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## SYNTHETIC LINEAR POLYAMIDES

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This invention relates to synthetic fibers and more particularly to improvements in nylon fibers and fabrics.

The nylon fibers with which this invention is concerned are made from high molecular weight synthetic linear polyamides. Fibers derived from these polyamides, of which polyhexamethylene adipamide is an example, resemble silk in that their resistance to degradation on exposure to light outdoors or to sunlight behind glass is not so good as might be desired. In this respect they are inferior to fibers of regenerated cellulose. Improved light stability is highly desirable in polyamide textiles subject to considerable exposure to light, as for example draperies, upholstery, and outer garments.

Among the methods proposed to improve the durability of polyamide fibers to light has been the incorporation in the fibers of small amounts of a phenol. The effective agents of this kind, which include hydroquinone, catechol and a number of other polyhydric phenols, are disadvantageous in that they are soluble in water and are easily removed from the fibers by washing.

This invention has as an object the preparation of a polyamide composition having a high degree of stability on exposure to light. A further object is the manufacture of polyamide fibers containing a light stabilizing agent which cannot be removed by laundering. Other objects will appear hereinafter.

The above objects are accomplished by forming a catechol-aldehyde resin in the polyamide.

We have discovered that light stable polyamides are obtained when the catechol contained therein is combined in a resin, and that when the catechol resin is formed in situ in the polyamide the resulting fibers and fabrics are not only highly light-fast but retain this property after laundering.

Several methods are applicable in forming the resin in situ in the polyamide. The polyamide can be impregnated with a mixture of catechol, formaldehyde and catalyst and then baked. Or the polyamide after incorporation of the catechol by impregnation, melt-blending, or by incorporating with the original polyamide-forming reactants, can be baked in formaldehyde vapor. By this method it is possible to incorporate the catechol with the polyamide in the massive state, e. g. by melting the catechol and polyamide together, spin the mixture into fibers, and then treat the fibers with formaldehyde. In another method the polyamide is impregnated consecutively with catechol, an N-methylol compound (substitute for formaldehyde), and catalyst and the product baked. A further method comprises incorporating into the polyamide the initial or intermediate reaction product of catechol and formaldehyde, namely, a hydroxymethyl catechol and then baking. The amount of the resin incorporated by the above methods generally varies from about 0.2% to 5% and is preferably in the range of from 0.5% to 2%.

The best method now known for carrying out our invention is as follows: The polyamide yarn or cloth which is to have incorporated in it the resin derived from catechol for the purpose of improving its light stability is laundered once to remove oily materials and sizes. The dried, laundered fabric or fiber is immersed at 25° C. for about five minutes in a solution containing one part of catechol (equivalent to the weight of the yarn or fabric) dissolved in about twenty parts of aqueous 37% formaldehyde solution and containing a trace of oxalic acid as catalyst along with a small amount of sodium bisulfite. The yarn or fabric is removed from the impregnating solution and either centrifuged or run through squeeze rolls so that the final weight when wet is about 50–75% greater than the dry weight. The yarn or fabric is not dried further but is baked immediately in a forced-draft oven maintained at 140° C. for a period of six minutes or for a longer period if the sample is a large one. The baking process usually causes the development of a light-straw color. The unreacted catechol and soluble, low molecular weight, resinous products are removed from the baked yarn or fabric by several launderings similar to the one first used to remove size. The treated, dry yarn or fabric now contains about 0.5–1% of resin derived from catechol and is a very pale flesh color. Its resistance to degradation by light, such as by sunlight behind glass, or by the light of a carbon arc, or by exposure outdoors, as measured by reduction in tenacity, has been increased from five- to ten-fold. The yarn or fabric containing these resins derived from catechol is not appreciably altered in hand, nor is it seriously discolored. The resin is not removed by further laundering.

In order to avoid discoloration in the fibers the catechol used is that obtained in the form of a pure white, high melting, well crystallized solid by a simple distillation under vacuum and by collecting the material boiling at 120° C./8 mm. In the case of some of the derivatives, such as p-tertiary-butylcatechol, similar purification is necessary.

