

1

3,454,351

PROCESS FOR TREATING NYLON PRODUCTS
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7 Claims

This invention relates to products produced from the polymer, polyhexamethylene adipamide. More particularly, the invention is concerned with a process for treating shaped articles produced from such a polymer to improve their dyeability with basic type dyes and their dye resistance to acid type dyes.

By the term "shaped articles" produced from polyhexamethylene adipamide is meant a fiber, fabric, filament, yarn, pellicle, and the like produced from the homopolymer prepared from the reaction of hexamethylene diamine and adipic acid, commercially known as nylon 66. The process of this invention is also applicable to other structures prepared from this polymer such as strands, rods, tubes, bristles and the like.

While it is known that textile products obtained from this polyamide possess properties of great value, they are deficient in dyeing properties, in that they have practically no affinity for basic type dyes. This is a disadvantage in that the bright shades of color are often demanded for textile fabrics which can be obtained only with basic type dyes. In general, the basic dyes are characterized by the brilliancy of the colors they produce in textile fibers, and their great tinctorial power. Thus, it is often possible to obtain full shades of color with as little as one percent based on the weight of the fiber of basic dyes.

A number of methods have been proposed to increase the affinity of polyamide fibers for basic dyes, but generally these have not proven satisfactory in practice. One such proposal has been to increase acidification of the polymer by way of viscosity stabilizers having acidic groups. This particular approach has not been successful, however, in that sufficient acidity could not be obtained without excessive sacrifice in the molecular weight and spinning performance of the resulting polymer.

Another deficiency of textile fibers obtained from this polyamide is that all such fibers possess the same acid dyeable characteristics and will dye to a single shade only. This is a distinct disadvantage since it eliminates the possibility of obtaining other dyeable color effects where some of the fibers do not absorb dye or absorb less dye. It is desirable, therefore, to produce polyamide filaments which have acid dye resist characteristics so that combining such polyamide filaments with other polyamide filaments of an unmodified type in varying amounts, it would be possible to produce a polyamide fabric or article which would be dyeable to different tones of the same color.

Accordingly, it is an object of the present invention to provide a process for increasing the basic dye uptake of articles formed from a synthetic linear polyamide.

Another object of the instant invention is to provide a method for increasing the resistance to acid dyes of filaments, fibers, and yarns, prepared from polyhexamethylene adipamide.

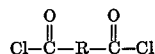
A further object of this invention is to provide a process for treating nylon articles which will increase their affinity for basic dyes and simultaneously increase their resistance to acid dyes.

These and other objects and advantages will become apparent in the course of the following detailed description of the invention when taken in combination with the claims appended thereto.

In general, these objects are accomplished by providing a process wherein a nylon article is treated so as to render the same more susceptible to accepting great amounts of

2

basic dyes and more resistant to the uptake of acid dyes. This process contemplates treating the already formed polyamide article with a diacid chloride of the following general formula:



in which R is a divalent hydrocarbon radical of from 2 to 30 carbon atoms and selected from the group consisting of alkylene, aralkylene, alkarylene, and arylene radicals, dissolved in a solvent selected from the group consisting of acetone, pyridine, dioxane, dimethylcarbamides and hydrocarbons containing 6 to 20 carbon atoms.

Representative examples of diacid chlorides which fit the above formula and are useful in the process of this invention are adipoyl chloride, succinoyl chloride, sebacoyl chloride, pimeloyl chloride, 1,12-dodecanedioyl chloride, 1,20-eicosanedioyl chloride, 1,22-docosanedioyl chloride, naphthalene-2,6-dioyl chloride, toluene 2,4-dioyl chloride, 4,4'-methylene-diphenyl dioyl chloride and the like.

The method of this invention is in general carried out by first completely drying the nylon product. After this drying step, the article is placed in a bath of solvent to which the diacid chloride reagent is added. Next, this bath is heated for a given period; the dwell time in the bath, the temperature of the bath and the reagent concentration all govern the amount of the reaction with the diacid chloride. After his reaction has taken place, the excess reagent is washed out and the article is dried. Articles treated by this process have greatly increased affinity for basic dyes as well as resistance to acid dyes.

As has been previously stated, the conditions of the treatment of this invention may be widely varied; time, temperature, reagent and reagent concentration may be varied over a wide range without adversely affecting the process of this invention. At the beginning of the process the nylon article should be dried. This drying can be accomplished by any conventional manner, such as by the use of a vacuum oven, a solvent bath, or treatment with a boiling solvent. Typical solvents useful in performing this drying step are: acetone, dioxane, pyridine, dimethylcarbamides, such as dimethylacetamide, and hydrocarbons containing 6 to 20 carbon atoms such as benzene, toluene, xylene, heptane, octane, and the like.

