MIXTURE OF FILAMENTS CAPABLE OF BEING DYED TO A MULTICOLOR PATTERN WITH ANIONIC DISPERSE DYSES

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Notice: The portion of the term of this patent subsequent to Jan. 2, 1985, has been disclaimed.

Filed: Sept. 13, 1968

Appl. No.: 759,776

U.S. Cl. ........................................... 8/15, 8/31, 8/39, 8/169, 8/171, 8/173, 8/21 C, 8/21 D, 8/17, 8/115.5, 8/100, 8/42 D, 8/168, 8/180, 57/140

Int. Cl. ........................................... D06p 8/02, D06p 1/16

Field of Search ................................ 8/180, 100, 115.5, 168, 21, 8/173, 15

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ABSTRACT

The present invention relates to a process for dyeing fibers, fabrics or other shaped articles made from blends of either poly(alpha-olefins) or polyesters and various thermoplastic nitrogen-containing basic polymers to a multicolor pattern.

50 Claims, No Drawings
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The process of the present invention consists of treating shaped articles made from poly(alpha-olefins) or polyesters and a thermoplastic nitrogen-containing basic polymer in discontinuous fashion with a Lewis acid composition which optionally may contain anionic dyes, anionic surfactants and other modifiers, and then subsequently dyeing the treated article, if said anionic dyes are not used in the Lewis acid composition. Due to differences in affinity for different classes of dyes or treated and untreated areas of the shaped articles, multicolor dyeings will be obtained. The present invention thus provides a method of treatment for imparting local differences in affinity for different dye classes to a filamentary assembly, which term is used to denote a fiber, yarn, fabric or other shaped article, so that by exposure of such fiber, yarn, fabric or article, either at the time of treatment or subsequently, to dyes of different classes, a multicolor effect will be obtained.

The base material used in this invention is an inherently undyeable or difficult to dye fiber, yarn, fabric or other shaped article made from a poly(alpha-olefin) or polyester. By blending this inherently undyeable material with a minor amount of a thermoplastic nitrogen-containing basic polymer capable of binding both disperse and anionic dyes, such material is made dyeable with disperse dyes, but is still impermeable and hence undyeable with anionic dyes. When fibers, yarns, fabrics or other shaped articles are made from the above-described blends, and localized areas of said articles are treated with Lewis acid or Lewis acid generating material compositions as described herein, the treated areas are rendered highly dyeable with anionic dyes. Dyeing the treated articles with anionic and optionally disperse dyes, either at the time of treatment or subsequently, yields a multicolor effect, since the treated areas are dyeable with both anionic and disperse dyes, whereas the untreated areas are dyeable only with disperse dyes.

The process of the present invention includes the following steps as explained herein:

1. Blending between about 0.5 and 5 percent of a thermoplastic nitrogen-containing basic polymer capable of binding anionic (i.e., acid-type) dyes, and optionally between about 0.5 and 5 percent of a hydrophobic compound containing ethylene oxide groups, with a fiber-forming poly(alpha-monoolefin) or polyester.

2. Forming said resulting blend into a fiber, yarn, fabric or other shaped article.

3. Optionally dyeing said shaped article with a disperse dye.

4. Contacting desired portions of said shaped article with an activating agent which means that the fiber, yarn or shaped article is treated with the Lewis acid only in certain areas or portions of the fiber, fabric or article, according to the wishes of the processor. When the article treated in this fashion is subsequently exposed to a dyebath, only the activated areas (i.e., areas treated by discontinuous activation) will absorb anionic dyes, whereas both treated and untreated areas will absorb disperse dyes. The result will be a two-color dyed effect. When more than two colors are desired this may be achieved by mixing different disperse dyes separately with the Lewis acid and applying each mixture of dye-Lewis acid separately to the article. Still another means for attaining multicolor effects would be by including natural (i.e., uncolored) or pigmentar fibers in a polyolefin or polyester yarn. Tone-on-tone effects, i.e., different intensities of the same color, may also be achieved alone or in combination with multicolor effects, by using combinations of fibers in the yarn or fabric, wherein one fiber is made from a polyolefin or polyester containing dye receptor alone and the other fiber from a polyolefin or polyester containing both dye receptor and hydrophobic compound containing ethylene oxide groups. The first fiber would be almost wholly undyeable with anionic dyes, while the second would have significant dyeability with anionic dyes. The activated portions of the two
fibers will show a similar difference in dyeability with anionic dyes as do the unactivated counterparts. The resultant product thus shows a tone-on-tone effect.

In the present invention, the shaped articles, fabrics or fibers made from alpha-monomolefin polymers comprise a major portion of inherently undyeable alphamonomolefin polymers comprising both homopolymers and copolymers of alpha-monomolefin; for example, copolymers with non-tertiary olefins or with one or more other alpha-olefins, as well as block copolymers of alpha-olefins with each other and graft copolymers of alpha-olefins with polymers of other alpha-olefins. The class includes polyethylene, propylene, poly(3-methyl-1-butene), poly(4-methyl-1-pentene), copolymers of propylene and 4-methyl-1-pentene, and copolymers of any of the foregoing monomers with each other and/or with other copolymerizable monomers. The preferred material of this class is polypropylene, by which we mean any polymer of propylene and any copolymer containing predominantly polymerized propylene together with any other comonomer copolymerized therewith.

The term "polyester" as used herein refers to polymers which are condensation polymers of dihydric alcohols with organic dicarboxylic acids or their anhydrides, particularly dicarboxylic acids, and self-condensation polymers of omega-hydroxy carboxylic acids. The preferred polyester materials in our invention are poly(ethylene terephthalate), poly(ethylene terephthalate-isophthalate), and poly(1,4-cyclohexylene dimethylene terephthalate), and further discussion in terms of polymers will be mainly in terms of these representative polymers. It will be understood however, that the invention is applicable to all fiber-forming polymers, in which the ester linkages are intralinear, including poly(alkylene alkanedioates), poly(cycloalkylenedimethylene alkanedioates), poly(alkylene arenedioates), poly(cycloalkylenedimethylene arenedioates), and analogous materials. Examples of the above-named polymers are respectively, poly(ethylene adipate), poly(1,4-cyclohexylenedimethylene adipate), poly(ethylene terephthalate), and poly(1,4-cyclohexylene dimethylene terephthalate).

