DYING AND LIGHT STABILIZING NYLON YARNS WITH SULFONATED DYES; STERICALLY HENDERED PHENOLS, AND ALKYL-NAPHTHALENE SULFONATES WITH OR WITHOUT OTHER ULTRAVIOLET LIGHT ABSORBERS

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ABSTRACT OF THE DISCLOSURE

Nylon yarns are dyed with a solution of a water soluble sulfonated acid dye, a 2,6-di-alkyl-4-phenyl phenol, an alkyl- or aralkyl-substitute naphthalene sulfonic acid ammonium or alkali metal salt. In addition, ultraviolet light absorbers, such as hydroxybenzophenones, hydroxybenzophenones, or aromatic substituted acrylonitrile can be used in the solution.

This invention relates generally to textile fibers and, more particularly, to a process for dying nylon yarns. It is now well known that streaking occurs in acid-dyed fabrics constructed with synthetic linear polyamide yarns, especially with continuous filament polyamide yarns. Therefore, the level-dyeing disperse dyes are broadly used for nylon fabrics, but not all disperse dyes have acceptable lightfastness. With these disperse dyes that provide acceptable dye lightfastness, a severe problem in fading results because of the NO₂ and the O₂ conventionally in the air. Level dyeing can be accomplished with acid dyes that are chemically stable to NO₂ and O₂ by using anionic leveling agents, but such acid dyeing processes do not produce lightfast fabrics. In the acid dyeing of carpets, an additional problem exists in the fugitive stain from the jute backing, and this problem is evidenced by both streakiness and insufficient lightfastness.

The principal object of this invention is to provide superior level-dyed polyamide yarns. A further object of this invention is to provide nylon yarns that are level-dyed, lightfast, and stable to gaseous atmospheric conditions that are recognized to fade disperse-type dyes.

Other objects will appear hereinafter.

These and other objects are achieved in a process for dyeing polyamide yarn in a dye bath containing (1) sulfonated, water soluble, acid dyes with molecular weight less than 850; (2) an antioxidant which is a phenolic compound of the formula

\[
\text{OH} \quad \text{R}_1 \quad \text{R}_2
\]

wherein \( \text{R}_1 \) and \( \text{R}_2 \) are alkyl groups of sufficient bulkiness to sterically hinder the phenol group; (3) a member of the class of leveling agents consisting of 2,6-di-tert-butyl-4-phenyl phenol sulfonate and a naphthalene compound of the formula

\[
\text{R}^{\prime \prime} \quad 8\text{O} \quad \text{R}^{\prime}
\]

wherein \( \text{R}^{\prime} \) is a monovalent substituent radical selected from the group consisting of propyl, isopropyl, butyl (normal, secondary and tertiary), amyl (normal, secondary and tertiary), and aralkyl, \( m = 1-3 \) and \( \text{R}^{\prime \prime} \) is a monovalent radical selected from the group consisting of NH₄⁺ and alkali metal cations, each of the substitution radicals —\( \text{R}^{\prime} \) and —SO₃—R²⁺ being attached at one of positions 1—8.

In the preferred process embodiment, the aforementioned dye bath also contains (4) a photostable, ultraviolet light absorber, said absorber being a member of one of the classes consisting of hydroxyphenylbenzotriazoles, hydroxybenzophenones, and aromatic substituted acrylonitriles, and being readily absorbed by polyamide yarn.

The phenolic compound is readily absorbed by polyamide yarns, remains substantially colorless during the dyeing process, and remains color-stable after dyeing. The bulky alkyl groups, \( \text{R}_1 \) and \( \text{R}_2 \), have generally at least 3 to 8 carbon atoms and are branched at the carbon atom alpha to the phenol ring. The preferred compound is 2,6-di-tert-butyl-4-phenyl phenol. The phenolic compound is preferably added as an emulsion.

The examples illustrate the advantages of the process in dyeing polyamide yarns, particularly in dyeing finished goods (such as carpets) containing nylon yarns and in dyeing polyethylene oxide (PEO) modified nylon yarns and fabrics. It is known that the tendency of filaments prepared from synthetic linear polyamides to acquire undesirable static charges has been overcome and that soil resistance has been enhanced by blending with the polyamide at least 2% by weight of a polyethylene oxide (PEO), prior to forming filaments thereof. After dyeing, however, the color of yarns and fabrics prepared from PEO-modified nylon filaments still can weaken at the higher temperatures required in many commercial finishing operations, leading to colorfastness deficiencies or to finishing limitations. The illustrative examples show that the process of this invention is equally efficient in dyeing these polyamide filaments containing 2% or more by weight of a polyethylene oxide having a molecular weight of 600 or more.

