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TONE-ON-TONE ACID DYEING BLENDED TEXTILE OF NYLON AND NYLONS WITH SMALL AMOUNTS OF PHTHALIC ACID SULFONIC ACID, PHOSPHORIC OR PHOSPHONIC ACID ESTER CONDENSED THEREIN AND THE TEXTILE SO PRODUCED

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V 26,362

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U.S. Cl. 8-21

7 Claims

ABSTRACT OF THE DISCLOSURE

Method of producing a tone-in-tone color pattern on a textile material by dyeing in a single bath with an acid dye at a pH of about 5.0 to 10.5 a textile product having at least two polyamide fibers and fibers of polyamide amides with a small amount of sulfophthalic acid phosphoric or phosphoric acid esters condensed with the polyamide forming amine and dicarboxylic acid or caprolactam according to a predetermined pattern.

The present invention is concerned with a method for producing a tone-in-tone mouliné design or similar tone-in-tone color patterns on textile materials such as cloth, fabrics, webs, mats or the like which are composed of synthetic polyamide fibers, yarns, threads, filaments, etc. More particularly, the invention relates to a method in which such tone-in-tone color patterns are produced on polyamide textiles by dyeing in a single bath.

The best known processes for the production of textiles with a mouliné effect are those in which differently colored threads are fabricated or woven together in a predetermined manner to give the desired pattern. However, one can also make use of the distinct dye affinity of various types of natural, artificial or synthetic threads and then piece dye the finished textile article. If one wishes to use threads or filaments of the same type, e.g., where all of the filaments are obtained from the same synthetic polymer, then some technique must be employed so that one group of fibers or filaments will exhibit a substantially higher or lower dyeability than the other group.

It has been determined that the affinity or absorptivity of dyestuffs with polyamides can be varied by the addition of a number of so-called viscosity stabilizers. Such compounds can be organic acids or amines which have been added in small amounts to the initial polyamide-forming monomers before carrying out the polycondensation. The addition of an acid such as acetic acid reduces the absorption of acid dyes on the resulting polyamide, whereas amines cause an increase in the absorption of acid dyes on the polyamide. However, the amount of such viscosity stabilizers which can be added to the polyamide-forming initial monomers must be kept quite small, because otherwise the formation of the polyamide linear chain is terminated too quickly during polycondensation and the resulting polymer products do not have satisfactory fiber-forming properties. On the other hand, if the acids or amines as viscosity stabilizers are used in sufficiently small amounts to guarantee proper spinning of the polyamide into fibers having said acceptable textile properties, there is only a trivial difference in the affinity of acid dyes for the two different polyamide fibers, and one cannot produce satisfactory tone-in-tone color patterns.

The principal object of the present invention is to provide an improvement in the bath dyeing of polyamide textiles so as to produce a very perceptible and distinct tone-in-tone color pattern without any substantial loss of the fiber-forming properties of the polyamide itself.

Another object of the invention is an improved method for producing tone-in-tone color patterns on polyamide textile materials which are prefabricated from at least two different groups or types of polyamide fibers, including unmodified polyamides and/or polyamides which have been modified by introducing specific additives along with the usual polyamide-forming initial monomers before or during polycondensation thereof, as explained more fully hereinafter.

It has now been found, in accordance with the present invention, that substantially improved results can be achieved in the production of tone-in-tone color patterns on polyamide textiles by dyeing with an acid dyestuff in a bath adjusted to a pH-value of about 5.0 to 10.0 a textile product obtained by: (1) selecting at least two of the following distinct groups of polyamide fibers (A) an unmodified polyamide, (B) a polyamide modified by condensing into the polymer a small amount of a monomeric component selected from the class consisting of phosphoric phosphonic acid esters, and (C) a polyamide modified by condensing into the polymer a small amount of an isophthalic sulfonate as a monomeric component, and (2) working each of the at least two distinct groups of polyamide fibers into said textile product according to a predetermined pattern. The resulting textile product dyed in a single bath brings out a very perceptible tone-in-tone color pattern corresponding to the manner in which the two or more different distinct groups of polyamide fibers, as threads, yarns or the like, have been woven or otherwise fabricated into the undyed textile product. When used in relatively small amounts, e.g., less than 5% by weight, the modifying additives of the polymers under (B) and (C) retain very satisfactory fibrous properties. The preferred embodiments of this invention will be apparent from the remainder of this detailed description.

