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DYEING WITH ANIONIC DYES OF NYLON SKEINS PARTIALLY METAL FOIL COVERED DURING MOIST HEAT TREATMENT BEFORE DYEING

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This application is a continuation-in-part of co-pending application Serial No. 65,608 filed October 28, 1960, now abandoned.

This invention relates to a process of producing ornamental effects on polyamide-containing textile materials, i.e., nylon-containing textile material and more particularly to the dyeing of nylon-containing textile material with anionic dyes to obtain pleasing tonal effects.

Commercially available polyamide-containing textile materials are produced from polyamide polymers, including nylon–6 derived from ε-caprolactam, nylon–66 derived from hexamethylenediamine and adipic acid, nylon–610 derived from hexamethylenediamine and decanoic acid, and nylon–11 derived from ω-aminoundecanoic acid. Textile fabrics, yarns and threads composed in whole or in part of these polyamides are used extensively in the production of garments, draperies, floor coverings and other products.

Heretofore, in order to produce ornamental effects on such fabrics, yarns and threads, which will hereinafter be referred to as nylon-containing textile material, it was generally necessary to combine blends of different fibers or filaments or to resort to a complicated and relatively expensive dyeing or printing procedure to produce the desired ornamental effects.

Furthermore the dyeing of nylon-containing textile material with anionic dyes and particularly the metallized azo dyes, which are noted for their light-fast properties, result in objectionable streaking known as barré effects.

It is a principal object of the present invention to provide a relatively simple, efficient and inexpensive procedure for the production of ornamental or multi-tonal effects on nylon-containing textile material.

A further object of this invention is to provide such process involving the pretreatment of nylon-containing textile material to modify the molecular structure of the polyamide content of such materials in selected areas so that upon subsequent dyeing with anionic dyes employing conventional dyeing procedures, the desired ornamental effects are produced.

Still another object is to provide a process of dyeing nylon-containing textile material with anionic dyes and without producing objectionable barré effects.

These and other objects and advantages of this invention will be apparent from the following description thereof.

In accordance with this invention, pleasing ornamental effects are produced on nylon-containing textile material by covering selected areas of the material with a solid, readily removable, protective covering substantially impervious to moisture under the conditions prevailing in the following treatment during which the partially protected material is subjected to moist heat at a temperature below the fusion point of the polyamide for a time interval sufficient for the moist heat to penetrate the surface of the unprotected areas. Thereafter, the protective covering is removed and the thus treated material is dyed by immersion in a dye bath containing an anionic dye capable of dyeing nylon, preferably poorly leveling dyestuffs. Especially preferred are the metallized azo dyestuffs.

Surprisingly, a pleasing variable or multi-toned dyeing results in which the exposed areas are more heavily hued than the protected areas, and the dyed nylon-containing textile material is free of objectionable barré effects. The contrast between the respective areas depends chiefly upon the polyamide subjected to treatment, the time and temperature of the moist heat treatment, and the particular anionic dyestuffs applied. In general, polyamide-containing textile materials made up of tightly twisted fiber require a longer moist heat treatment at substantially the same temperature as a material made from loosely woven or twisted fiber to obtain substantially the same penetration of the heat and moisture and hence substantially the same orientation of the polyamide molecules and the same tonal effects. By selecting proper conditions and anionic dyes, desired tonal effects can be obtained.

The moist heat treatment effects a change in the orientation of the polyamide molecules in the area subjected to such treatment, i.e., a reorientation of these molecules. The time required for this reorientation depends upon the condition of the fiber or filament, or in other words, the accessibility of the heat and moisture to the unprotected areas. A 6-denier monofilament will respond in about 1/10 of a second. A 2100-denier monofilament will require a longer time to respond to the same extent. The number of filaments in the yarn bundle, how tightly they are wound, the particular polyamide of which they are composed, etc., affect the accessibility of the moisture and heat to the unprotected areas and hence the time required to produce the reorientation desired, which reorientation starts immediately upon exposure to moisture and heat and the extent thereof increases with increase in the time of exposure.

By subjecting the nylon-containing textile material to successive moist heat treatments under different conditions of temperature and for different time intervals and exposing different areas during the successive treatments, controlled variations in the reorientation of the molecules can be obtained in which three, four, or even more distinctively different degrees of reorientation are produced in the material. Alternatively, by varying the degree of exposure or intensity of the treatment, for example, by running a yarn, thread or fabric, having portions thereof protected by the readily removable, moisture-impervious, solid covering in static contact therewith, through the zone where they are subjected to the moist heat at variable speeds so that the exposed portions are subjected to the moist heat treatment for different periods of time, the resultant treated material will have in the exposed areas different degrees of reorientation of the polyamide molecules. Upon dyeing with an anionic dyestuff suitable for dyeing nylon by immersion in a dye bath, as conventional for the dyeing of nylon, as many different tonal effects result as there are distinctively different degrees of molecular reorientation. The dye pick-up in general is proportional to the degree of molecular reorientation; the less highly oriented the molecules are in a given area, the greater the dye intensity in that area.