The basic dye receptor polymers which may be incorporated in the polyolefins or polymers listed previously are thermoplastic basic nitrogen-containing materials capable of binding anionic and disperse dyes, and are illustrated by:

1. Polymers of vinyl-substituted mono- and polycyclic pyridines, either homopolymers or copolymers with each other, or with other vinyl compounds, including graft copolymers.

2. Polyamides, including condensation homopolymers and copolymers, in which the amide groups are an integral part of the polymer chain, and addition homopolymers and copolymers having pendant groups consisting or consisting of amide groups.

3. Amine polymers, including condensation homopolymers and copolymers, in which the amine group is an integral part of the polymer chain, and addition homopolymers and copolymers having pendant groups which include or consist of amine groups.

Other basic nitrogen polymers which may be used in this process are polyurethanes, poly(vinylcarbazoles), aniline-formaldehyde resins, etc. The major requirement for the type of structure of this nitrogen containing material is that it be capable of binding anionic dyes.

The basic nitrogen polymers employed should not be extractable from the mixtures thereof with the polyolefin or polyester under the conditions of treating and dyeing used, since of course this would lower or eliminate the dyeability. As a diagnostic test, a 1-hour extraction of the fiber or shaped article with boiling water at a pH of 3 for 1 hour should not extract more than 90 percent of the originally added nitrogen polymer. The amount of the basic nitrogen polymer added to the polyolefin or polyester polymer should be sufficient so that, after the acid treatment of the invention, it will bind the amount of dye required to produce the shade desired.

The vinyl-substituted monomeric and polycyclic pyridine base dye-receptor polymers may be incorporated in the hydrocarbon polymer either as a homopolymer, or as a copolymer with another vinyl-substituted pyridine or any other vinyl monomer copolymerizable therewith, or as a graft copolymer with a hydrocarbon high polymer. The vinyl-substituted mono- and polycyclic pyridine base dye receptor polymers used are those based, for example, on monovinyl pyridines and monovinyl quinolinolines.

The monovinylpyridines useful in making the above described dye-receptive polymers employed in the invention include 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine, 2-ethyl-5-vinylpyridine, 2-methyl-5-vinylpyridine, 2-ethyl-6-vinylpyridine, 2-isopropenylpyridine, etc. Polymerizable olefinic monomers with which the monovinylpyridine may be copolymerized include acrylic and methacrylic esters typified by ethyl acrylate and methyl methacrylate, vinyl aryl hydrocarbons typified by styrene and vinyltoluenes, and butadiene-1,3. Alternatively, the monovinylpyridine may be graft-copolymerized, by well-known methods, with a previously formed linear high polymer, typified by polyethylene, propylene, polystyrene, and polybutadiene. In instances where a hydrophilic compound containing ethylene oxide units (-CH2-CH2-O-) is incorporated into blends containing a polyolefin or a polyester it is preferable to employ nitrogen base polymers containing pyridinic groups only, i.e., ones which are not copolymerized with non-nitrogen base monomers.) It is always desirable that the basic polymer contain no more than a minor proportion of non-basic material copolymerized with a monovinylpyridine, since only the pyridine portion of the polymer additive is active in enhancing dyeability.

The polyanilides useful as the dye-receptors employed in this process include homopolymides such as poly(hexamethylene adipamide), poly(hexamethylene sebacamide), poly-pyrrolidone, polycaprolactam, polyanhydrolactam, and copolyamides such as Zytel 61 (a trademark of Du Pont de Nemours and Company), an interpolymer of hexamethylene adipamide and hexamethylene sebacamide with caprolactam.

As examples of vinyl polymers with pendant groups consisting of or containing amide groups there are the substituted poly(vinylpyrrolidinones), (e.g., polymers of N-vinyl-3-alkylpyrrolidone) and N-substituted polyacrylamides, (e.g., N-butylpyrrolidone). Also usable are copolymers of the amide-containing vinyl monomers with other olefinic monomers such as acrylic and methacrylic esters typified by ethyl acrylate and methyl methacrylate, vinylaryl hydrocarbons typified by styrene and vinyltoluenes, and butadiene-1,3. Alternatively, the vinylpyrrolidinones or acrylamides may be graft-copolymerized, by well-known methods, with a previously formed linear high polymer, typified by polyethylene, polypropylene, polystyrene, and polybutadiene. It is always desirable that the basic polymer contain no more than a minor proportion of material copolymerized with the vinylpyrrolidinones or acrylamides, since only the amide portion of the polymer additive is active in enhancing the dyeability of the hydrocarbon polymer.

As examples of amine polymers useful as the dye receptor employed in this invention there are the condensation products of epichlohydrins or dihaloaryls with one or more amines, such as those disclosed in Belgian Pat. No. 606,306, exemplified by the condensation product of dodecylamine, piperazine and epichlorohydrin; as examples of addition polymers with pendant groups consisting of or containing amines there are the reaction product of a styrenemalene anhydride copolymer with 3-(dimethylamino)propylamine (the product being a polyamino-polyamide), and styrene-allylamine copolymers such as those disclosed in U.S. Pat. No. 2,456,428.

