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POLYMERIC MATERIAL

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This invention relates to synthetic linear polyamides, and more particularly to a process for improving the properties of shaped articles prepared from fiber-forming synthetic linear polyamides.

The synthetic linear polyamides used in the practice of this invention are of the type described in Patents 2,071,250 and 2,071,253, and in application Serial Number 136,031 filed April 9, 1937 by W. H. Carothers. These polyamides may be spun into filaments which can be cold drawn into fibers exhibiting by X-ray examination molecular orientation along the fiber axis. This orientation may also be obtained by cold rolling the polyamide in the form of sheets or ribbons. The polyamides from which the filaments, fibers, fabrics, bristles, films, and the like are made are of two types, namely, those obtainable from polymerizable monoaminomonocarboxylic acids or their amide-forming derivatives, and those obtainable from suitable diamines by reaction 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.

An object of this invention is to improve the properties of filaments, fibers, bristles, films, fabrics, and the like derived from synthetic linear polyamides. Further objects are to increase the recovery from deformation of such polyamides, and to increase their resistance to deterioration in the presence of ultraviolet light. Other objects will appear hereinafter.

These objects are accomplished by subjecting fiber-forming synthetic linear polyamides, preferably in the form of filaments, fibers, bristles, films, fabrics, or the like, to the action of hot formaldehyde or formaldehyde-liberating substances. During the treatment with formaldehyde the pH of the reaction medium should not go below 3.0.

The treatment of the polyamide articles with formaldehyde results in several beneficial effects. The formaldehyde treatment, for instance, effects a setting action which imparts to the polyamide articles a more or less permanent form to which they tend to recover after deformation. Thus formaldehyde treatment of crimped polyamide fibers improves the permanency of the crimp. As a further example, formaldehyde treatment of polyamide bristles increases their ability to recover from deformation; in other words, it decreases their tendency to curl in use. Under certain conditions treatment with formaldehyde decreases the stiffness of polyamide bristles. When the treatment is with certain formaldehyde-liberating compounds, as for instance dimethylol urea, there is a marked increase in their resistance to oxidative degradation under the influence of ultraviolet light. Thus the loss in tensile strength is only about 30% of that of an untreated control after 120 hours' exposure under a carbon arc. When polyamide fabrics are treated with reactive formaldehyde derivatives containing long chain aliphatic radicals, as for instance methylol stearamide, the fabric is given a water-repellent finish. Impregnation with stearamide, followed by treatment with formaldehyde, drying and baking also gives water-repellency. I have also found that the intrinsic viscosity of the polyamides is increased by heating with aqueous formaldehyde.

The following examples are illustrative of the methods used in practicing my invention:

Example I

A sample of 10-filament yarn, spun from melt at about 280° C. from polyhexamethylene adipamide (i. e., the polymer obtainable from hexamethylenediamine and adipic acid) having an intrinsic viscosity of 0.71, was cold drawn 275%, while wet with water, and kept wet with water. Yarns prepared in this way assume a spontaneous crimp upon drying in the relaxed condition. A portion of this yarn was immersed for a short time in a solution composed of 1000 parts of 10% aqueous formaldehyde containing 5 parts of ammonium chloride as catalyst, and then allowed to crimp by drying in the relaxed condition. After baking for 3 minutes at 150° C., the "crimp retentivity from stretch" (a measure of the permanency of the crimp) of the yarn was determined. This was done by determining the original crimped length (the length of the yarn in the crimped condition), the straightened length (the length of the yarn when the crimp is pulled out), and the crimped length after the yarn was stretched 10% (based on the original straightened length), immersed in boiling water in the stretched condition for 30 seconds, and then dried in the relaxed condition. The "crimp retentivity from stretch" was then calculated by substituting the values obtained in the following expression:

$$\text{Crimp retentivity from stretch (in \%)} = 100 \times \frac{\text{initial straightened length} - \text{final crimped length}}{\text{initial straightened length} - \text{initial crimped length}}$$

The "crimp retentivity from stretch" of the yarn treated in the above manner was 60%, while that of a similarly treated yarn in which the formaldehyde treatment was omitted was 3%.

