., and was then laundered and ironed according to standard procedures.

The finished fabric possessed an excellent combination of softness, crease resistance, liveliness and fullness. The fabric had been rendered insoluble in boiling 88% aqueous phenol, it did not melt at 295° C., and its affinity for acid dyestuffs, e. g., du Pont Anthraquinone Blue RXO (Color Index Number 1076), was increased. It contained 2.60% of combined formaldehyde, based on the weight of the nylon.

The following tabulation indicates the marked improvement in resilience properties which was obtained.

Tests	Greige Fabric	Glycol-set Fabric	Glycol-set and formaldehyde-treated fabric
Crease Angle.....degrees..	45	35	20
Flexometer Resilience...per cent..	45	43	69
Flexometer Stiffness.....ergs..	2,600	2,000	2,000

In the above table the crease angle test is described in the previously mentioned Patent 2,365,931. It is the angle remaining 60 seconds after removal of the one kilogram weight from the folded fabric. The flexometer stiffness and

resilience are determined in the manner described by H. F. Schiefer in Bureau of Standards Journal of Research 10 647 (1933). Bends were made through a 70° angle so that fill threads were bent, with the face side of the satin in.

Example II

Fabric woven from mixed nylon/viscose staple was treated according to the conditions described in Example I. The treated fabric was markedly improved in softness, liveliness, and crease resistance.

The increased fullness obtained by the present procedure is a subjective quality, since the treated fabric feels thicker but is actually thinner by mechanical measurement.

If the procedure described herein is varied by including an alcohol, as by adding ethylene glycol to the catalyst impregnating bath, the product is deficient in crease resistance, liveliness and dye receptivity. If the heat-setting step is omitted, the product is considerably stiffer, and if the fabric is not maintained at fixed dimensions during the treatment with formaldehyde vapor, the dye receptivity is lowered rather than raised. If no catalyst is used, only traces of formaldehyde are combined, and none of the improved fabric properties are obtained; similar results are encountered if the fabric is not thoroughly dried after impregnating with catalyst, or if the formaldehyde vapor is not essentially anhydrous. If the fabric is treated with aqueous formaldehyde containing an acidic catalyst, followed by drying and baking, the improvements of this invention are obtained only to a minor extent.

The fabrics treated in accordance with the present invention can contain the nylon either as continuous filaments or as staple yarn. These fabrics can contain other types of fibers with the nylon fibers present in amount of at least 5%, and preferably at least 25% of the weight of the fabric.

The treatment of heat-set fabrics which have already been fabricated into garments comprises a preferred embodiment of this invention, since such treatment serves to set or fix the garment in desirable folds, creases, pleats, etc., in addition to improving its general liveliness, crease-resistance, and resilience.

Further examples of particular polyamide-forming reactants that can be used in making the nylon fibers are dibasic carboxylic acids such as glutaric, adipic, pimelic, suberic, azelaic, sebacic, diglycolic, terephthalic, and p-phenylene diacetic acids; diamines, such as tetra methylenediamine, pentamethylenediamine, hexamethylenediamine, m-phenylenediamine, p-xylylenedi-

amine, triglycoldiamine and bis(-p-aminocyclohexyl)methane; and primary monoaminomono-carboxylic acids such as 6-aminocaproic and 12-aminostearic. Interpolymers can be used in the practice of this invention; that is, those obtained from a mixture of polyamide-forming compositions.

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 we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A process of improving a fabric comprising oriented nylon fibers in which the nylon contains hydrogen-bearing amide groups, said fabric having been heat-set by heating at a temperature within 25° C. of the softening point of the nylon, the said process comprising impregnating said fabric with an aqueous solution of a non-volatile acid catalyst, said catalyst being one which yields a saturated aqueous solution thereof having a pH below 3, heating the impregnated fabric at a temperature of 100° C. to 250° C. until essentially all the moisture is removed from the fabric, and then heating the dried impregnated fabric while maintained at fixed dimensions with anhydrous formaldehyde vapor at a temperature of 100° C. to 250° C. in the absence of other reactants until the nylon in said fabric contains at least 1.5% by weight thereof of combined formaldehyde.

2. Process as set forth in claim 1 wherein the dried impregnated fabric is heated at a temperature of 130° C. to 150° C.

3. Process as set forth in claim 1 wherein the nylon is polyhexamethylenedipamide.

BOYNTON GRAHAM.

ORION EDWIN SCHUPP, JR.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
995,852	Eschallier	June 20, 1911
2,177,637	Coffman	Oct. 31, 1939
2,311,080	Pinkney	Feb. 16, 1943
2,430,953	Schneider	Nov. 18, 1947
2,434,247	Lewis et al.	Jan. 13, 1948

FOREIGN PATENTS

Number	Country	Date
463,472	Great Britain	Mar. 22, 1937