The hydrophilic compounds, optionally blended in the amounts of about 0.5 and 7 percent with the hydrocarbon polymer or polyester used in this invention, are selected from the following groups of compounds.
1. Polyethylene glycol (also referred to herein as PEG) having a degree of polymerization (DP) of at least 4.
2. Copolymers of ethylene oxide with other alkylene oxides having a degree of polymerization of the ethylene oxide units of at least 4 and containing a minimum of 60 percent by weight ethylene oxide. These compounds are exemplified by the series of block copolymers produced by condensing ethylene oxide with a product formed by the condensation of propylene oxide with propylene glycol (formula of such copolymers: HO—(CH₂O)₃(C₃H₆O)₇) and sold under the trademark “Fluronic”). Other useful copolymers are derived from the polymerization of ethylene oxide and propylene oxide.
3. Derivatives of polyethylene glycol, such as its ethers and esters having a degree of polymerization of ethylene oxide of at least 4 and an ethylene oxide content of at least 60 percent by weight. Examples of such derivatives are: (a) polyethylene glycol alkyl ethers; (b) alkylaryl polyethoxyalkyl alcohols sold under the trade name “Triton” (octylphenylpolyethylene ether series); (c) polyoxyethylene glycol ethers of long chain fatty acid esters of hexitol anhydrides including sorbitan, sorbitides, mannitis and mannites, such as polyethylene glycol hexitol carboxylates, polyoxyethylene sorbitan monolaurate and polyethylene glycol carboxylate esters such as polyglycerol mono- and polyglycerol distearate.

The mixtures of the hydrocarbon polymer or polyester and the nitrogen-containing dye receptor polymers are made by blending, tumbling or any convenient method and then can be shaped by vacuum molding, extrusion or in the case of fibers, may be spun into yarns using a conventional melt spinning process. The articles made from the polymers are treated with the Lewis acid composition after shaping. If the article is to be treated is a fabric made from yarns, the physical form of said fibers which are woven into the fabric may vary widely. They may be monofilament or multifilament; plain, bulked or texturized; staple, tow or stock. The treatment with the Lewis acid composition may be done in any convenient fashion such as roller printing, screen printing, spraying or dipping. By means known to those skilled in the art, random or regular color effects can be produced. If a sharply defined pattern or design is desired, a thickener which is compatible with the Lewis acid may be employed to prevent migration, which is the tendency of the activated material to diffuse or wrinkle away from the site of application and thus produce a blurred rather than a sharply defined area. The duration of the acid activation treatment with the Lewis acid composition may be from a few seconds to several hours, or for practical reasons is preferably kept between 10 seconds to 30 minutes duration. In order to hasten the diffusion of the Lewis acid and the other modifiers present in the activating material into the treated article, it may be heated at a temperature below the melting temperature of the material. Usually a temperature not greater than 140°C. for poly(alpha-olefins) and 200°C. for polyesters is satisfactory and sufficient in most cases.

The activating material which is used in accordance with the present invention, may contain, in addition to the Lewis acid, an anionic surfactant, an anionic dyestuff and a suitable amount of water and thickening agent to form a paste of desired consistency. The following are examples of the Lewis acids which may be used in the present invention. They are illustrative and in no way limiting.
1. Concentrated inorganic acids such as hydrochloric acid, hydrobromic acid, sulfuric acid, nitric acid, sulfuric acid, phosphoric acid and perchloric acid, or the anhydrides thereof.
2. Organic carboxylic and sulfonic acids including aliphatic, aromatic, hydroxy-substituted aromatic acids, monocarboxylic and dicarboxylic acids, monosulfonic and disulfonic, saturated and unsaturated acids. Suitable acids are exemplified by formic, acetic, propionic, stearic, and other alkanic acids in the C₂-C₄ range, undecylenic, oleic, benzoic, salicylic, succinic, adipic, phthalic, bromoacetic, benzenesulfonic, p-toluensulfonic, chloroacetic and lactic acids.

Examples of preferred acids used in the present invention are hydrochloric, formic, acetic, mono- or dichloroacetic and para-toluensulfonic acids. Any Lewis acid or Lewis acid generating material which can be applied to the yarn, fabric or shaped article may be used, including hydrolyzable halides such as aluminum, zinc and tin halides, benzylic halides, allylic halides, acyl halides and sulfonl halides, phenols, borate esters and the like. The acid may be used in the liquid or molten state (when its melting point is below the temperature selected for the treatment) or in solution in an aqueous or organic solvent. The concentration of the Lewis acid used in the activating composition of the present invention is not critical since low concentrations of the acid may be applied in solution in a volatile solvent, with the solvent being evaporated during the heating period. Concentrations of Lewis acid in the activating composition of between 4 and 100 percent (on the weight of treating composition) are most convenient, when used in the absence of anionic surfactants. Lower concentrations (i.e., between about 0.1 and 4 percent) as well as the higher ones are operative in the presence of anionic surfactants.

The anionic surfactants optionally employed in the present invention have the general formula (R-A), wherein R represents a hydrophobic group which is either a saturated or unsaturated alkyl, aryl or alkylaryl group having six or more carbon atoms (preferably between nine and 40 carbon atoms) per "A" group; and A is an anionic group exemplified by one or more of the following groups: (1) sulfonate; (2) sulfoate; (3) phosphate or polyphosphate; 4) carboxylate etc. The "A" group can be in the free acid form or in the salt form, but acid conditions (i.e., a pH of about 5 or less) must always be present. Another type of anionic surfactant which can be used is where R may contain a polyoxalkylene group. Additional operative materials include those generating anionic surfactants in situ during the process of this invention.
Anionic surfactants, when used in the activating composition of this invention, permit the use of lesser amounts and lower concentrations of Lewis acid as described above. Any concentration above about 0.5 percent of anionic surfactant in the Lewis acid treating composition is operative but concentrations in said composition between about 0.5 and 5 percent are preferred. Attendant to this are savings in cost, the use of less expensive metals and alloys in storage and application equipment, decreased corrosion and lower toxicity hazards. Their incorporation in the activating composition is thus highly beneficial.