Examples I, IV, VI, and VII below are of the preferred process embodiment wherein the dyes, antioxidant, levelling agent and ultraviolet light absorber are combined in a dye bath. Examples I and VI show the preferred method of adding the antioxidant as an emulsion, resulting in unexpectedly superior level-dyed, lightfast, carpeting that is stable to atmospheric conditions. The second example shows the benefits of having only the acid dyes, levelling agent and phenyl-phenol in the dye bath. Example III shows unsatisfactory lightfastness obtained when the antioxidant is omitted. The fifth example shows the unsatisfactory lightfastness obtained when the phenyl-phenol of this invention is replaced with a methyl phenol that is otherwise structurally identical. Example VII shows that the same results are obtained when a PEO-modified nylon yarn is dyed by the process of this invention. All percentages, except where otherwise noted, are based on carpet weight. Also, for convenience, the approximate Metric System equivalent of the English units have been given in parentheses.

EXAMPLE I

Approximately 700 square yards (585 square meters), weighing 1540 pounds (600 kilograms), of jute-backed carpeting comprising 21 ounces per square yard (496 grams/square meter) of face nylon is tufted with 3700denier, 204-trifilament, continuous-filament, melt-spun from poly(hexamethylene adipamide) flake. The yarn is jet bulked with the jet taught by Hallden et al. in U.S. Patent 3,005,251. Said carpeting is placed in a
nominally 15-foot-wide (4.56 meters) beck containing approximately 5500 gallons (21,000 liters) of a scouring bath which is an alkaline aqueous solution at 130° F. (54°C.) comprising (1) 0.1% "Antifoam" B (a silicone emulsion to reduce foaming), (2) 0.25% the condensation product of 15-25 mols of ethylene oxide with 1 mol of either a long-chain fatty alcohol containing 12-18 carbon atoms or a mixture of fatty alcohols each containing 12-18 carbon atoms, and 0.15% the sodium salt of the sulfate ester of either a long-chain, fatty alcohol containing 12-18 carbon atoms or a mixture of fatty alcohols each containing 12-18 carbon atoms, (3) 0.75 NaOH, and (4) 1.5% of a solution of 50 weight parts H₂O₂ and 70 weight parts H₂O. This solution is raised to 140° F. (60°C.) and then 0.25% sodium dichromate is added and next, the temperature of this resultant dichromate solution is raised to 200° F. (90°C.) at a rate of 5° F. (1.66°C.) per minute. Then, the scouring bath is dropped, the beck is filled again with 5500 gallons (21,000 liters) of water at 130° F. (54°C.) and this rinse bath is run for 10 minutes and then dropped.

The beck is refilled, this time with a bath of 5500 gallons (21,000 liters) of water and the carpeting is level-dyed in said beck according to the following procedure.

(1) Set the dye-bath at not more than about 80° F. (27°C.) and add 1.75 pounds (794 grams) of "Antifoam" B.

(2) In a separate piece of equipment, provide an aqueous solution of 11.2 pounds (5 kilograms) of the sodium sulfonate of di-sec-butyl naphthalene, and 35 pounds (16 kilograms) of phosphoric acid; and then supply this solution to the beck to attain a pH of about 3.3 in said beck.

(3) Dissolve in 50 gallons (189 liters) of water in another piece of equipment, a mixture of 0.25% C.I. Acid Brown 10 [sodium P-(4-diethylamino)hydroxy-1-naphthylazo]benzenesulfonate, 0.04% C.I. Acid Red 57 [sodium 6-amino-5-[O-(ethylphenylsulfonamido)phenylazo] 4-hydroxy-2-naphthalenesulfonate], and 0.041% C.I. Acid Blue 40 [C.I. 62125], to make a cocoa shade, and continuously add this solution to the beck over a period of 15 minutes.

(4) Run this bath for 15 minutes at 80° F. (27°C.) and then raise the temperature to 140° F. (60°C.) at a rate of 3° F. (1.66°C.) per minute.