The temperature of the moist heat treatment is within the range of from 212° F. to below the fusion point of the polyamide, preferably at from about 230° to 260° F. The time of treatment is at least that required to penetrate the unprotected surface of the polyamide-containing textile material and will depend upon the material treated and the temperature of the treatment. At a temperature of about 250° F., from 10 to 30 minutes will suffice.

As the source of the moist heat, steam is used which should not be superheated to a temperature such that

it is dry; preferably staturated steam under a pressure of from 10 to 25 p.s.i.g. is employed. Instead of steam, heating in contact with water under pressure to prevent evaporation can be used.

The present invention is applicable to the production of ornamental effects on fabrics woven from yarns containing only polyamide fibers or filaments or woven from blends of polyamide fibers or filaments with other fibers or filaments, as well as to such yarns and threads containing polyamides in whole or in part.

Selected or predetermined areas of such polyamide-containing textile materials, whether in the form of fabrics, yarns, or threads, are covered with a readily removable, solid covering which is substantially moisture impermeable under the conditions of the subsequent moist heat treatment, i.e., will prevent the moist heat from penetrating the surface of the covered areas. Such protective covering can be a plastic film made, for example, from synthetic or natural rubber, polyvinyl polymers or copolymers or other substantially water-impervious plastic materials. In lieu of a plastic film, metal foils such, for example, as aluminum, copper, or other metal foil can be used. The protective covering can be in the form of metal sheets or foil having open design areas and adapted to cover one or both surfaces of the fabric subjected to moist heat so that the moist heat penetrates only the uncovered areas of the fabric, i.e., those areas which are exposed by the openings in the moisture-impervious, readily removable sheet or foil in static contact with the fabric. In the case of yarn or threads, they may be wrapped with the protective covering in selected areas leaving the remainder of the areas uncovered so that the moist heat can penetrate the surface of the uncovered areas. Alternatively, the yarns or threads can have selected portions thereof positioned within or covered by metal sleeves, such as stainless steel sleeves, designed or positioned to leave uncovered selected areas which are subjected to moist heat to effect reorientation of the nylon molecules in the uncovered selected areas.

The moist heat treatment of the thus protected nylon-containing textile material can be carried out in any suitable apparatus, conveniently in an autoclave under controlled conditions of humidity and heat. Preferably the thus protected material is introduced into the autoclave in a loose or relaxed state. The moist heat treatment may be continuous, i.e., the fabric, yarn or thread suitably protected, as herein described, is passed continuously through a chamber wherein it is subjected to moist steam at a temperature below the fusion point of the polyamide. Alternatively, the treatment can be effected in a discontinuous manner. For example, successive batches of the partially protected polyamide-containing textile materials are introduced into autoclaves where they are subjected to moist heat at a temperature below the fusing point of the polyamide for a period of time sufficient for the moist heat to penetrate the unprotected areas, the moist heat treatment discontinued, each batch removed from its autoclave and then dyed by immersion in a dye bath, as herein described.

The polyamide-containing textile materials can have selected areas covered with the protected material subjected to moist heat, the protective covering removed from some but not all of the covered areas and again subjected to moist heat under conditions which are different from the initial moist heat treatment. Thereafter the protective covering is removed and the thus treated polyamide-containing textile material dyed by immersion in the dye bath. In this way, contrasting tonal effects are obtained having at least three distinct shades, namely, the darker shade is produced in the areas subjected to the most intense moist heat treatment, a somewhat lighter shade in the areas subjected to a less intense moist heat treatment, and the lightest shade in the areas which were covered during both moist heat treatments. By

varying the number of moist heat treatments and the conditions of each, the desired number of different shades can be obtained.