The synthetic linear polyamides used in the

practice of this invention are of the general type disclosed in U. S. Patents 2,071,250, 2,071,253 and 2,130,948. The polyamide of this kind, generally speaking, comprise the reaction product of a linear polymer-forming composition, for example, one consisting essentially of bifunctional reacting material, which comprises in substantial amount molecules containing two amide-forming groups each of which is complementary to an amide-forming group in other molecules in said composition. The polyamides can be obtained, for example, by self-polymerization of monoaminomonocarboxylic acid, by reacting a diamine with a dibasic carboxylic acid in substantially equimolecular amounts, or by reacting a monoaminomonohydric alcohol with a dibasic carboxylic acid in substantially equimolecular amounts, it being understood that reference herein to the amino acids, diamines, dibasic carboxylic acids, and amino alcohols is intended to include the equivalent amide-forming derivitives of these reactants. In the polyamides obtained from these reactants the average number of carbon atoms separating the amide groups is at least two.

These linear polyamides include also polymers obtained by admixture of other linear polymer-forming reactants, as for instance, glycol-dibasic acid mixtures or hydroxy acids in the case of polyester-amides, with the mentioned polyamide-forming reactants. 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.

*Example I*

Two parts of a polyhexamethylene adipamide yarn is immersed for five minutes at 25° C. in a solution of 2 parts of catechol, 0.2 part of sodium bisulfite and 0.3 part of oxalic acid in 40 parts of aqueous 37% formaldehyde. The wet yarn is run through a wringer to give an increase in weight between 50 and 75% and baked five minutes at 140° C. without drying. In order to remove unreacted materials, the yarn is washed five different times in 100 parts of 0.5% soap solution for ten minutes at 70° C., each wash being followed by four rinses in 50 parts of water. The treatment produces a gain of about 0.70% in weight. Further washing does not appreciably change this weight. The loss in tenacity after 600 hours' exposure to the light of a carbon arc is 22% as compared to 83% for the untreated polyhexamethylene adipamide contral. Under the same conditions the loss in tenacity is 91% for silk and 16% for regenerated cellulose.

*Example II*

Two parts of polyhexamethylene adipamide yarn is immersed for one hour at 25° C. in a solution of 2 parts of catechol and 0.34 part of hydrochloric acid (sp. g. 1.19) in 40 parts of aqueous 20% formaldehyde. The yarn is rinsed rapidly in water and dried in the air. It is baked for five minutes at 140° C. and is then washed in soap solution to remove unreacted material. The net gain in weight is 1.4%. After 600 hours' exposure to the light of a carbon arc the treated yarn is found to lose but 18% of its original tenacity compared to a loss of 87% of the original tenacity of an untreated polyhexamethylene adipamide control.

*Example III*

Two parts of polyhexamethylene adipamide yarn is immersed for one hour at 25° C. in a solution of one part of catechol, 0.1 part of diammonium hydrogen phosphate and 0.1 part of ammonium chloride in 40 parts of 20% formalin. The yarn is squeezed between rollers to remove adhering solution and is dried in the air. It is baked five minutes at 140° C. and washed as described in Example II to remove unreacted material. The net gain in weight produced by this treatment is 0.84%. After 600 hours' exposure to the light of a carbon arc the polyamide yarn showed a loss in tenacity of 24% as compared to 77% for yarn made from the untreated polyamide. After eight weeks' outdoor exposure to the sun the treated polyamide yarn showed a loss in tenacity of 36%, the untreated control 53%, and yarn from regenerated cellulose 50%. After eight weeks' exposure to sun behind glass the treated polyamide yarn lost but 9% in tenacity as compared to 60% for the untreated polyamide yarn and 19% for the regenerated cellulose yarn.