EXAMPLE II

Samples of cold dawn polyhexamethylene adipamide bristles 15 mils in diameter which had been conditioned by immersion in boiling water for 2 hours, were heated in a sealed vessel at 100° C. for 24 hours, with 50 parts of a formaldehyde solution. The formaldehyde solution was composed of 1.02 parts of potassium hydrogen phthalate as a buffer to prevent excessive acidity, and 0.04 part of 0.02 normal sodium hydroxide in 100 parts of 37% formaldehyde solution. The pH of the solution was originally 4.6, but changed to 4.1 during the heating. The dry stiffness (modulus of elasticity of dry bristle $\times 10^{-6}$) was found to be lowered from 0.43 to 0.15 and the wet stiffness was changed from 0.17 to 0.07.

The residual deformation of bristles treated with formaldehyde in this way is decreased as may be seen by inspection of Table I. Measurement is carried out by soaking the bristle in water for at least 3 hours, wrapping the bristle four turns (1440° bend) around a mandril 0.094″ in diameter, holding it in this position for four minutes, releasing it, and then measuring the angle of deflection after recovery has ceased. The per cent residual deformation is expressed by the equation:

$$\text{Percent residual deformation} = \frac{100\alpha}{1440}$$

The per cent improvement in recovery of the formaldehyde treated bristle over the untreated bristle is expressed by the equation:

$$\text{Percent improvement} = \frac{100(\alpha' - \alpha)}{\alpha'}$$

In the above equations, α represents the residual angle of deflection of the formaldehyde treated bristle and α' the residual angle of deflection of the untreated bristle or control.

Table I

Bristle treatment	Percent residual deformation	Percent improvement in recovery
Conditioned 2 hours in boiling water (control)	25.2	
Conditioned as above and then treated with formaldehyde	8.3	67.3

EXAMPLE III

A sample of 83-denier, 10-filament yarn, which was obtained by spinning polyhexamethylene adipamide and cold drawing the resultant filaments 425% (i. e. until their length was increased 5.25 times), was treated with formaldehyde as described for the bristles in Example II. After washing with water and drying, the intrinsic viscosity of the yarn was found to have risen from 0.82 to 0.99. The tensile strength was not impaired by this treatment, whereas a sample of the same yarn heated in a similar bath containing potassium acid phthalate and sodium hydroxide but no formaldehyde suffered a drop in tensile strength from 4.35 to 1.64 grams per denier.

EXAMPLE IV

Samples of oriented polyhexamethylene adipamide bristles 15 mils in diameter, which had been conditioned by immersion in boiling water for 2 hours, were heated in a sealed vessel at 100° C. for 24 hours with 60 parts of a solution composed of 40 parts of dimethylol urea (containing 10–25% water) in 60 parts of water. The bristles were then washed with hot water and dried. Table II gives the per cent residual deformation of these bristles as compared with untreated bristles.

Table II

Bristle treatment	Percent residual deformation	Percent improvement in recovery
Conditioned 2 hours in boiling water (control)	25.2	
Conditioned as above and treated with formaldehyde	8.7	65.3

EXAMPLE V

A sample of 85-denier, 10-filament yarn composed of polyhexamethylene adipamide filaments which had been cold drawn 425% was treated with a dimethylol urea solution as in Example IV. The treated yarn was exposed under the carbon arc under conditions similar to those for an untreated sample of the same yarn. As may be seen in Table III below, the treated material has a much greater resistance to degradation by ultraviolet light as measured by the loss in tenacity and elongation.

In a second experiment a sample of the same yarn was heated in a closed vessel at 130° C. for 20.5 hours with 25 parts of a solution composed of 30 parts of dimethylol urea (containing 10–25% water) in 70 parts of water. The pH of the reagent solution changed from 7.0 to 7.8 during the heating. Upon exposing the treated sample to the carbon arc simultaneously with a sample of the untreated yarn, the treated material was found to have an increased stability toward degradation by ultraviolet light, as measured by tenacity and elongation. This may be seen in Table III.