(5) Dissolve in about 12 gallons (45 liters) of water in a separate piece of equipment, 70 ounces (2 kilograms) of NaOH, 1.2 ounces (34 grams) of the condensation product of 15-25 mols of ethylene oxide with one mol of either a long-chain fatty alcohol containing 12-18 carbon atoms or a mixture of fatty alcohols each containing 12-18 carbon atoms, and 7 pounds (3.2 kilograms) of 2-(2-hydroxy-5'-methyl phenyl)benzotriazole. This solution is brought to a boil to form the sodium salt of the benzotriazole and then diluted to about 40 gallons (150 liters) of solution to reduce solution temperature to about 120° F. (49°C.).

(6) To the 140° F. (60°C.) bath (Step 4), continuously add the cooled solution of Step (5) to the beck over a period of 15 minutes. The pH of the dye bath in the beck is now about 3.7.

(7) Raise the dye-bath temperature to 180° F. (82°C.) at a rate of 3° F. (1.66°C.) per minute.

(8) Add 13.4 pounds (6 kilograms) of 2,6-di-tert-butyl-4-phenyl phenol as an emulsion. Said emulsion is made up by first preparing 61 parts by weight of A and 39 parts by weight of B. Part A consists of 24 parts by weight of 2,6-di-tert-butyl-4-phenyl phenol, 36 parts by weight of toluene, and 1 part by weight of oleic acid. Part B consists of 30 parts by weight of a 10% ammonium caseinate solution in water, 1.2 parts by weight sodium salt of technical lauryl alcohol, 1 part by weight KOH, and 3 parts by weight water. The 1.2 parts of Part B is added to 6 parts of Part A and then this mixture is added to the beck with high speed agitation to provide a stable, water-dispersible, antioxidant for the dye bath.

(9) Add approximately 4 pounds (1.8 kilograms) of phosphoric acid to attain a pH of approximately 3.7 in the dye bath.

(10) Raise the temperature of the dye bath to 205° F. (96°C.) at the rate of 3° F. (1.66°C.) per minute.

(11) Dye for 1 hour at a temperature as close as possible to 205° F. (96°C.).

(12) Drop the dye bath, rinse the carpeting well, extract the rinse water, and dry the carpeting at about 285° F. (140°C.). Then latex-back the carpeting at 250° F. (120°C.).

This carpeting is observed to be attractively level-dyed, substantially streak-free, and desirably unstained by the amide-backing. It is then tested for lightfastness by exposure to Florida sunlight for 4500 hours. The Gray Scale rating, 4, resulting from such an exposure to sunlight, indicates a sufficiently small shade change to rate the carpeting to have good lightfastness. For an exposure to Florida sunlight for 65 sun hours, the Gray Scale rating is between 4 and 5.

EXAMPLE II

152 grams of face nylon yarn is used to prepare jute-backed, tufted carpeting comprising 22 ounces per square yard 520 grams/square meter) of said face nylon. Said yarn is 3700-denier, 240 trilobal, continuous-filament, jet-bulked yarn, melt-spun from poly(hexamethylene adipamide). The yarn is jet-bulked with the jet taught and jet plied in the same laboratory according to the following procedure:

(1) Set the dye bath at not more than 100° F. (38°C.).

(2) Add approximately 4 pounds (1.8 kilograms) of phosphoric acid to attain a pH of approximately 3.7 in the dye bath.

(3) Raise the temperature of the dye bath to 205° F. (96°C.) at the rate of 3° F. (1.66°C.) per minute.

(4) Dye for 1 hour at a temperature as close as possible to 205° F. (96°C.).

(5) Drop the dye bath, rinse the carpeting well, extract the rinse water, and dry the carpeting at about 285° F. (140°C.). Then latex-back the carpeting at 250° F. (120°C.).

This carpeting is observed to be attractively level-dyed, substantially streak-free, and desirably unstained by the amide-backing. It is then tested for lightfastness by exposure to Florida sunlight for 4500 hours. The Gray Scale rating, 4, resulting from such an exposure to sunlight, indicates a sufficiently small shade change to rate the carpeting to have good lightfastness. For an exposure to Florida sunlight for 65 sun hours, the Gray Scale rating is between 4 and 5.