The term "unmodified polyamide" is employed herein with reference to such common polymers as polycaprolactam and polyhexamethylene adipamide, characterized by a recurring-NHCO-group in an otherwise linear alkylene chain, but is also intended to include those modifications of said common polymers which do not perceptibly alter the dye absorptivity thereof, e.g., where the alkylene chain may vary from about 4 to 12 carbon atoms or where various intermediate or terminal groups are added to the polymer chain without changing its dyeing characteristics.

Throughout this specification, percentages by weight of various monomeric components which form the polyamides are given with reference to the total weight of the initial polyamide-forming reactants which make up the unmodified polymer, e.g., with reference to the total weight of caprolactam or the total weight of the so-called AH-salt (hexamethylene diamine-adipate). However, in the appended claims, these same percentages are used with reference to the total weight of the polymer since the calculated amounts are substantially the same for all practical purposes when working in a low range of up to 5% by weight. Also, slight variations of these percentages of the additives are permissible, particularly where at least one of the groups of fibers in the textile product is composed of unmodified polyamide.

For the production of the unmodified polyamide fibers, one can use polyamides prepared from conventional monomers including lactams, preferably caprolactam, or those prepared from aliphatic dicarboxylic acids and aliphatic diamines, preferably adipic acid and hexamethylene diamine. The modified polyamides are obtained under

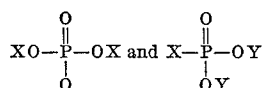
the conditions of the usual polycondensation process by adding to the initial conventional monomers about 0.1 to 5% by weight, preferably 0.5 to 3% by weight, of the phosphoric acid ester or the phosphonic acid ester, or by adding about 0.02 to 3% by weight, preferably 0.1 to 2% by weight, of the isophthalic sulfonate.

When modifying the polyamide with a phosphoric acid ester or a phosphonic acid ester and especially when using caprolactam as the initial polyamide-forming material, the addition of a small excess amount of an alkylene diamine of 4 to 12 carbon atoms, particularly hexamethylene diamine, is recommended. In this case, one can add about 0.1 to 1% by weight, most expediently about 0.3 to 0.5% by weight, of excess hexamethylene diamine, e.g., with reference to the caprolactam.

If the polyamide is modified with the isophthalic sulfonate, there can also be separately added to the caprolactam or AH-salt a small excess amount of these alkylene diamines and preferably hexamethylene diamine, e.g., in an amount of about 0.02 to 2% by weight, advantageously about 0.1 to 1% by weight, in each case with reference to the initial polyamide-forming material. It is even more expedient to use the hexamethylene diamine salt of the isophthalic sulfonate (i.e., the 1:1 salt of the isophthalic sulfonate and the diamine), and in this instance, one can choose an additive amount of this diamine salt of about 0.1 to 5% by weight, preferably about 0.5 to 3% by weight.

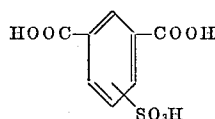
In referring to an excess of an aliphatic diamine, such as hexamethylene diamine, an amount is specified as one of the monomeric reactants in forming the modified polyamides which is in excess to any aliphatic diamine normally required for production of the unmodified polyamide. In the polycondensation of the monomeric reactants, this excess of the aliphatic diamine can be added as such or as the "salt" of one of the modifying components specified under (B) and (C).