Table III.—Ultraviolet exposure tests (Carbon arc)

Sample	Original tenacity g./denier	Tenacity percent loss after—		Original elongation, percent	Elongation percent loss after—	
		65 hrs.	120 hrs.		65 hrs.	120 hrs.
Untreated sample	4.38	46	55	23	64	66
Sample treated with dimethylol urea at 100° C	4.29	6	17	23	9	24
Sample treated with dimethylol urea at 130° C	4.17	8	16	22	14	32

EXAMPLE VI

A crepe de Chine type fabric woven of yarn spun from polyhexamethylene adipamide and cold drawn was impregnated with a 0.3% solution of monobasic sodium phosphate and dried. Immersion of the impregnated fabric in a 3% solution of methylol stearamide in 95% ethyl alcohol for 30 minutes, followed by drying and baking at 150° C., imparted a good degree of water repellency.

Measurement of the water repellency by a spray test involving the use of a constant five-foot head of water and the determination of the percentage water absorbed (Am. Dyestuff Reporter 26, 323

(1937)) showed that the treated fabric absorbed 32% of water both before and after washing as compared to about 72% for the untreated fabric both before and after washing.

The reaction mixture (solution of formaldehyde or formaldehyde-generating material) should not contain enough acid to cause hydrolysis of the polyamide. For this reason the pH value of the formaldehyde solution should not be permitted to go below 3.0. Buffers, such as potassium hydrogen phthalate, may be added to the reaction mixture when necessary to prevent the formaldehyde from becoming too acidic. With pure formaldehyde, however, the formaldehyde solution can be refluxed for 24 hours without developing sufficient acidity to affect materially the strength of the polyamide fibers.

The foregoing examples illustrate the application of this invention to synthetic linear polyamides in the form of yarns, bristles and fabrics. It will be apparent that other polyamide articles, e. g., ribbons, films, and sheets, can be similarly treated.

The invention is not limited to the particular polyamide cited in the foregoing examples but is applicable generally to synthetic linear polyamides containing amide groups as integral members of the main chain of atoms. As examples of other polyamides of the diamine-dibasic acid type may be mentioned polytetramethylene sebacamide, polytetramethylene adipamide, polypentamethylene adipamide, polypentamethylene sebacamide, polyhexamethylene sebacamide, polyoctamethylene adipamide, polydecamethylene adipamide, and poly-p-xylylene sebacamide. Polyamides of the amino acid type, such as those obtainable by polymerizing 5-aminocaproic acid, caprolactam, 9-aminononanoic acid and 11-aminoundecanoic acid may also be used. Interpolyamides, i. e., polyamides derived from a mixture of polyamide-forming reactants capable of yielding more than one polyamide if reacted in suitable combinations, can also be successfully treated with formaldehyde and certain of its derivatives as described above. As an example of such an interpolyamide, the polymer derived from equimolecular quantities of hexamethylenediamine, decamethylenediamine, adipic acid, and sebacic acid may be cited. Synthetic linear polyamides containing other groupings, such as ester groups, are within the scope of this invention, as an example of such a polyamide may be mentioned that prepared from adipic acid, hexamethylenediamine and hexamethylene glycol. A further example of such a polyamide may be prepared from adipic acid, hexamethylenediamine, and ω-hydroxydecanoic acid.

For many purposes it is advantageous to apply the formaldehyde treatment to polyamide articles containing modifying agents, e. g., plasticizers, pigments, dyes, agents for the modification of luster, antioxidants, oils, and resins. The polyamide treated may also contain urea or a phenol, in which case the formaldehyde reacts also with the urea or phenol to give novel effects. The invention can also be applied to mixed yarns and fabrics, i. e., yarns and fabrics composed of filaments of more than one polyamide or yarns and fabrics containing types of filaments other than polyamides.