The Lewis acid-containing activating compositions of the present invention are frequently applied by conventional textile printing techniques which involve thickening them so they do not spread excessively after printing. Suitable thickening agents include polyvinyl alcohol, sold under various trademarks such as "Elvanol," "Vinol," etc.; polyethylene glycols of various molecular weights, sold under trademarks such as "Carbowax," "Polysor," etc.; methyl-substituted cellulose sold under the trademark "Methocel;" purified natural gum ethers sold under the name Polygum 260, 261 or 262 LV; or carboxymethylcellulose sold under the trademark "CMC Cellulose Gum." The amount of viscosity increasing (thickening) agent used may be varied to give the desired degree of viscosity and spreading of the applied pattern, as desired. Other dyeing assistants, such as retarding agents, wetting agents and leveling agents may likewise be added to the activating paste in accordance with the effects to be obtained.

When dyeing is subsequent to activation, a two-color dyed effect may be realized with the treated yarn, fabric or shaped article. By incorporating dyes in the activating paste, however, multiple-pass printing techniques may be used with different dyes in separate pastes to achieve multicolor effects. By dyeing the entire fabric with a disperse dye prior to activation, and then printing with the activating paste, over-printed effects may be obtained. Swelling agents (carriers) to open the fiber to dyes, such as ortho-dichlorobenzene, aromatic hydrocarbons, etc. may be used in the paste, but the effect of the present invention does not depend upon the use of a carrier. The following anionic dyes can be utilized in the practice of the present invention:

**Acid Red 209**
**Acid Blue 168**
**Acid Black 60**

Another category of anionic dyes which may be used in this invention are the direct dyes typified by the following:

- Direct Yellow 44 (C.I. No. 29900)
- Direct Red 13 (C.I. No. 22155)
- Direct Blue 67 (C.I. No. 27925)

Other categories of anionic dyes which are applicable to our invention are the reactive dyes, typified by Reactive Orange 1, and the mordant acid dyes, typified by Mordant Red 3 (C.I. No. 58002).

In addition to anionic dyes, disperse dyes may also be used in the present invention, as previously described. Examples of this class are:

- Disperse Yellow 23 (C.I. No. 26070)
- Disperse Orange 21
- Disperse Blue 27 (C.I. No. 60667)
- Cibacron Pink FG
- Disperse Yellow 42 (C.I. No. 10338)
- Interchem Blue RLF 40

As indicated herein previously the dye penetration into the Lewis acid-treated yarn fabric or shaped article is increased and deeper colors are produced when the activating paste is heated. This can be accomplished by heating the fabric or shaped article with the paste thereon to a temperature below the melting point of the polymers used (i.e., 140° to 200°C.), or the paste may be heated prior to application to the article. If the paste includes a dye, both activation and dyeing are accelerated by the heating step. Otherwise, dyeing is carried out subsequent to the treatment, which has the practical advantage than an undyed fabric may be stored and then dyed to any desired two- (or multicolor with natural or pigmented yarns) shade as needed. For the heating step, either steam or dry heat may be used. Steam at about 100°C. for 3 to 20 minutes is, however, preferred for optimum results.

The following examples are included to illustrate but not necessarily to limit our invention.

**EXAMPLE 1**

A blend of 97.1% isotactic polypropylene and 2.9 percent poly-2-vinylpyridine was melt-spun into fiber, drawn 5:1 and the resultant yarn knit into tubular fabric.

An activating paste was prepared by mixing 100 grams of 90 percent formic acid, 10 grams of hydroxyethy cellulose and 10 grams water. The activating paste was printed on a sample of the tubular fabric in the form of an X. The treated fabric was then heated on a ferrotype plate at 260°F. for 10 minutes, and then rinsed in water containing a small amount of nonionic detergent which is the nonylphenol/ethylene oxide condensate known as Triton X-100. After being scoured at 93°C. for 20 minutes in water at pH 10 containing a small amount of nonionic detergent, the fabric was dyed for 1 hour at 200°F. in a dyebath containing 3 percent owf (on the weight of fiber) Capryl Orange R (Acid Orange 60) and 3 percent owf Calcosperse Yellow 4 RL (Disperse Yellow 23). The fabric was finally post-scoured for 10 minutes at 160°F. in water containing a small amount of nonionic detergent.

The sample was dyed orange where the acid-containing activation paste had been applied and yellow where it had not been applied. The contrast was marked and the borders were clearly defined.

**EXAMPLE 2**

The procedure of Example 1 was duplicated except that methoxycellullose was used as thickener, and spots of paste, rather than an X, were applied to the fabric. After scouring, the fabric was dyed as in Example 1, using only Capryl Orange R. After dyeing, orange spots resulted where the paste had been applied, while the untreated areas were colored only a very pale pink.
EXAMPLE 3

An intimate mixture of 97.1 percent isotactic polypropylene and 2.9 percent poly(2-vinylpyridine) was melt-spun and drawn into a 52-filament 4,000 denier yarn. Three of these yarns were plied together, texturized, and tufted into jute carpet backing. The tufted carpet was then simultaneously activated and dyed using the following procedure:

The face yarn of the carpet was printed with a paste made up of 5 percent Nealon Red BRE (Acid Red 212), 5 percent Lyogen VU (a nonionic allylphenolpolyether glycol used as levelling agent), 5 percent Polygum 261, a purified natural gum ether thickening agent, 6 percent formic acid and 81 percent water. The carpet containing the paste thereon was put into a saturated steam atmosphere at 212° F. for 20 minutes, removed from the atmosphere and scoured for five minutes at 140° F. with an aqueous solution containing 0.5 percent owf Triton X-100. A carpet having a red pattern printed on it resulted, with good pattern definition of the printed area and negligible migration into and staining of the untreated area.