*Example IV*

Two parts of a skein of polyhexamethylene adipamide yarn is immersed for one hour at 25° C. in a solution of 3 parts of urea, 0.75 part of tertiary-butylcatechol and 0.2 part of phosphoric acid in 36 parts of 30% aqueous ethanol, followed by three rapid rinses in small portions of the same solvent. After drying the yarn is baked in formaldehyde vapor for ten minutes at 135° C. It is washed five times as described in Example I to remove unreacted material. The treated yarn is found to have gained 1.91% in weight. Comparable exposure tests of the treated and untreated polyamide yarn and of silk and regenerated cellulose shows a similar large improvement in tenacity retention in the treated polyamide yarn over the untreated control on exposure to the carbon arc. After five weeks' exposure to sunlight outdoors the treated polyamide yarn is found to be markedly superior to silk and also superior to regenerated cellulose yarn.

*Example V*

Two parts of polyhexamethylene adipamide yarn is immersed for two hours at 25° C. in a solution of 0.5 part of catechol and 0.2 part of tartaric acid in 40 parts of water, followed by three rinses in small portions of water. After drying, the skein is baked for 15 minutes at 140° C. in acetaldehyde vapor. It is then washed five times as described in Example I, the net gain in weight being about 0.70%. After 300 hours' exposure in the carbon arc, this treated yarn is found to lose but 59% of its original tenacity as compared with a loss of 73% of the original tenacity of an untreated polyhexamethylene adipamide control.

*Example VI*

Two parts of polyhexamethylene adipamide yarn is immersed for one hour at 25° C. in a solution of 1 part of catechol, 0.2 part of ammonidm chloride, and 0.2 part of diammonium hydrogen phosphate in 40 parts of 20% formalin. The yarn is removed from this solution and shaken quickly to remove adhering liquid. It is rinsed once in a solution of 3 parts of urea

in 17 parts of water, shaken, and dried. It is baked five minutes at 140° C. and is then washed five times as described in Example I. It is found to have gained 2.53% in weight. After 600 hours' exposure in the carbon arc, the treated yarn is found to have lost only 37% of its original tenacity, compared with a loss of 87% in the tenacity of the untreated polyhexamethylene adipamide control.

*Example VII*

Polyhexamethylene sebacamide yarn is improved in resistance to deterioration on exposure to light by a procedure which consists in immersing this yarn of 56 denier-10 filaments for five minutes at 25° C. in a solution of 2 parts of catechol and 0.34 parts of hydrochloric acid in 40 parts of 37% formalin. The yarn is shaken to remove adhering solution and is baked without drying at 140° C. for five minutes. It is washed as described in Example II. This treatment produces a net increase in weight of 3.0%.

*Example VIII*

A solution of 2 parts of hydroxymethyl catechol (prepared by reacting catechol with formaldehyde in alkaline medium followed by acidification) is made up in 40 parts of 50% aqueous ethanol. Two parts of a skein of polyhexamethylene adipamide yarn of approximately 50 filaments-175 denier is immersed in this solution at 75° C. for five minutes. The skein is removed from the impregnating solution and rinsed three times rapidly in fresh portions of 50% aqueous ethanol. After drying the skein is baked ten minutes at 125° C. in an electrically heated forced-draft oven. The skein is washed once in 0.5% soap solution for ten minutes at 100° C. followed by four rinses in water to remove any unreacted material. The treatment causes an increase in weight of the skein of 2.2%. The treated yarn, after 600 hours' exposure in the carbon arc is found to lose but 73% of its original tenacity, as compared with a loss of 90% of the original tenacity of a simultaneously exposed, untreated polyhexamethylene adipamide control.

It is to be observed that the use of phenols other than catechol for forming the resin in the polyamide is ineffective to accomplish the objects of this invention. In fact it has been found by experiment consisting of essentially repetition of Example I with phenol substituted for the catechol that there is a decrease in the inherent light stability of the resulting polyamide. Thus after 600 hours' exposure to the carbon arc the polyamide containing the phenol resin lost 92% of its original tenacity as compared to a loss of 87% for the untreated yarn. Likewise the use of formaldehyde alone without the catechol yields a polyamide yarn showing a greater loss in tenacity than the untreated polyamide.