The dried carpeting of this example is also tested for chemical fading. For testing stability in O₃, the dried and finished dried carpeting is placed in a commercial ozone, oven manufactured by Ozone Research & Equipment Corporation, 3840 N. 40th Ave., Phoenix, Ariz. Said oven exposes the carpeting to 10 parts of O₃ in one hundred million parts of air for 120 hours at 95°F. (35°C.) and between 90% and 95% relative humidity. The Gray Scale rating, 4, results from such an exposure to O₃ indicates a sufficiently small shade change to rate the dyed carpeting to be stable to atmospheric conditions wherein O₃ is present. For testing stability at 3% O₂, the dried and finished dyed carpeting is tested following the American Association of Textile Chemists and Colorists Test No. 23-1962 for 2 cycles and then the Gray Scale rating is 4, to indicate sufficiently small shade change to rate the dyed carpeting to be stable to atmospheric conditions wherein NOₓ is present.
and add 0.75% of the α-sodium sulfonate of di-sec-butyl naphthalene, and 1% 2,6-di-tert-butyl-4-phenyl phenol in 30 cc. acetone.

(2) Run this bath for 5 minutes; then slowly add as a mixture 0.05% C.I. Acid Brown 10, 0.06% C.I. Acid Red 57, and 0.05% C.I. Acid Blue 40.

(3) Run this bath for an additional 5 minutes at 100° F. (38° C.) and then add diluted phosphoric acid dropwise for about 15 minutes to attain a pH of 4.0 and then bring the bath to a boil at a rate of about 2-3° F. per minute.

(4) Run this bath for 45 minutes and then add 10 cc. of a 10% phosphoric acid solution to obtain a pH of about 3.1.

(5) Complete the dyeing for one hour at a temperature as close to the boil as possible.

(6) Drop the dye bath, rinse the carpeting twice with warm water, extract, and finally dry the carpeting at about 275°F. (135° C.).

This carpeting is observed to be substantially streak-free and is tested for lightfastness by exposure to the light of a Xenon arc in an Atlas Xenon Weather-Ometer (Model 60-WR) to simulate 80 sun hours. The Gray Scale rating for the carpeting of this Example II is 2.

**EXEMPLARY III**

Example II is repeated except that in Step 1 of the level-dyeing procedure, instead of 2,6-di-tert-butyl-4-phenyl phenol, 0.15% the condensation product of 15-25 mols of ethylene oxide and 1 mol of either a long-chain fatty alcohol containing 12-18 carbon atoms or a mixture of fatty alcohols each containing 12-18 carbon atoms is added. The Gray Scale rating observed in the carpeting of this Example III is 1 for simulated 80 sun hours.

**EXEMPLARY IV**

Example II is repeated except that no 2,6-di-tert-butyl-4-phenyl phenol is added in Step (1), and instead in Step (5) of the level-dyeing procedure, 1.5% on weight of yarn of 2,6-di-tert-butyl-4-phenyl phenol in 30 cc. of acetone is added dropwise, and then 0.5% 2-(2'-hydroxy-5'-methyl phenyl)benzotriazole in 30 cc. acetone is also added dropwise. Also, in Step (5) the dyeing is 30 minutes. The Gray Scale rating observed in the carpeting of this Example IV is 3 for 80 simulated sun hours.

**EXEMPLARY V**

Example II is repeated except that instead of 2,6-di-tert-butyl-4-phenyl phenol, 1% on weight of yarn of 2,6-di-tert-butyl-4-phenyl is added in Step (1). Furthermore, the dyeing in Step (5) is completed in only 30 minutes. The Gray Scale rating observed in the carpeting of this Example V is 1 for 80 simulated sun hours.