The phosphoric and phosphonic acid esters which are especially useful for the modification of the polyamide have the formulae:



in which X represents aryl, aralkyl or alkyl, and Y represents hydrogen, aryl or alkyl. Aryl groups are preferably restricted to phenyl and aralkyl groups are preferably restricted to phenylmethane, i.e., benzyl, with not more than one of these aromatic groups as a substituent, while the alkyl groups are preferably lower alkyl of about 1 to 4 carbon atoms such as methyl or ethyl. Suitable phosphoric and phosphonic acid esters include the following specific compounds: phosphoric acid triethyl ester, ethanephosphonic acid diethyl ester, phenylmethane-phosphonic acid diethyl ester, phosphoric acid triphenylester, phosphoric acid trimethylester, methanephosphonic acid dimethyl ester, phenyl phosphonic acid dimethyl ester.

The isophthalic sulfonate is represented by the formula



wherein M represents an alkali metal, preferably sodium, and this compound is most advantageously employed in the form of its alkali metal salts, especially the sodium salt of 5-sulfoisophthalic acid or in the form of its 1:1 salt with hexamethylene diamine. Other useful sulfonates of this type include the 4-sulfoisophthalic acid.

Both the unmodified and the modified fibers, threads or filaments used in accordance with the invention can contain delustering agents such as TiO_2 or other conventional additives or finishing agents which do not cause any substantial change in the dye absorption properties. In addition,

all of these polyamide fibers can be subjected to any of the conventional texturizing processes in order to provide crimping, loop formation or the like.

Textile products of all types, including woven and knitted goods and especially carpets, can be fabricated by the use of the above-noted polyamide fibers in the form of filaments, threads, yarns or the like by using various combinations of the unmodified polyamides (A) with one or two of the differently modified polyamides (B) and (C), in a predetermined pattern. And conventional apparatus can be employed to weave or otherwise arrange the fibers in the textile product.

A special advantage of the process according to the invention will be apparent from the fact that the textiles can be dyed in a bath, i.e., by piece dyeing in a single bath. As the dye liquor, it is desirable to use aqueous solutions of acid dyes and to carry out the dyeing at a pH-value of about 5.0 to 10.0, preferably about 8 to 9. Under these conditions, the acid dye is moderately strongly taken up by the unmodified polyamide fibers or threads. By comparison, the polyamide fibers or threads modified with phosphoric or phosphonic acid esters, are colored very intensely by the acid dye, while the polyamide fibers or threads which contain the isophthalic sulfonate have only a very slight receptiveness for acid dyes and remain practically undyed.

Thus, by suitable choice of the fibrous components in a predetermined woven, knitted or otherwise fabricated pattern, one can produce textile materials dyed in two or three perceptibly distinct colorations. These colorations exhibit a very good tone-in-tone shading. At the same time, the modified polyamides retain desirable fibrous properties. The process of the invention is especially advantageous as applied to carpets, rugs or the like which have a jute backing, in that the dyeing is carried out in an alkaline pH-range and under these conditions the impurities of the jute do not appear on the polyamide fibers as is the case when the dyeing is attempted in an acid pH-range.

The invention is further illustrated by the following examples but is not to be limited to these examples.

EXAMPLE 1

A polyamide is produced from caprolactam according to the conventional polycondensation process and this is spun into multifilament thread with a titer of 1000 denier (72 individual filaments). In an analogous manner, caprolactam is polycondensed with an addition of 1.8% by weight of ethane-phosphonic acid ethyl ester and 0.31% by weight of hexamethylene diamine (amounts with reference to the caprolactam), and a multifilament thread of the titer 1000 denier (72 individual filaments) is likewise produced from the polyamide modified in this manner. Two threads of non-modified polyamide and one thread of modified polyamide are textured by press-crimping and then drawn together with a twist of 75S (right-hand turns per meter). From the yarn of 3000 denier obtained in this manner, a carpet is tufted with the aid of a jute backing. The finished carpet is dyed in an aqueous bath which contains 1% Telon Fast Marine Blue G at a pH-value of 8.5 and a temperature of 100° C. for a one-hour period in a winch vat. The ratio of textile to liquor amounts to 1:50. After completion of the dyeing, the modified polyamide yarn receives a deep marine blue coloration, while the non-modified portion becomes cornflower blue. The carpet shows a very good two-shaded blue tone-in-tone mouliné effect.