EXAMPLE 4

A carpet prepared as in Example 3 was printed with paste containing 3 percent Crocein Scarlet SS (Acid Red 73, C.I. No. 27090), 5 percent Polygum 261, a natural purified gum ether thickening agent, 40 percent of a 1:1 mixture of monochloro- and dichloroacetic acid, 0.1 percent Triton X-100 and 51.9 percent water. The carpet containing the paste was put into a superheated steam atmosphere at 120° C. for 3 1/2 minutes and scoured for 5 minutes with an aqueous solution of 0.5 percent owf Triton X-100 at 140° F. The resultant carpet had a printed scarlet pattern with deep color penetration and negligible dye migration and staining to the untreated areas.

EXAMPLE 5

A carpet prepared as in Example 3 was printed with a paste containing 3 percent Cibalon Grey BL (Acid Black 60), 5 percent Polygum 261, a natural purified gum ether thickener, 40 percent of a 1:1 mixture of monochloro- and dichloroacetic acid, 0.1 percent Triton X-100 and 51.9 percent water. The carpet containing the paste was put into a superheated steam atmosphere at 120° C. for 3 1/2 minutes. It was then removed from the steam atmosphere and scoured for 5 minutes with an aqueous solution of 0.5 percent owf Triton X-100 at 140° F. The resultant carpet had a printed gray pattern with deep color penetration and negligible dye migration and staining to the untreated areas.

EXAMPLE 6

A carpet prepared as in Example 3 was printed with paste containing 3 percent Pilate Fast Blue RRN (an acid metallized anionic dye), 5 percent Polygum 261, a natural purified gum ether thickener, 40 percent of a 1:1 mixture of monochloro- and dichloroacetic acid, 0.1% Triton X-100 and 51.9 percent water. The carpet containing the paste was put into a superheated steam atmosphere for 3 1/2 minutes at 120° C. It was then removed from the steam atmosphere and scoured for 5 minutes with an aqueous solution of 0.5 percent owf Triton X-100 at 140° F. The resultant carpet had a printed blue pattern with deep color penetration and negligible dye migration and staining to the untreated areas.

EXAMPLE 7

A carpet prepared as in Example 3 was printed with a paste containing 2% percent Carbolan Brilliant Blue 2-GS (a strong acid type anionic dye), 2% percent formic acid, 2% percent of an anionic surfactant made from the reaction of fatty alcohols with phosphorus pentoxide, and 92.5 percent water. The printed carpet was heated at 212° F. by steam for 15 minutes in a closed chamber, and then rinsed in water containing 0.5 percent owf nonionic surfactant at 180° F. for 20 minutes. The resultant carpet was dyed to a deep blue shade in the areas where the dye paste has been applied, and sharp definition of the printed pattern was obtained without staining of adjacent untreated material.

EXAMPLE 8

This example illustrates the technique in the present invention of overprinting with an acid dye on a previously disperse-dyed background. For this purpose, a sample of carpet prepared by the same procedure as in Example 3 from a blend of 2.9 percent of the 1:1 copolymer of 2-vinylpyridine and 2-methyl-5-vinylpyridine with 97.1 percent isotactic polypropylene was dyed with 0.25 percent owf of Terasil Blue GLF (Disperse Blue 27, C.I. 60767) in conventional fashion, using 1 percent owf acetic acid in the dye bath and dyeing at the boil for 1 hour. The dyed carpet was then postscoured and dried.

The light blue product was then screen printed with the following paste formulation:

- 1 percent Wool Yellow (Acid Yellow 23, C.I. 19140)
- 3 percent Diethanolamine salt of a 1:1 mixture of mono- and di-fatty alcohol phosphates
- 5 percent Formic acid
- 2.5 percent Polygum 275
- 88.5 percent water

(Percentages are on the weight of paste)

The printed carpet was steamed for 10 minutes at 100°-105° C. and post-scoured, yielding a green print on a light blue background. The printed pattern was sharply defined with deep color penetration.

EXAMPLE 9

This example illustrates the technique in the present invention of overprinting with an acid dye on an acid-dyed background. A sample of the carpet used in Example 8 was prescoured and dyed with the following dyebath:

- 1 percent owf Carbolan Brilliant Blue 2GS (Acid Blue 175)
- 4 percent owf Sodium laurylsulfate
- 5 percent owf Acetic acid
- 0.5 percent owf Lyogen MS (a cationic leveling agent for anionic dyes)

The carpet was dyed for 1 hour at the boil, rinsed, post-scoured and dried. It was medium blue in color.

The dyed carpet was then roller printed with the same paste used in Example 8 and aftertreated in the same fashion as the printed carpet in Example 8. The resultant product had a green pattern on a medium blue background, the pattern being sharply defined and deeply dyed.

EXAMPLE 10

This example illustrates printing with a mixture of Lewis acid and anionic surfactant, followed by dyeing with a mixture of acid and disperse dyes. A sample of the carpet used in Example 8 was screen printed with the following paste:

- 4 percent Tergitol 15-S-3S
- 3 percent para-Toluensulfonic acid
- 3 percent Polygum 275
- 90 percent Water

The printed carpet was steamed and scoured as in Example 8. It was then dyed in the following dyebath for one hour at the boil:

- 1 percent owf Alizarine Cyanine Green G (Acid Green 25, C.I. 61570)
- 0.25 percent owf Terasil Blue GLF (Disperse Blue 27, C.I. 60767)
- 3.0 percent owf Acetic Acid
- 0.5 percent owf Lyogen MS

After scouring, the product was a carpet of blue background with a green pattern. The pattern was clearly defined and deeply dyed.
A carpet yarn made from a blend of 97 percent isotactic polypropylene and 3 percent of a copolymer composed of 75 percent 2-methyl-5-vinyl-pyridine and 25 percent styrene was tufted into carpet and dyed to a light yellow color in the following dyebath:

0.20 percent owf Wool Yellow (Acid Yellow 23, C.I. 19140)
3.0 percent owf Sandopan 6624 (C₆H₄H₂−(CH₂CH₂O)₇)−
CH₂−COONa
5.0 percent owf Acetic acid
After dyeing for 45 minutes at the boil, the carpet was postscoured and dried. It was then roller printed with the following composition:
1 percent Anthraquinone Blue SWF (Acid Blue 25, C.I. 62055)
5 percent Sodium cetyl sulfate
5 percent Formic acid
85.25 percent Water
The printed carpet was steamed for 3 minutes in a superheated steam atmosphere and then postscoured. It had a green pattern of good definition on a yellow background.