**EXEMPLARY VI**

159 Grams of face nylon are used to prepare carpeting similar to the carpeting prepared for Example II, and this carpeting is scorched and rinsed in a laboratory beak in the same manner as is the carpeting for Example II. Then the laboratory beak is refilled with water, and the carpeting is level-dyed in said laboratory beak according to the following procedure:

(1) Set the dye bath at not more than 100° F. (38° C.), add 0.15% the condensation product of 15-25 mols of ethylene oxide with 1 mol of either a long-chain fatty alcohol containing 12-18 carbon atoms or a mixture of fatty alcohols each containing 12-18 carbon atoms, and then 18 grams of dispersed emulsion in 20 parts of water at 170° F. (77° C.). Said dispersed emulsion is made as follows:

A melt at 221° F. (105° C.) is made of a mixture of 24 grams of 2,6-di-tert-butyl-4-phenyl phenol, 12 grams of 2-(2'-hydroxy-5'-methyl phenyl)benzotriazole, and 12 grams of the condensation product of 1-5 mols of ethylene oxide with 1 mol of either a long-chain fatty alcohol containing 12-18 carbon atoms or a mixture of fatty alcohols each containing 12-18 carbon atoms. Twelve grams of said melt is added, with mixing, to 48 grams of a 15% water solution (cooled in water to 50° F. (10° C.)) of the α-sodium sulfonate of di-sec-butyl naphthalene to form a thick creamy dispersed emulsion.

(2) Run this bath for 10 minutes; then slow add as a mixture 0.5% C.I. Acid Brown 10, 0.06% C.I. Acid Red 57, and 0.05% C.I. Acid Blue 40.

(3) Run this bath for an additional 10 minutes at 100° F. (38° C.) and then add 2% acetic acid to attain a pH of 4.5 and then bring the bath to a boil.

(4) Boil for 45 minutes and then add phosphoric acid solution to obtain a pH of about 3.0.

(5) Continue the dyeing for about 30 minutes more at a temperature as close to boil as possible. The pH is then about 3.2.

(6) Drop the dye bath, rinse the carpeting twice with warm water, extract, and finally dry the carpeting at about 275°F. (135° C.).

This carpeting is observed to be substantially streak-free, and is tested for lightfastness as is the dyed carpeting of Example II. The Gray Scale rating for the carpeting of this Example VI is 3.

**EXEMPLARY VII**

Three grieeve skeins of 3700 denier, 204 trilobal, cross-section filaments, zero twist, semi-dull luster, bulked yarn constructed of filaments spun from a 95/5 melt blend of poly(hexamethylene adipamide)/polyethylene oxide ether glycol of 20,000 molecular weight are secured for 20 minutes at 145° F. (60° C.) in a 30:1 aqueous bath previously set at 80° F. (27° C.) with 0.06% of the condensation product of 15-25 mols of ethylene oxide with one mol of either a long-chain fatty alcohol containing 12-18 carbon atoms or a mixture of fatty alcohols each containing 12-18 carbon atoms, and 0.25% tetrasodium pyrophosphate. After rinsing, one of the skeins is level-dyed in a dye-bath according to the following procedures:

(1) Set the dye bath, containing the skeln, at not more than 80° F. (27° C.) with 0.75% the α-sodium sulfonate of di-sec-butyl naphthalene, and 0.75% "Lycoll" HW, a leveling agent which is an anionic, aromatic sulfonate.

(2) Run this bath for 10 minutes and then add 0.5% of 2-(2'-hydroxy-5'-methyl phenyl)benzotriazole, and 1% 2,6-di-tert-butyl-4-phenyl phenol dissolved in 30 cc. acetone.

(3) Run this bath for 10 minutes and then slowly add, as a mixture, 1% C.I. Acid Brown 10, 0.12% C.I. Acid Red 57 and 0.08% C.I. Acid Blue 58 (C.I. 62125) dyes.

(4) Run this bath for an additional 10 minutes at 80° F. (27° C.).

(5) Slowly add sufficient acetic acid (concentrated) to give a pH of about 4.5.

(6) Raise the bath temperature to 130° F. (54° C.) at the rate of about 1° F. (6° C.) per minute and then run this bath again for 10 minutes.

(7) Raise the bath temperature to 160° F. (71° C.) at the rate of about 1° F. (6° C.) per minute.

(8) Raise the bath temperature to 200° F. (93° C.) at the rate of about 2° F. (1.1° C.) per minute, adding 1.5% phosphoric acid at the end of 30 minutes.

(9) Dye for 1 hour at a temperature as close to 200° F. (93° C.) as possible.

(10) Cool back to 180° F. (82.2° C.) slowly, rinse well, extract, and then dry the yarn at 280° F. (138° C.).

Another skein is similarly dyed except that no ultraviolet light absorber is added in Step (2), although the phenyl phenol is present. The third skein is similarly dyed except that Step (2) is omitted.