Formaldehyde derivatives other than those mentioned above may be used, as for instance polymers of formaldehyde, hexamethylene tetramine, formaldehyde in the gaseous state, methylol mercaptans, methylol ureides, methylol amines, and hydroxymethyl ethers (semiacetals of formaldehyde). Treatment and reaction may be carried out in the presence of catalysts, particularly those of a weakly acidic or basic nature such as phthalic acid, boric acid, dilute formic acid, sodium acetate, borax, and sodium bisulfate.

Although the preferred media for carrying out the treatment is water or other oxygenated organic liquids such as alcohols or ketones, the invention may be practiced with other non-solvents for polyamides.

Reaction temperatures below the melting point of the polyamide are preferred, temperatures between 100 and 150° C. being most desirable. The reaction may be carried out at atmospheric, superatmospheric or subatmospheric pressure, in the light or in the dark.

The time required for optimum reaction is dependent upon the temperature and catalysts used. In most cases reaction is completed within 24 hours and usually within 15 minutes to 5 hours.

In general, it is desirable to work with 1 to 25 parts by weight of formaldehyde, or formaldehyde derivative, per part of polyamide to be treated, and to use the formaldehyde in concentrations of 10 to 50%. Use of an excess of formaldehyde promotes rapid reaction. The excess formaldehyde can be recovered.

This invention furnishes a convenient and economical method for improving polyamide articles. As has been mentioned before, the beneficial effects include increasing the resiliency and decreasing the stiffness of polyamide filaments, yarns, fabrics and bristles, increasing the crimp retention of crimped polyamide filaments, stabilizing polyamide articles to ultraviolet light and imparting water repellency to polyamide filaments and fabrics.

The invention is useful in producing fibers, fabrics, and bristles with improved properties for a number of uses. Thus, for example, polyamide bristles treated with formaldehyde are suitable for the manufacture of brushes where recovery from deformation is important. As another example, formaldehyde-treated polyamide bristles are suitable for the production of surgical sutures and fishing leaders where a low degree of stiffness is required. As a further example, dimethylol urea treatment of a polyamide fabric results in a desirable product for uses such as flags where stability toward sunlight is desirable. As a still further example, methylol stearamide treatment of polyamide yarns or fabrics results in a product having desirable properties for the manufacture of splash-proof stockings where water repellency is necessary.

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 improving the properties of articles formed from fiber-forming synthetic polyamides which comprises treating such articles with a compound of the class consisting of formaldehyde and formaldehyde-liberating substances.

2. A process which comprises heating a fiber-forming synthetic linear polyamide below its melting point in the presence of a solution of a compound of the class consisting of formalde-

hyde and formaldehyde-liberating substances in a non-solvent for the polyamide.

3. A process for improving the properties of articles formed from fiber-forming synthetic linear polyamides which comprises heating such articles with a solution of a compound of the class consisting of formaldehyde and formaldehyde-liberating substances in a non-solvent for the polyamide, said solution having a pH not substantially below 3.0.

4. A process for improving the crimp retentivity of crimped filaments of synthetic polyamide which comprises heating the crimped fibers in the presence of a compound of the class consisting of formaldehyde and formaldehyde-liberating substances.

5. A process for improving the properties of articles in the form of filaments, fibers, fabrics, bristles, and the like formed from synthetic linear polyamide which comprises heating said articles in the presence of a compound of the class consisting of formaldehyde and formaldehyde-liberating substances.

6. The process set forth in claim 1 wherein said polyamides are those obtainable by condensation polymerization of diamines and dibasic carboxylic acids.

7. The process set forth in claim 1 wherein said polyamides are those obtainable by polymerization of monoaminomonocarboxylic acids.

8. A process which comprises heating a fiber-forming synthetic polyamide with a compound of the class consisting of formaldehyde and formaldehyde-liberating substances.

9. A process which comprises heating a fiber-forming synthetic polyamide containing phenol with a compound of the class consisting of formaldehyde and formaldehyde-liberating substances.

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