A sample of the carpet described in Example 11 was dyed to a medium yellow shade with 0.5 percent owf Calcopersene Yellow 4RL (Disperse Yellow 23, C.I. 26070). When printed with the paste described in Example 11, followed by steaming and postscouring as in Example 8, a green pattern on a yellow background was obtained.

A sample of the carpet described in Example 11 was printed with a paste containing 40 percent of a 1:1 mixture of mono- and dichloroacetic acids, 5 percent Poly gum 261 and 55 percent water. The printed carpet was steamed for 3½ minutes at 120°C, postscoured and dyed with the dyebath of Example 1. An orange print on a yellow background was obtained. Example 14
A blend of 100 parts of isotactic polypropylene, 3.5 parts of the 1:1 copolymer of 2-vinylpyridine with 2-methyl-5-vinyl-pyridine and 2 parts of polyethylene glycol of molecular weight 600,000 was converted to carpet yarn by the procedure of Example 1 and tufted into jute carpet backing. Samples of this carpet when treated according to the procedures of Examples 8, 9 and 10 gave results similar to those described in these examples except that the colors were darker.

This example demonstrates the process of the present invention in making effects of more than two colors by multiple over-printing. A sample of the carpet described in Example 8 was pad-dyed with the following composition:
1.0 percent Capracryl Orange R (Acid Orange 60)
3.0 percent Diethanolamine salt of a 1:1 mixture of mono- and di-fatty alcohol phosphates
5.0 percent Formic acid
The carpet was padded with the above composition to ca. 100 percent wet pickup, steamed 10 minutes at 100°-105°C, postscoured and dried. It was then screen printed with three different screens, each screen having a pattern which was not coincident with either of the other two screens. The printing pastes all contained 3 percent Poly gum 275, 5 percent formic acid, dye and water to make 100%. The following dyes were separately used in the above paste formulation to make the three overprints:
Supralan Yellow NR (a neutral metallized dye, Acid Yellow 121, C.I. 18690)
Calcicod Brown RD (Acid Brown 14, C.I. 20195)

A carpet yarn made from a blend of 100 parts of polyethylene terephthalate, 2 parts of poly-2-vinylpyridine and 6 parts of polyethylene glycol of molecular weight 4 million was melt-spun at 540°F. into 70-filament yarn and drawn 4 to 1 to form a final yarn of 20 denier per filament. Two of these yarns were then plied together, texturized and the texturized yarn tufted into jute carpet backing. To form the background color, the carpet was dyed for 45 minutes at the boil with the following dyebath:
0.75 percent owf Cibacet Orange 2RN (Disperse Orange 3, C.I. 11005)
0.50 percent owf Acetic acid
2.0 percent owf Diammonium phosphate
0.5 percent Lyogen MS
The orange-dyed carpet was postscoured and dried. It was then screen printed with the following composition:
1 percent Anthraquinone Blue SKY (Acid Blue 78, C.I. 62055)
5 percent Formic acid
3 percent Diethanolamine salt of a 1:1 mixture of mono- and di-fatty alcohol phosphates
3 percent Poly gum 260
88 percent water
The printed carpet was steamed for 12 minutes at 100°C and then postscoured, yielding a product having a green print on an orange background.

A sample of the carpet used in Example 16 was dyed for one hour at the boil with the following dye bath:
0.75 percent owf Alizarine Blue SAP (Acid Blue 45, C.I. 63010)
5 percent owf Formic acid
3 percent owf Sodium lauryl sulfate
0.5 percent owf Triton X-100
The dyed carpet was postscoured, dried and screen printed with the following formulation:
1 percent Wool Yellow (Acid Yellow 23, C.I. 19140)
10 percent 1:1 mixture of mono- and dichloroacetic acids
3.2 percent Poly gum 260
85.8 percent water
The printed carpet was steamed for 10 minutes and scoured yielding a product having a green pattern of sharp definition on a blue background.

A sample of the carpet used in Example 16 was roller printed with the following paste:
15 percent Formic acid
3.2 percent Poly gum 260
81.8 percent Water
The printed carpet was steamed for 10 minutes at 100°C, scoured and dyed in the following dyebath:
1 percent owf Croceine Scarlet SS (Acid Red 73, C.I. 27090)
0.15 percent owf Cibacet Orange 2RN (Disperse Orange 3, C.I. 11005)
3.0 percent owf Acetic acid
0.5 percent owf Lyogen MS
After scouring the carpet showed a medium red print on a light red background.

A sample of the carpet used in Example 16 was roller printed with the acid paste used in Example 18, steamed for 5 minutes at 120°C and then scoured. When dyed with 1 percent owf Carbolan Brilliant Blue 2GS (Acid Blue 175) in the
presence of 5 percent acetic acid, the resultant carpet was colored medium blue with a dark blue pattern.

**EXAMPLE 20**

A sample of the carpet used in Example 16 was screen printed with the following paste:

- 5 percent Formic acid
- 3 percent Diethanolamine salt of a 1:1 mixture of mono- and di-fatty alcohol phosphates
- 3.5 percent Polygum 260
- 88.5 percent Water The printed carpet was steamed for 10 minutes at 100°C, scoured and dyed with the same dyebath as used in Example 10. After scouring, the polyester carpet had a sharply defined green print on a blue background.