In order to better ascertain the difference in the intensity of the dyeing, strands of the above described polyamides having a weight of 3 grams in each case were dyed in the same bath with the same acid dyestuff. The dyestuff taken up on the threads was then completely dissolved out with a pyridine-water mixture. By measurement of the extinction of both dyestuff solutions, the amount of dye may be determined which was taken up

by the dye samples. It was determined that the modified polyamide fibers took up 4.1 times as much dyestuff as the non-modified fibers.

EXAMPLE 2

As described in Example 1, there were produced a nonmodified polyamide from caprolactam and a modified polyamide from caprolactam with the addition of 1.8% by weight of ethane-phosphonic acid diethyl ester and 0.31% by weight of hexamethylene diamine as well as a polyamide from caprolactam with 1.07% by weight of the hexamethylene diamine salt of sodium isophthalic sulfonate and 0.75% by weight of sodium isophthalic sulfonate. Each of the multifilament threads, which were obtained from the melt of the polyamide and subjected thereafter to a press-crimping process, were finally collected together into a yarn of 3000 denier. A carpet was produced from this yarn, which was dyed with Telon Fast Marine Blue G while observing the conditions set forth in Example 1. The carpet exhibits a three colored tone-in-tone mouliné effect in weak-light blue/deep marine blue/cornflower blue. In the above described examination of the amounts of dyestuff taken up by the individual threads, it was determined that the polyamide modified with isophthalic acid sulfonate had been practically undyed, both of the other thread tests exhibiting the same results as in Example 1.

EXAMPLE 3

One thread from an unmodified polyamide of caprolactam and two identical threads of a modified polyamide (caprolactam with 2.0% by weight of phosphoric acid triethyl ester and 0.31% by weight of hexamethylene diamine) were twisted together. A carpet was produced therefrom and then dyed with the use of Anthralan Blue B (C. I. Acid Blue 41, 62130) as an acid dye. The conditions in the dyeing corresponded to those which are set forth in Example 1, with the exception that the bath was adjusted to a pH-value of 9. The dyed carpet shows as two-colored blue tone-in-tone mouliné effect. By extinction measurement, it was found that the modified polyamide had 3.2 times more dyestuff than the non-modified polyamide.

EXAMPLE 4

A modified polyamide was produced from caprolactam with 0.75% by weight of phosphoric acid triethyl ester and spun into a fibrous tow, which was then crimped and cut into staple lengths. The resulting fibers were worked together with fibers of an unmodified polyamide of caprolactam into a yarn, in a mixture of 2:1. The fiber yarn was used for the production of a fabric in a twill weave. Dyeing was carried out with the use of an aqueous dye liquor containing 1% Anthralan Blue B at a pH-value of 9. The fabric exhibits a blue two-toned mouliné effect. By means of the above explained extinction measurement, it was determined that the modified polyamide took up 1.7 times as much dyestuff as the unmodified polyamide.

EXAMPLE 5

A fabric was produced from a fiber yarn composed of one part of an unmodified polyamide of adipic acid and hexamethylene diamine and two parts of a modified polyamide of the same initial materials with 0.74% by weight of phosphoric acid triethyl ester. This fabric was dyed in the above described manner with Telon Fast Marine Blue G at a pH-value of 8.5. The fabric then exhibits a blue tone-in-tone mouliné effect. The modified polyamide takes up 2.2 times as much dyestuff as the unmodified polyamide.