These three dried and dried skeins are tested for dye light-fastness by exposure to the light of a Xenon arc in air in an Atlas Xenon Weather-Ometer (Model 60-WR) to simulate 80 sun hours. They are then compared with otherwise identical, unexposed skeins. The results
are shown in the table below with a numerical rating according to the Gray Scale:

<table>
<thead>
<tr>
<th>Shade change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl phenol</td>
</tr>
<tr>
<td>Dyeed with ultraviolet light absorber plus 1% phenyl phenol</td>
</tr>
<tr>
<td>Dyeed with 1% phenyl phenol but without the ultraviolet light absorber</td>
</tr>
<tr>
<td>Dyeed with neither the ultraviolet light absorber nor the phenyl phenol</td>
</tr>
</tbody>
</table>

The above example indicates that the effect of the phenolic antioxidant and the ultraviolet light absorber is more than additive because, when they are both present, the improvement is more than twice the improvement due to the presence of the phenolic antioxidant alone.

As hereinbefore indicated, Example I specifies the preferred process embodiment wherein the ultraviolet light absorber is added to the dye bath in the form of a sodium salt with subsequent regeneration to the free phenol. The temperature is raised, and then 2,6-di-t-butyl-4-phenyl phenol is added as an oil-in-water emulsion. Finally, the carpeting is rinsed, dried and latex-backed. Example VI illustrates another process wherein the antioxidant is in the form of an emulsion.

Examples II, IV and VII indicate that the process is likewise operable when the antioxidant is added in acetone. Example VII further illustrates the beneficial results obtained on PE0-modified yarns.

The process of this invention has utility for fabrics as well as for yarns, for bulked, as well as for unbulked, yarn, for film, as well as for unfoamed, and is particularly useful in dyeing carpets, rugs and upholstery, whether or not the yarn is PE0-modified.

The preferred levelling agent is the aforementioned sodium sulfonate of di-sec-butyl naphthalene. Also operable are the sodium sulfonate of di-sec-butyl naphthalene, the sodium sulfonate of di-isopropyl naphthalene, the sodium sulfonate of di-isopropyl naphthalene, the sodium sulfonate of diaminonaphthalene, the sodium sulfonate of triaminonaphthalene, the sodium sulfonate of trimethyl naphthalene, the sodium sulfonate of di-isopropyl naphthalene, the sodium sulfonate of tributyl naphthalene, the sodium sulfonate of dibenzyl naphthalene, the sodium sulfonate of dibenzyl naphthalene, and 2,6-di-t-butyl-4-phenyl phenol sulfonate. The preparative range of levelling agents for the purpose of this invention is (based on yarn weight) from 0.25% to 2%, and 0.75% is the preferred concentration.

The preparative range of antioxidants for the purpose of this invention is (based on yarn weight) 2% to 1% (preferably 1%) based on yarn weight. The preferred antioxidant is 2,6-di-t-butyl-4-phenyl phenol.

2-(2'-hydroxy-5'-methyl phenyl)benzotriazole is the preferred ultraviolet light absorber for the process of this invention, and it has an absorption maxima on nylon of 350-360 nm. Other ultraviolet light absorbers which are also operable with nylon in the dye bath, are those that are also photosolable, also have a useful absorption maxima on nylon, and are members of the classes comprising hydroxypyhenylbenzotriazoles, hydroxybenzhenones, and aromatic substituted acrylimides. Examples of such other ultraviolet light absorbers are 2,4-dihydroxybenzophenone and the ethyl ester of 2-cyano-3,3-diphenyl acrylic acid. Ultraviolet light absorbers for this invention are operable in the range of 0.25 to 1.5% (preferably 0.3 to 0.75%) based on yarn weight.

The phenolic acid dyes for this invention include C.I. Acid Yellow 29 [C.I. 18900], C.I. Acid Brown 10, C.I. Acid Red 57, C.I. Acid Blue 23 [C.I. 61125], C.I. Acid Blue 40, C.I. Acid Blue 41 [C.I. 62130], C.I. Acid Blue 58, C.I. Acid Yellow 17 [C.I. 18963], and C.I. Acid Red 37 [C.I. 17045]. The concentration of dyes is not critical, but a range of about 0.05 to 3.00% based on yarn weight. It has been found that acid dyes with molecular weights more than about 850 do not disperse to a satisfactory degree of uniformity.