**EXAMPLE 21**

Three batches of print paste and dye were made up, each containing 100 parts of the paste used in Example 20 and one part of dye. The batches contained the following dyes:
- Batch No. 1: Buffalo Black SS (Acid Black 1, C.I. 20470)
- Batch No. 2: Calcost Brown RD (Acid Brown 14, C.I. 20195)
- Batch No. 3: Capracll Orange R (Acid Orange 60)

The three batches of paste were separately printed, using silk screens with non-incident patterns, on a sample of the polyester carpet used in Example 16. The printed carpet was steamed for 5 minutes at 120°C, scoured and dried. It had a printed pattern of black, brown and orange on a white background.

**EXAMPLE 22**

A sheet of 300 of the 52-filament 4,000 denier yarns prepared in Example 3 was randomly printed with the acid paste of Example 13, steamed for 4 minutes at 120°C, scoured and dried. The yarn was then tufted into jute carpet backing and the resultant carpet dyed in a bath identical with the one used in Example 10. After scouring, the product was a space-dyed carpet composed of random blue and green colored areas.

**EXAMPLE 23**

A sheet of yarns identical with those used in Example 21 was successively randomly printed with three different pastes. The pastes all contained the ingredients of the paste used in Example 10, to which was added 3 percent of the following dyes:
- Paste A: Crocine Scarlet SS (Acid Red 73, C.I. No. 27090)
- Paste B: Wool Yellow (Acid Yellow 23, C.I. 19140)
- Paste C: Alizarine Cyanine Green G (Acid Green 25, C.I. 61570)

The printed sheet was then steamed for 4 minutes at 120°C, scoured and dried. The yarns were then tufted into jute carpet backing to yield a space-dyed carpet which was composed of red, yellow, green, orange, chartreuse and gray areas.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. A mixture of filaments capable of being dyed to a multicolor pattern through exposure to anionic and disperse dyes, said filaments having been prepared from a blend comprising:
   A. a fiber-forming poly(alpha-olefin) or polyester,
   B. between about 0.5 and 5 percent of a thermoplastic nitrogen-containing basic polymer capable of binding anionic dyes,
   wherein at least some of the filaments contained in said mixture are contacted discontinuously along their length with between about 4 and less than 100 percent on weight of the fiber, of a concentrated Lewis acid or Lewis acid-generating material of sufficient concentration to form a reaction product with said nitrogen-containing polymer, said treatment occurring prior to or during the dyeing step and resulting in the presence of said filaments so treated being dyeable with anionic and disperse dyes, and the portions of said filaments not so treated being dyeable with disperse dyes only.

2. The mixture of filaments defined in claim 1, in which the blend contains between about 0.5 and 7 percent by weight of a hydrophilic compound which is a homopolymer of ethylene oxide, an ether or ester derivative thereof, or copolymer of ethylene oxide, said hydrophilic compound having a degree of polymerization not less than 4, and an ethylene oxide content not less than 60 percent by weight, the total amount of the thermoplastic nitrogen-containing polymer and said hydrophilic compound in said blend being greater than 3 percent by weight of total blend.

3. The mixture of filaments of claim 1 wherein the poly(alpha-olefin) is selected from polyethylene, polypropylene, poly(3-methyl-1-butene) or poly(4-methyl-1-pentene) and the polyester is selected from the poly(ethylene terephthalate), poly(1,4-cyclohexylene-dimethylene terephthalate).

4. The mixture of filaments of claim 1 wherein the basic nitrogen-containing polymer is selected from the group consisting of homopolymers of vinylpyridines, alklyvinylpyridines, vinylquinolines, alklyvinylquinolines, or copolymers of vinylpyridine monomers with each other or with alklyvinylpyridine monomers, or copolymers of vinylpyridine monomers with each other or with alklyvinylpyridine monomers, or copolymers of vinylpyridine monomers with a monoethylenically unsaturated monomer.

5. The mixture of filaments of claim 4 which is a yarn.

6. The mixture of filaments of claim 4 which is a fabric.

7. The mixture of filaments of claim 4 which is included in a carpet.

8. The fabric of claim 6 which contains uncolored non-dye receptor-containing poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dyeing.

9. The carpet of claim 7 which contains uncolored non-dye receptor-containing poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dyeing.

10. The fabric of claim 6 which contains pigmented poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dyeing.

11. The carpet of claim 7 which contains pigmented poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dyeing.

12. The fabric of claim 8 which contains pigmented poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dyeing.

13. The carpet of claim 9 which contains pigmented poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dyeing.

14. The mixture of filaments defined in claim 4 in which the basic dye receptor polymers is selected from the group consisting of:
   a. poly(2-vinylpyridine)
   b. poly(2-methyl-5-vinylpyridine)
   c. poly(4-vinylpyridine)
   d. poly(2-vinylquinolone)
   e. the copolymer of 2-vinylpyridine and 2-methyl-5-vinylpyridine
   f. the copolymer of 2-vinylpyridine and styrene
   g. the copolymer of 2-methyl-5-vinylpyridine and styrene.

15. The mixture of filaments defined in claim 14 in which the poly(alpha-olefin) is selected from the group consisting of polyethylene, polypropylene, poly(3-methyl-1-butene) or poly(4-methyl-1-pentene) and the polyester is selected from the group consisting of poly(ethylene terephthalate), poly(ethylene terephthalate-isophthalate) or poly(1,4-cyclohexylene-dimethylene terephthalate).
16. The mixture of filaments of claim 15 in which the Lewis acid or Lewis acid-generating material is selected from the group consisting of:
   a. Concentrated inorganic acids, or their anhydrides.
   b. Organo-carboxylic or sulfonic acids.
   c. Hydrolyzable halides.
   d. Borate esters.
   e. Phenol.

17. The mixture of filaments of claim 16 which has been treated under acid conditions with an anionic surfactant either prior to or during said Lewis acid or Lewis acid-generating material treatment, said anionic surfactant having the general formula R-A wherein:
   R represents a substituted or unsubstituted alkyl aryl, or alkylaryl group having at least six carbon atoms and
   A represents an anionic group selected from the group consisting of:
      a. Poly(2-vinylpyridine)
      b. Poly(2-methyl-5-vinylpyridine)
      c. Poly(4-vinylpyridine)
      d. Poly(2-vinylquinoline)
      e. The copolymer of 2-vinylpyridine and 2-methyl-5-vinylpyridine
      f. The copolymer of 2-vinylpyridine and styrene
      g. The copolymer of 2-methyl-5-vinylpyridine and styrene.