The moist heat treatment, while effecting reorientation of the molecules in the uncovered areas of the nylon-containing textile material, does not result in deformation of the fibers as takes place when the nylon-containing textile material is subjected to calendering under pressures such as produce glazed effects. The nylon-containing textile material subjected to the moist heat treatment as herein described is indistinguishable to the eye from similar nylon-containing material not subjected to moist heat treatment. For example, in the case of skeins of yarns, selected areas of which are wrapped with aluminum foil, subjected to moist heat treatment, and the aluminum foil removed, the portions of the yarn which were covered by the aluminum foil, are indistinguishable to the eye from those which were uncovered, i.e., the areas of the yarn in which reorientation of the nylon molecules had taken place. That is to say the uncovered portions of the yarn subjected to moist heat in which reorientation of the nylon molecules has taken place cannot be distinguished on observation from the covered portions of the yarn in which reorientation of the nylon molecules had not been effected. Yet when the treated yarn is dyed with an anionic dye a pleasing contrasting tonal effect is obtained, the uncovered portions being dyed a darker hue than the covered portions, resulting in contrasting tonal effects. The production of objectionable barré effects produced when dyeing the untreated skeins with the same anionic dyestuff under the same conditions are thus obviated by the present invention.

Any anionic dyestuff, including the acid dyes, suitable for dyeing polyamides can be used in the dyeing step which is carried out in a conventional manner. Preferably poorly leveling anionic dyestuffs are used because such dyestuffs accentuate the ornamental effect, i.e., the treated areas have a markedly greater affinity for the dye than the untreated areas. Preferred are the metallized azo dyestuffs, particularly the neutral dyeing metallized azo dyestuff. Examples of preferred anionic dyes are:

Chromium complex of 2(1 - hydroxy-4-sulfo-naphthyl-azo)-5,8-dichloro-1-naphtol

Cobalt complex of 2(2-hydroxy-4-sulfamylphenylazo)-5,8-dichloro-1-naphthol

Cobalt complex of 1(2-hydroxy-5-N(3-sulfamylphenyl) sulmaylphenylazo)-2-naphthol

Chromium complex of 1(2-hydroxy-5-nitrophenylazo)-2-naphthol

Cobalt complex of 4(2-hydroxy-5-sulfamylphenylazo)-1-phenyl-3-methyl-5-pyrazolone

Chromium complex of 1(2-hydroxy-5-N-methylsulfamyl-phenylazo)-8-acetamido-2-naphthol

Chromium complex of 4(2-hydroxy-5-N-methylsulfamyl-phenylazo) - 1(3 - chloro-phenyl)-3-methyl-5-pyrazolone

Cobalt complex of the above

Chromium complex of 4(2-carboxy-phenylazo)-1-phenyl-3-methyl-5-pyrazolone

Cobalt complex of 1(2-hydroxy-4-sulfamylphenylazo)-2-naphthol

Cibalan Blue BL

Chromium complex of 2-(2-hydroxy-4-sulfamylphenl-azo)-5,8-dichloro-1-naphthol

Chromium complex of 1(2-hydroxy-4-sulfamyphenyl-azo)-8-acetamido-2-naphthol

New C.I. 16150

New C.I. Acid Brown 19

New C.I. 18050

New C.I. 16185

New C.I. Acid Green 10

New C.I. 27275

The folowing examples are given for illustrative purposes; it will be understood that the invention is not limited to these examples. In these examples, parts and percentages are given on a weight basis and temperatures in degrees Fahrenheit.

Example I

A skein of 2100-denier 112-filament textured nylon–6 yarn, weighing 20 parts, was leased and a portion of the leased skein was wrapped tightly with aluminum foil. The skein then was placed in an autoclave and treated with saturated steam for 5 minutes at 248°. The treated skein was removed from the autoclave and the aluminum foil wrapping was removed. Thereafter the skein was dyed in an aqueous dye bath containing ½% (on the weight of the fiber) of the chromium complex of 1(2-hydroxy-4-sulfamylphenyl-azo) - 8-acetamido-2-naphthol for one hour at 210°. The resulting dyed skein after being washed and dried was colored light grey in those areas which had been protected by the aluminum foil during the moist heat treatment and a darker grey in the unprotected areas. This ornamental two-tone effect was pleasing and striking.

Example II

A 100 part skein of 200-denier 34-filament nylon–66 yarn was leased and a portion of the skein was wrapped tightly with aluminum foil. The skein was placed in an autoclave and steamed at temperature of 252° for 30 minutes. The treated skein was removed from the autoclave, stripped of the aluminum foil wrapping and dried at 130°. The treated skein was dyed for one hour at 210° in an aqueous dye bath containing ¼% Triton X–100 (an alkylarylether sulfate wetting agent) and ½% of the same dyestuff used in Example I. The resulting dyed product was dyed an ornamental two-tone grey shade, dark grey in the unprotected areas and a lighter grey shade in the protected areas.