In treating the nylon article with the diacid chloride reagent, it has been found that the concentration of the reagent in the solvent bath should be somewhere between 0.1 to about 1.0 mole per liter of solvent. The solvent employed in the treatment bath may conveniently be any of the ones employed in the drying step as listed above. A preferred concentration of the reagent is from 0.2 to 0.8 mole per liter of solvent. It has been found that if the concentration of the diacid chloride is increased to much in excess of 1.0 mole per liter of solvent the treatment may degrade the nylon polymer. The concentration of the nylon article in this treatment bath may be as low as one gram per liter of solution or as high as approximately 200 grams per liter of solution.

The time the nylon product is reacted in the solvent-diacid chloride reagent bath may also vary over a wide range. This time interval should preferably be at least one hour and may vary up to 24 hours and more; however, periods of treatment in excess of 24 hours tend to degrade the polymer molecules. A preferred range of the time of treatment would vary 2 to 24 hours.

The reaction may be carried out at any temperature from room temperature to reflux temperature of the solvent; a preferable range would be from 60° C. to about 110° C. If the reaction is carried out at excessively high temperatures for long periods of time the nylon article may be degraded; therefore, a maximum of 110° C.

should not be exceeded for long intervals of time. It is contemplated that the process of this invention may be carried out on a continuous basis. That is to say, that by choosing the proper conditions for the variables of this invention, the treatment of this invention may be performed as a continuous operation.

In order to illustrate the invention and advantages thereof with greater particularity, the following specific examples are given. It is to be understood that they are intended to be only illustrative and are in no way intended to limit the invention. In these examples parts and percentages are given by weight unless otherwise indicated.

Example I

The process of this invention was carried out in this example and all following examples with samples, weighing approximately one gram each, of nylon 66 yarn. The yarn used was a 140-filament yarn having a tenacity of 8.1 grams per denier and an elongation of 18.6 percent. The polyhexamethylene adipamide polymer from which is was melt spun contained 0.032 percent titanium dioxide, based on the weight of the fiber, as delusterant.

A one-gram sample of this yarn was completely dried for a period of 24 hours by use of a vacuum oven which was maintained at 100° C. The yarn was next placed in a bath containing 25 milliliters of toluene and 0.525 mole per liter of adipoyl chloride. The bath containing the yarn was heated to 110° C. and the yarn was treated in the bath for a time period of 2.5 hours. After this treatment the sample was rinsed with 100 milliliters of toluene and any remaining unreacted reagent was extracted by treating the sample with a further 100 milliliters of toluene for a period of 24 hours. Finally, the sample was dried in a vacuum oven for a period of 24 hours, the temperature of which was maintained at 100° C.

In this example as well as in the other examples of this specification, the extent of the reaction was found by comparing the weight increase of the treated sample with a control sample treated in exactly the same manner but without reaction with the diacid chloride reagent. The amount of reaction in this example, as measured by a percent increase in weight, was determined to be 1.4 percent.

Example II

In this example a one-gram sample of nylon 66 yarn was treated in a manner identical to that of Example I, with the following exceptions: the treatment bath of toluene and adipoyl chloride was maintained at 68° C., and the treatment was carried out for a period of 24 hours. The extent of the reaction in this example was found to be a 0.22 percent gain in weight.

Example III

A sample, weighing approximately one gram, of nylon 66 yarn as described in Example I, was completely dried in a vacuum oven, which was maintained at 100° C. for a period of 24 hours. The fiber sample was then immersed in a toluene bath containing 25 milliliters of the solvent. To this bath was added a sufficient amount of the reagent sebacyl chloride to make the final concentration of the reagent in the toluene 0.525 mole per liter of solvent. The bath was next heated to 110° C. and the yarn sample was treated at this temperature for 24 hours. After this period of reaction the yarn was rinsed with 100 milliliters of toluene, and any unreacted sebacyl chloride was extracted by treating the sample with another 100 milliliters of toluene for 24 hours. Subsequently, the sample was dried as before in a vacuum oven for a period of 24 hours. The amount of reaction of the sample with the reagent in this example was determined to be an increase in weight of 2.0 percent.

Example IV

In this example a yarn sample, weighing approximately one gram, of nylon 66 yarn as described in Example I

was put through the treatment as described in Example III. However, in this example the reagent pimeloyl chloride was used in lieu of sebacyl chloride. The other variables of this invention, i.e., solvent, reagent concentration, temperature of treatment bath, and time of treatment remained identical to those used in Example III. The extent of the reaction in this example was found to be a percent increase in weight of 1.7 percent.

Example V

A sample of nylon 66 yarn as described in Example I and weighing approximately one gram was treated in this example by procedures and practices similar to those set forth in Example III. The treatment bath in this case was composed of toluene and the reagent naphthalene-2,6-diyl chloride which had a concentration of 0.525 mole per liter of the solvent. The yarn was reacted in this bath at a temperature of 110° C. for a period of approximately 24 hours. The percent increase in weight, used as an indicator of the extent of the reaction, of the sample in this instance was determined to be 1.9 percent.