Examples of other polyamides that can be used in the practice of this invention to obtain fibers of improved durability and high resistance to the degrading action of continued exposure to light are those disclosed in the patents referred to above. Typical examples include polydecamethylene adipamide, polyhexamethylene sebacamide, 6-aminocaproic acid polymers, the polyamide derived from ethanolamine and sebacic acid, interpolyamides derived from various mixtures of diamines, dibasic acids, and amino acids, and polyester-amides in which a portion of the diamine or amino acid of the polyamide forming ingredients has been replaced by an equimolar quantity of a glycol or hydroxy acid, respectively.

The polyamides treated according to the process of this invention can contain modifying agents, such as plasticizers, pigments, delusterants, dyes, cellulose derivatives, other polymers, and fillers. Polyamide fibers containing the catechol-aldehyde resins can be dyed, crimped, and in general treated like unmodified polyamide fibers.

It will be understood that the reference herein to catechol is intended to include also the derivatives that are well known to yield resins with aldehydes. These derivatives must not have the hydrogen of the hydroxyl groups replaced. Examples are p-tertiary octylcatechol, benzylcatechol, phenylcatechol, methylcatechol, dodecylcatechol, and methoxycatechol.

Of the aldehydes, formaldehyde is the most desirable resin-forming reactant from the standpoint of availability, ease in incorporation, and effectiveness. Compounds other than formaldehyde included by the mention herein of aldehydes are acetaldehyde ,butyraldehyde, furfuraldehyde, benzaldehyde, and glyoxal as well as the formaldehyde derivatives which are known to react similarly to formaldehyde and which comprise such compounds as hexamethylenetetramine, hydroxymethylphenols, hydroxymethylureas, hydroxymethylmelamines, hydroxymethyl derivatives of dibasic acid amides, and the ethers of these hydroxymethyl compounds.

The fastness of the resin to repeated washing can be improved somewhat by the addition of urea to the catechol and aldehyde reactants. Compounds which act similarly to urea are melamine, uron, biuret and other nitrogen compounds which yield methylol compounds on reaction with formaldehyde.

The reaction between catechol and aldehydes takes place without the addition of added catalysts. The reaction is, however, accelerated greatly by the addition of traces of acidic materials. The optimum pH for the reaction lies below 3.0. Suitable acids for catalyzing the reaction between catechol or substituted catechols and aldehydes or aldehyde derivatives are mineral acids, such as hydrochloric, sulfuric, or phosphoric, and organic acids such as citric, tartaric, oxalic, dichloroacetic, maleic, phthalic, benzoic, and acetic. Acidic compounds which are also strong antioxidants, such as thioglycolic acid and sodium bisulfite, can advantageously be used to replace part or all of the acid catalyst since they tend to prevent formation of color during the baking treatment. Certain ammonium salts can also be used as catalysts for the formation of catechol resins since in the presence of formaldehyde they form hexamethylenetetramine and liberate free acids. Although the use of ammonium salts as catalysts causes some discoloration of the yarn the color is not sufficient to preclude its use in most outlets.

The resin-forming reaction between the catechol and aldehyde is best carried out at temperatures above 50° C. and not exceeding 200° C. The reaction proceeds at room temperature but it is too slow to be practical, whereas very high temperatures cause undue oxidation of the catechol with formation of undesirable color. The best results are obtained at temperatures between 100° and 150° C. At this temperature the time of heating required is usually from about 2 to 30 minutes. Heating in an inert atmosphere is de-

sirable, particularly when high temperatures are used.

When the catechol is added to the finished yarn by impregnation from solution, a variety of solvents having no deleterious effect on the polyamide and capable of dissolving the catechol can be used. Solvents which have a swelling action on the polyamide can be used. Examples of suitable solvents are water, alcohols, esters, aromatic hydrocarbons, and halogenated aliphatic hydrocarbons. Solutions containing 1 to 10% catechol are used to greater advantage. Impregnations from solution can be carried out at ordinary or elevated temperatures, a shorter time usually being required for the same degree of impregnation when carried out at an elevated temperature. The aldehyde component, such as the formaldehyde, can be added by impregnation simultaneously with the catechol, by impregnation from solution either preceding or following the impregnation with catechol, or by treating the catechol-containing polyamide with the aldehyde in the vapor state. When the aldehyde is used in solution, concentrations ranging from 5 to 40% are normally used.