33. The shaped article of claim 32 in which the poly(alphaolefin) is selected from the group consisting of polyethylene, propylene, poly(3-methyl-1-butene) or poly(4-methyl-1-pentene) and the polyester is selected from the group consisting of poly(ethylene terephthalate), poly(ethylene terephthalate-isophthalate) or poly(1,4-cyclohexylene-dimethylene terephthalate).

34. The mixture of filaments of claim 33 in which the Lewis acid or Lewis acid-generating material is selected from the group consisting of:
   a. Concentrated inorganic acids or their anhydrides.
   b. Organo-carboxylic or sulfonic acids.
   c. Hydrolyzable halides.
   d. Borate esters.
   e. Phenol.

35. The mixture of filaments of claim 34 which has been treated under acid conditions with an anionic surfactant either prior to or during said Lewis acid or Lewis acid generating material treatment, said anionic surfactant having the general formula R-A wherein:
   R represents a substituted or unsubstituted alkyl aryl, or alkylaryl group having at least six carbon atoms and
   A represents an anionic group selected from the group consisting of:
      a. Poly(2-vinylpyridine)
      b. Poly(2-methyl-5-vinylpyridine)
      c. Poly(4-vinylpyridine)
      d. Poly(2-vinylquinoline)
      e. The copolymer of 2-vinylpyridine and 2-methyl-5-vinylpyridine
      f. The copolymer of 2-vinylpyridine and styrene
      g. The copolymer of 2-methyl-5-vinylpyridine and styrene.

36. The mixture of filaments of claim 35 which has been treated with a mixture of 0.1 percent or greater of Lewis acid or Lewis acid-generating material based on the total treating composition weight, and greater than 0.5 percent of said anionic surfactant based on the total treating composition weight and a viscosity increasing agent.

37. The mixture of filaments of claim 36 which has been dyed with an anionic or disperse dyestuff prior to treatment with said mixture.

23. The filamentary assembly of claim 22 which is a fabric.

24. The mixture of filaments of claim 22 which is a carpet.

25. The mixture of filaments of claim 22 which is included in a carpet.

26. The fabric of claim 24 which contains uncolored non-dye receptor-containing poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dying.

27. The carpet of claim 25 which contains uncolored non-dye receptor-containing poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dying.

28. The fabric of claim 24 which contains pigmented poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dying.

29. The carpet of claim 25 which contains pigmented poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dying.

30. The fabric of claim 26 which contains pigmented poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dying.

31. The carpet of claim 27 which contains pigmented poly(alpha-olefin) or polyester fibers which are not susceptible to dyeing by anionic and disperse dyes under the conditions of dying.

32. The mixture of filaments defined in claim 22 in which the basic dye receptor polymer is selected from the group consisting of:
   a. Poly(2-vinylpyridine)
   b. Poly(2-methyl-5-vinylpyridine)
   c. Poly(4-vinylpyridine)
   d. Poly(2-vinylquinoline)
   e. The copolymer of 2-vinylpyridine and 2-methyl-5-vinylpyridine
   f. The copolymer of 2-vinylpyridine and styrene
   g. The copolymer of 2-methyl-5-vinylpyridine and styrene.

42. The process defined in claim 40 in which an anionic dye is added to the treating composition.

43. A process for making the mixture of filaments defined in claim 1 comprising the following steps in sequence:
   a. Blending between about 0.5 and 5 percent of a thermoplastic nitrogen-containing basic polymer capable of binding anionic dyes with a fiber-forming poly(alphaolefin) or polyester,
   b. Forming the resulting blend into fiber,
   c. Forming said fiber into a mixture of filaments,
   d. Discontinuously contacting the surface of said filaments with a treating composition which contains between about 4 percent and 100 percent of a Lewis acid or Lewis acid generating material,
   e. Heating said mixture of filaments containing the treating composition for such time to allow penetration of same,
   f. Removing the excess treating composition,
   g. Dyeing the treated filaments with an anionic dyestuff alone or in combination with a disperse dyestuff.

40. The process defined in claim 39, in which between about 0.5 and 7 percent by weight of a hydrophilic compound has been added to the blend prior to forming said blend into fiber, said hydrophilic compound being a homopolymer of ethylene oxide, an ether or ester derivative thereof, or copolymer of ethylene oxide, said hydrophilic compound having a degree of polymerization not less than 4, and an ethylene oxide content not less than 60 percent by weight, the total amount of the thermoplastic nitrogen containing polymer and hydrophilic compound in said blend being greater than 3 percent by weight of the total blend.

41. The process defined in claim 39 in which an anionic dye is added to the treating composition.

42. The process defined in claim 40 in which an anionic dye is added to the treating composition.
43. The process as defined in claim 39 in which the mixture of filaments has been dyed with a disperse dye prior to treatment with the treating composition, said treating composition containing an anionic dye.

44. The process defined in claim 44 in which the mixture of filaments is dyed with a disperse dye after said treatment with the treating composition defined therein.

45. The process defined in claim 39 in which the treating composition contains a viscosity increasing agent.

46. The process defined in claim 41 in which the treating composition contains a viscosity increasing agent.

47. The process as defined in claim 40 in which the mixture of filaments has been dyed with a disperse dye prior to treatment with the treating composition, said treating composition containing an anionic dye.

48. The process defined in claim 42 in which the mixture of filaments is dyed with a disperse dye after said treatment with the treating composition defined therein.

49. The process defined in claim 40 in which the treating composition contains a viscosity increasing agent.

50. The process defined in claim 42 in which the treating composition contains a viscosity increasing agent.

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