Example VI

In this example, the one gram sample of nylon 66 yarn was treated under conditions and procedures identical to those set forth in Example III, with the exception that the diacid chloride reagent used was succinoyl chloride. Again, the concentration of this reagent was 0.525 mole per liter of the solvent toluene and the yarn was reacted at 110° C. for a period of 24 hours. The extent of the reaction in this example was found to be an increase in weight of 12.3 percent.

In order to demonstrate the practical usefulness of the process of the present invention, comparative tests of the yarns treated in the above examples were conducted to determine relative receptivity for basic dyes. The treated yarn samples of each of the above examples were dyed with comparable concentrations (10.0 percent based on the weight of the yarn) of the commercial basic dye, Sevron Blue 2G (C. I. Basic Blue 22). The dyeing was conducted in a bath having a liquor to fiber ratio of 40:1 and a pH of 6.7, adjusted by the use of ammonium acetate. The bath temperature was maintained at 100° C. and the dyeing period was 2 hours in length. The dye absorption values were determined by measuring spectrophotometrically the changes in dye bath concentration, i.e., the difference between the original dye concentration and the dye concentration after equilibrium (saturation) conditions have been reached. In addition to the yarn samples of the above examples, the control (a yarn sample treated in an identical manner, with the exception of the exposure to the diacid chloride reagent) of each example was dyed in a similar manner and used as a basis of comparison. In these basic dye tests the following results were obtained:

Example	Degree of treatment recorded as percent gain in weight	Equilibrium basic dye absorption recorded as percent of control
I.....	1.4	325
II.....	0.22	116
III.....	2.0	175
IV.....	1.7	250
V.....	1.9	236
VI.....	12.3	2,620

It is readily apparent from the foregoing test data that the yarns treated in accordance with the process of this invention are markedly improved over untreated yarns in their receptivity for basic dyes. Additionally, it is noted that the basic dye absorption appears to be a function of the degree of treatment or reaction, i.e., the greater the degree of treatment, the greater the basic dye absorption.

To further demonstrate the utility of the process of this invention, comparative tests of the yarn samples in Examples I and II were conducted to determine relative

5

resistance to acid dyes. Samples of the treated yarn of each of these two examples were dyed with comparable concentrations (3.0 percent based on the weight of the yarn) of the commercial acid dye, Scarlet 4 RA Conc. CF (C.I. Acid Red 18). The dyeing was conducted in a bath having a liquor to fiber ratio of 40:1 and a pH, adjusted by the use of acetic acid, of 3.3. The bath temperature was maintained at 100° C. and the dyeing period was 2 hours in length. Again, dye absorption values were determined by measuring spectrophotometrically the changes in dye bath concentration, i.e., the difference between the original dye concentration and the dye concentration after equilibrium (saturation) conditions had been reached. As before, the controls (similar yarn which had been treated in the same manner, but without being exposed to the diacid chloride treatment) of these two examples were dyed in identical fashion and used as a basis of comparison with the yarn samples treated by the process of this invention. The following results were obtained:

Example:	Equilibrium acid dye absorption recorded as percent of control, percent
I -----	49.6
II -----	60

It is noted in the above table that the yarns treated in accordance with the process of this invention are substantially improved over untreated yarns in their ability to resist acid dyes. As shown in Example I, the acid dye absorption is approximately one-half of that absorbed by a similar, but untreated, yarn.

Although a particular acid dye and basic dye were employed in the examples used to illustrate this invention, it is understood, of course, that the advantages of the invention are realized with all types of acid dyes and basic dyes which are capable of dyeing polyamide articles.

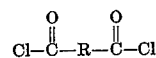
As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited by the specific embodiments set forth herein, but only by the claims which follow.

I claim:

1. A process for increasing the basic dye receptivity and the acid dye resistance of the articles produced from polyhexamethylene adipamide, comprising the steps of:

6

- (a) completely drying said polyhexamethylene adipamide article;
- (b) reacting said article, for a period of between 1 and 24 hours, with a solution, maintained between 60° C. and 110° C., said solution consisting essentially of 0.1 to 1.0 mole per liter of a reagent of the general formula,



wherein R is a divalent hydrocarbon radical of from 2 to 30 carbon atoms and selected from the group consisting of alkylene, aralkylene, alkarylene, and arylene radicals, dissolved in a solvent selected from the group consisting of acetone, pyridine, dioxane, dimethylcarbamides, and hydrocarbons containing from 6 to 20 carbon atoms;

- (c) washing said article with said solvent to extract all unreacted reagent; and
 - (d) drying said article.
2. A process as defined in claim 1 wherein said article is in the form of a filament.
 3. The process of claim 2 wherein said reagent is adipoyl chloride.
 4. The process of claim 2 wherein said reagent is sebacyl chloride.
 5. The process of claim 2 wherein said reagent is pimeloyl chloride.
 6. The process of claim 2 wherein said reagent is succinoyl chloride.
 7. The process of claim 2 wherein said reagent is naphthalene-2,6-dioyl chloride.

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