The polyamides comprised by this invention are synthetic, linear polyamides characterized by recurring amide linkages as an integral part of the polymer chain. These polyamides are produced by reacting amino acids or their amide-forming derivatives, or of diamine and dicarboxylic acids or their amide-forming derivatives. Examples of the first group are poly(amidoamines), poly(hexamethylene adipamide), poly(m-xylene sebacamide), poly(p-xylene sebacamide), poly(m-xylene adipamide), poly(p-xylene adipamide), and the polyamide from bis(p-aminocyclohexyl) methane and sebacic acid. Co-polyamides within or among these groups may also be employed. With these polyamides, there may be melt-blended 2% or more by weight of a polyethylene oxide. The polyethylene oxide ether glycols having a molecular weight of at least 1000 are particularly suitable. Alternatively the polyethylene oxide may have, as end caps, either one or two radicals of oxyhydrocarbon such as methoxy, ethoxy, phenoxy, dodecyl phenoxy, nonyl phenoxy, and the like. The capped polyethylene oxides, especially when capped by aromatic radicals, should have a molecular weight of 600 or more. The molecular weight and concentration requirements are imposed by the necessity that enough of the oxide be added to provide a two-phase conductive system, i.e., to render the fiber uniformly conductive, which has ends reactive with the polyamide are excluded since they do not form such a two-phase system. These polyamides, with or without polyethylene oxide, may also contain conventional polyamide additives such as delusterants, pigments, plasticizers, and adjuvants to increase dyeability. Typical additives are disclosed in U.S. Patent Nos. 2,205,722, 2,510,777, 2,887,462, and 2,345,533.

This application is a continuation-in-part of Application Ser. No. 315,362, filed Oct. 10, 1963.

It is apparent that many variations and modifications of the disclosed process may be accomplished without departing from the spirit of the present invention which is accordingly intended to be limited only by the scope of the appended claims.

What is claimed:

1. A process including the steps of dyeing, rinsing and drying nylon yarns, said dyeing step comprising heating said yarn in a bath containing (1) sufonated, water-soluble, acid dyes with molecular weight less than 850; (2) 0.25 to 2.00% by weight, based on yarn weight, of a phenolic compound of the formula

\[
\text{HO} \quad \text{R}_1 \quad \text{R}_2 \quad \text{R}_3 \quad \text{OH}
\]

wherein R₁ and R₂ are alkyl groups of sufficient bulkiness to sterically hinder the phenol group; (3) 0.25 to 2.00% by weight, based on yarn weight, of a member of the class of levelling agents consisting of 2,6-di-t-butyl-4-phenyl phenol sulfonate and a naphthalene compound of the formula

\[
\text{HO} \quad \text{R}_3 \quad \text{SO}_3 \text{R''}
\]

wherein R’ is a monovalent substituent radical selected from the group consisting of propyl, isopropyl, normal butyl, secondary butyl, tertiary butyl, normal amyl, secondary amyl, tertiary amyl, and aralkyl, m is 1–3 and R” is a monovalent radical selected from the group consisting of NH₄⁺ and alkaloid metal cations, each of the sub-
3,363,969

1. A process for the modification of nylon yarn comprising the steps of:

(a) selecting, said nylon yarn containing 0.25 to 2.00% by weight, based on yarn weight, of a nonionic surfactant formed by sulfonation of a naphthalene compound of the formula

\[
\text{OH} \quad \text{R} \quad \text{R}_2
\]

wherein \( R \) and \( R_2 \) are alkyl groups of sufficient bulkiness to sterically hinder the phenol group; and (3) 0.25 to 2.00% by weight, based on yarn weight, of a member of the class of leveling agents consisting of 2,6-di-tert-buty1-4-phenyl phenol sulfonate and a naphthalene compound of the formula

\[
(R')_n\text{SO}_2\text{R''}
\]

wherein \( R' \) is a monovalent substituent radical selected from the group consisting of propyl, isopropyl (normal butyl, secondary butyl, tertiary butyl, normal amyl, secondary amyl, tertiary amyl), and aralkyl, \( m \) is 1-3 and \( R'' \) is a monovalent radical selected from the group consisting of \( \text{NH}_4^+ \) and alkali metal cations, each of the sub-