The formation of small amounts of catechol-aldehyde resins in the fiber-forming polyamides yields products which have a durability on exposure to sunlight considerably greater than either natural silk or the untreated polyamide and which retain this superiority after washing inasmuch as the agent is not removed in laundering. This invention makes possible the extension of nylon fabrics to purposes for which the many advantages inherent in these fabrics could not be fully realized heretofore because of the degration resulting from continued exposure to sunlight. For this reason the improved fabics of this invention are valuable in textiles subjected to continued light exposure such as in fabrics for men's and women's outer garments, tapes for Venetian blinds, sail cloth, draperies, umbrellas and upholstery. While the advantages of the products of this invention are of greatest significance in the case of fibers and fabrics, the products are also useful in making films, coating compositions, molded articles, and other products for which the unmodified polyamides are useful.

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 synthetic linear polyamide of improved durability on exposure to sunlight and containing in amount from about 0.2% to about 5% of a light stabilizing agent which is not removed on washing and which is a resin formed in situ in the polyamide from an aldehyde and a substance selected from the group consisting of catechol and monoalkyl-, monoaryl-, and monoalkoxy-substituted catechols, said polyamide being one which with hydrochloric acid yields a hydrolysis product selected from the class consisting of (*a*) monoaminomonocarboxylic acid hydrochloride, (*b*) a mixture of diamine hydrochloride and dibasic carboxylic acid, and (*c*) a mixture of amino alcohol hydrochloride and dibasic carboxylic acid.

2. A synthetic linear polyamide of improved durability on exposure to sunlight and containing in amount from about 0.2% to about 5% of a light stabilizing agent which is not removed on washing and which is a resin formed in situ in the polyamide from complementary resin-forming components comprising catechol and formaldehyde, said polyamide being one which with hydrochloric acid yields a hydrolysis product selected from the class consisting of (*a*) monoaminomonocarboxylic acid hydrochloride, (*b*) a mixture of diamine hydrochloride and dibasic carboxylic acid, and (*c*) a mixture of amino alcohol hydrochloride and dibasic carboxylic acid.

3. A fiber composed of the synthetic linear polyamide set forth in claim 1.

4. A fiber composed of the synthetic linear polyamide set forth in claim 2.

5. A method for obtaining a synthetic linear polyamide which contains an agent which imparts to said polyamide improved durability on continued exposure to sunlight and which is not removed by washing, said method comprising forming in situ in said polyamide in amount from about 0.2% to about 5% of a resin comprising the reaction product of an aldehyde and a substance selected from the group consisting of catechol and monoalkyl-, monoaryl-, and monoalkoxy-substituted catechols, said polyamide being one which with hydrochloric acid yields a hydrolysis product selected from the class consisting of (*a*) monoaminomonocarboxylic acid hydrochloride, (*b*) a mixture of diamine hydrochloride and dibasic carboxylic acid, and (*c*) a mixture of amino alcohol hydrochloride and dibasic carboxylic acid.

6. A method for obtaining a synthetic linear polyamide which contains in amount of from about 0.2% to about 5% of an agent which imparts to said polyamide improved durability on continued exposure to sunlight and which is not removed by washing, said method comprising impregnating said polyamide with a solution of resin-forming components comprising catechol, formaldehyde and an acidic catalyst, and heating the polyamide so treated, said polyamide being one which with hydrochloric acid yields a hydrolysis product selected from the class consisting of (*a*) monoaminomonocarboxylic acid hydrochloride, (*b*) a mixture of diamine hydrochloride and dibasic carboxylic acid, and (*c*) a mixture of amino alcohol hydrochloride and dibasic carboxylic acid.

7. The composition of matter defined in claim 1 in which said resin is the reaction product of tertiary butyl catechol and formaldehyde.

8. The composition of matter defined in claim 1 in which said resin is the reaction product of catechol and acetaldehyde.

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