Example III

A 100 part skein of 2100-denier 408 filament nylon–6 yarn was leased and a portion wrapped with aluminum foil. The partially protected skein was then placed in an autoclave and steamed for 15 minutes at 248°. The treated skein was removed from the autoclave and after the aluminum foil had been removed from the skein it was dried at 150°. The skein was dyed for one hour at 210° in an aqueous dye bath containing ¼% Triton X–100 and ½% of the chromium complex of 1(2-hydroxy - 4 - nitrophenyl-azo)-2-naphthylamine-6-sulfonic acid. The skein was dyed a two-tone shade of green, the dark shade in the unprotected areas and the lighter shade in the protected area.

Example IV

Carpet material weighing 70 parts and tufted from 4200-denier 224-filament textured nylon–6 yarn was placed between two aluminum sheets. The top sheet was cut out exposing portions of the carpet according to a design while the bottom sheet was solid covering the entire back of the material. The partially exposed carpet material was placed in an autoclave wherein it was treated with saturated steam at 250° for 15 minutes. Thereafter, the piece was removed from the autoclave and the aluminum sheets were stripped from the material. The treated material was dried at 150° and then dyed for one hour at 180° in an aqueous dyebath containing ½% of the chromium complex of 1(2-hydroxy-4-sulfamylphenylazo) - 8 - acetamido-2-naphthol. The carpet was dyed an ornamental two-tone grey, the unprotected areas being colored a darker grey than the protected areas.

Example V

A similar 70 part piece of carpeting as that treated in Example IV was covered front and back with two aluminum sheets with matching cutout design. The partially protected carpet was treated with moist steam at about 212° under atmospheric conditions for three minutes. The aluminum shields were removed and the carpet was dried at 130°. It was then dyed for one hour at 180° in an aqueous dyebath containing ½% of the chrome complex dye used in Example IV. The resulting dyed material was colored an ornamental two-tone grey shade, the unprotected area being colored a darker grey than the protected area. The combination of light and dark grey areas gave a striking ornamental effect.

In the above examples, instead of aluminum foil as the protective material, other metal foils, metallic sleeves, plastic films or other material substantially non-pervious to moisture under the conditions of the examples can be used to protect the areas of the polyamide textile material, which areas are covered so that the steam does not penetrate same. The protective material can be shaped in any desired manner to provide protection to predetermined portions of the polyamide-containing textile material; thus, for example, in the case of yarn the protective material can be used to cover only a portion of the periphery and not the entire circular extent along selected areas, if desired.

The treated polyamide textile material after the moist heat treatment can be stored and later dyed and/or further manipulated whenever desired. For example, the thus treated yarns, alone or along with other yarns from the same or other fibers or filaments, can be woven into fabrics, and the latter dyed to produce pleasant contrasting tonal effects.

It will be noted that the present invention provides a simple, effective and inexpensive method for the dyeing of nylon-containing textile material with light-fast anionic dyes to obtain attractive ornamental effects, i.e., pleasing contrasting tonal effetcs, as distinguished from objectionable barré or streaking effects.

It is to be understood that this invention is not restricted to the present disclosure otherwise than as defined by the appended claims.

What is claimed is:

1. The process of producing multitone effects on nylon-containing yarn, which process comprises the following steps:

Step 1, covering selected surface areas of a skein of said yarn by tightly wrapping spaced portions of said skein in a relaxed state with metal foil, so as to completely enclose said selected surface areas of said skein and prevent them from being contacted by the moist steam applied in Step 2 of the process while leaving uncovered remaining surface areas of said skein in a relaxed state;

Step 2, applying moist steam to the assembly of said skein of yarn and metal foil at a temperature below the fusion point of the nylon and above 212° F., said moist steam being applied for a time interval at least sufficient for the moist steam to penetrate the surface of the uncovered areas of said yarn to effect selective reorientation of the nylon molecules in said uncovered areas and impart thereto a markedly greater affinity for dyes capable of dyeing nylon than is possessed by the nylon in the covered areas;

Step 3, removing the metal foil wrapping from the skein of yarn; and

Step 4, immersing the thus treated skein of yarn, from which the wrapping has been removed, in a dye bath containing an anionic dye capable of dyeing nylon, thus imparting different tonal effects to the areas of the yarn which had been covered with metal foil and the remaining areas.

2. The process as defined in claim **1**, in which in Step 2 the assembly of skein of yarn and metal foil is exposed to moist steam at a temperature within the range of from 230° to 260° F. for from 10 to 30 minutes.

3. The process as defined in claim 1, in which the anionic dye is a metallized azo dye.

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