2. The process of claim 1 wherein the phenolic compound is added as an emulsion.

3. The process of claim 1 where the nylon yarn is a PEO-modified nylon yarn.

4. The process of claim 1 wherein the phenolic compound is 2,6-di-tert-butyl-4-phenyl phenol.

5. The process of claim 4 wherein the 2,6-di-tert-butyl-4-phenyl phenol is added as an emulsion.

6. A process including the steps of dyeing, rinsing and drying nylon yarns, said dyeing step comprising heating said yarn in a bath containing (1) sulfonated, water-soluble, acid dyes with molecular weight less than 850; (2) 0.25 to 2.00% by weight, based on yarn weight, of an emulsion of a phenolic compound of the formula

\[
\text{OH} \quad \text{R} \quad \text{R}_2
\]

wherein \( R \) and \( R_2 \) are alkyl groups of sufficient bulkiness to sterically hinder the phenol group; and (3) 0.25 to 2.00% by weight, based on yarn weight, of a member of the class of leveling agents consisting of 2,6-di-tert-buty1-4-phenyl phenol sulfonate and a naphthalene compound of the formula

\[
(R')_n\text{SO}_2\text{R''}
\]

wherein \( R' \) is a monovalent substituent radical selected from the group consisting of propyl, isopropyl (normal butyl, secondary butyl, tertiary butyl, normal amyl, secondary amyl, tertiary amyl), and aralkyl, \( m \) is 1-3 and \( R'' \) is a monovalent radical selected from the group consisting of \( \text{NH}_4^+ \) and alkali metal cations, each of the sub-

7. The process of claim 6 wherein said phenolic compound is 2,6-di-tert-butyl-4-phenyl phenol.

8. A process including the steps of dyeing, rinsing and drying nylon yarns, said dyeing step comprising heating said yarn in a bath containing (1) sulfonated, water-soluble, acid dyes with molecular weight less than 850; (2) 0.25 to 2.00% by weight, based on yarn weight, of an emulsion of a phenolic compound of the formula

\[
\text{OH} \quad \text{R} \quad \text{R}_2
\]

wherein \( R \) and \( R_2 \) are alkyl groups of sufficient bulkiness to sterically hinder the phenol group; and (3) 0.25 to 2.00% by weight, based on yarn weight, of a member of the class of leveling agents consisting of 2,6-di-tert-buty1-4-phenyl phenol sulfonate and a naphthalene compound of the formula

\[
(R')_n\text{SO}_2\text{R''}
\]

wherein \( R' \) is a monovalent substituent radical selected from the group consisting of propyl, isopropyl (normal butyl, secondary butyl, tertiary butyl, normal amyl, secondary amyl, tertiary amyl), and aralkyl, \( m \) is 1-3 and \( R'' \) is a monovalent radical selected from the group consisting of \( \text{NH}_4^+ \) and alkali metal cations, each of the sub-

9. The process of claim 8 wherein the nylon yarn is a PEO-modified nylon yarn.

10. A process including the steps of dyeing, rinsing and drying nylon yarns, said dyeing step comprising heating said yarn in a bath containing (1) sulfonated, water-soluble, acid dyes with molecular weight less than 850; (2) 0.25 to 2.00% by weight, based on yarn weight, of an emulsion of a phenolic compound of the formula

\[
\text{OH} \quad \text{R} \quad \text{R}_2
\]

wherein \( R \) and \( R_2 \) are alkyl groups of sufficient bulkiness to sterically hinder the phenol group; and (3) 0.25 to 2.00% by weight, based on yarn weight, of a member of the class of leveling agents consisting of 2,6-di-tert-buty1-4-phenyl phenol sulfonate and a naphthalene compound of the formula

\[
(R')_n\text{SO}_2\text{R''}
\]

wherein \( R' \) is a monovalent substituent radical selected from the group consisting of propyl, isopropyl (normal butyl, secondary butyl, tertiary butyl, normal amyl, secondary amyl, tertiary amyl), and aralkyl, \( m \) is 1-3 and \( R'' \) is a monovalent radical selected from the group consisting of \( \text{NH}_4^+ \) and alkali metal cations, each of the sub-

11. The process of claim 10 wherein the nylon yarn is a PEO-modified nylon yarn.

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