EXAMPLE 6

A fiber yarn was produced from separate threads composed of (A) unmodified polyamide of adipic acid-hexamethylene diamine, (C) the same polyamide modified

by condensing in 2.22% by weight of sodium isophthalic acid sulfonate and 0.96% by weight of hexamethylene diamine, and also (B) the same polyamide modified by condensing in 2.4% by weight of phenylmethane-phosphonic acid diethyl ester. This yarn is formed into a fabric, which is then dyed with Anthralan Blue B at a pH-value of 8. A three-toned mouliné effect is obtained. While the polyamide modified with the isophthalic sulfonate takes up practically no dyestuff, the dye take-up in the material modified with the phosphonic acid ester amounts to 3.5 times as much as the unmodified polyamide.

In addition to the acid dyes named in the foregoing examples, similar results in the form of a mouliné effect or another color pattern on mixtures or fabricated patterns of the modified and unmodified polyamide fibers can be achieved with all of the well-known class of acid dyes.

Other useful acid dyes includes by way of example: Acilan Marine Blue, Acilan Marine Blue B, Alizarin Cyanine Green, Alizarin Cyanine Green 5G (C. I. Acid Green 41 C. I. 62560). Acilan Naphthalene Red G, Acilan Ponceau 4GBL (C. I. Acid Orange, C. I. 15970), Diacilan Grenadine 5, and Acilan Orange GX (C. I. Acid Orange 10 C. I. 16230). It is necessary to apply these acid dyes while observing conventional conditions and precautions and also while adjusting the aqueous dye bath to a pH-value of about 7.5 to 9.5. The optimum conditions of the dye bath and the dyeing process for any particular acid dye, for example with respect to the textile to dye liquor ratio, the temperature, the length of the dyeing time and the pH-value within the prescribed range, can be readily determined for each mixture of modified and unmodified polyamide fibers, threads or yarns by a simple preliminary test.

The invention is hereby claimed as follows:

1. An improved method of bath dyeing polyamide textiles to produce a tone-in-tone color pattern, which comprises dyeing with an acid dyestuff in a bath adjusted to a pH-value of about 5.0 to 10.0 a textile product obtained by:

(1) selecting at least two of the following distinct groups of polyamide fibers

(A) an unmodified polyamide

(B) a polyamide modified by condensing into the polymer a small amount of a monomeric component selected from the class consisting of phosphoric and phosphonic acid esters, and

(C) a polyamide modified by condensing into the polymer a small amount of an isophthalic acid alkali metal sulfonate salt as a monomeric component, and

(2) working each of the at least two distinct groups of polyamide fibers into said textile product according to a predetermined pattern.

2. A process as claimed in claim 1 wherein the unmodified polyamide is a polymer selected from the class consisting of polycaprolactam and polyhexamethylene adipamide.

3. A process as claimed in claim 1 wherein the modified polyamide (B) contains about 0.5 to 3% by weight, with reference to the total weight of the polymer, of said monomeric component selected from the class consisting of the phosphoric and phosphonic acid esters, and the modified polyamide (C) contains about 0.1 to 3% by weight, with reference to the total weight of the polymer, of said an isophthalic acid alkali metal sulfonate salt.

4. A process as claimed in claim 3 wherein said modified polyamide (B) contains an excess of about 0.3 to 0.5% by weight, with reference to the total weight of the polymer, of an alkylene diamine, condensed into the polymer and said modified polyamide (C) contains an excess of about 0.1-3.0% by weight, with reference to the total weight of the polymer, of an alkylene diamine condensed into the polymer.

5. A process as claimed in claim 4 wherein the alkylene diamine condensed into each of the modified polyamides (B) and (C) is hexamethylene diamine.

6. A process as claimed in claim 1 wherein the dye bath is adjusted to a pH-value of about 8 to 9.

7. The textile product having a tone-in-tone color pattern as produced by the method of claim 1.

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8—15, 55; 57—140; 161—172

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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October 28, 1969

Ernst Meyer et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 64, "SO₃H" should read -- SO₃M --. Column 6, line 40, "10.0" should read -- 10.5 --.

Signed and sealed this 31st day of March 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents