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3,439,999

CROSS-DYED CARPETS

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This invention relates to fabrics and textile articles suitable for being dyed to multi-color patterns by a mixture of types of dyes in a single dyeing step and to the process of assembling such fabrics.

The advantages of piece-dyeing fabrics as compared to weaving, knitting or otherwise assembling them from pre-dyed yarns and fibers are well known to those skilled in the art. To obtain these advantages many fabric articles are piece-dyed to a single color by any one of a number of well-known dyeing procedures, such as beck dyeing, jig dyeing, etc. However, where the fabric or textile article is to be multi-colored, no generally applicable piece goods dyeing processes are available. It has been necessary, in order to achieve multiple color effects in piece-dyed goods, to prepare the fabric article out of a combination of pigmented or natural color undyeable yarns with yarns dyeable in the piece-dyeing process to which it is to be subjected.

In U.S. Patent 3,101,522, Hopper et al. describe a 3-ply yarn which can be converted to a variegated colored textile article by exposure to a single dye bath. The plies of this yarn are, respectively, a color-pigmented yarn, a natural color poly(alpha-olefin) fiber yarn and a dyeable artificial yarn of a fundamentally different polymeric structure. During subsequent dyeing, only the last of these plies is changed in color. The dyeing step imparts only one of the component colors of the multiple color pattern to the yarn, the other component color of necessity being introduced as a pigment into the first of the three plies. The poly(alpha-olefin)ply never achieves any color in the process of Hooper et al. Therefore the natural color of such poly(alpha-olefin) yarn is one of the component colors of the multiple color pattern. Furthermore the 3-ply yarn, and therefore the fabric articles created therefrom, is composed of fibers which differ from each other fundamentally in their respective polymeric structures. As a result the tendency toward shrinking, the modulus, the resiliency, the wearability, the luster and many of the other fundamental physical properties of each of the three plies of the yarn will differ from those of the other two, making the composite yarn difficult to process and undesirable for many textile applications.

It is an object of this invention to provide a fabric capable of being piece-dyed to a multi-color pattern. It is another object of this invention to provide a fabric composed of yarns of a given polymeric composition capable of being piece-dyed to a multiple color pattern.

It is still another object of this invention to provide a fabric of yarns composed predominantly of polypropylene capable of being piece-dyed to a multiple color pattern.

A still further object of this invention is that such dyeing to a multiple color pattern of such fabrics can be accomplished in a single dyeing step with a mixture of acid type dyes and other types of dyes.

Other objects of our invention will be apparent to one skilled in the art from a consideration of this specification.

These objects can be achieved by assembling a fabric or textile article, such as a carpet pile, from two or more classes of yarns, of all of which have been formed from a polymeric composition which is substantially undyeable by acid dyes but susceptible to dyeing by another type of

dye; some, but less than all, of said classes of yarns having been treated, before their assembly into said fabric, to render them dyeable by acid type dyes. Exposure of such a fabric to acid and such other types of dyes will result in the yarns which have been so treated being dyed by all of the types of dyes whereas the yarns which have not been so treated being dyed only by the said other types of dyes, so that the fabric achieves a multi-color pattern predetermined by the arrangement of the classes of yarns in the fabric. Where the types of dyes are mutually compatible in the dye bath, these fabrics can be dyed to their multi-color pattern in a single dyeing step by a mixture of the acid type with the other types of dyes.

Certain classes of high polymeric materials are not susceptible to dyeing by one or more types of dyes because the polymer lacks functional groups, known as dye receptors, with which the dye molecules may combine. Hydrocarbon high polymers as a class are not susceptible to dyeing by acid type dyes or disperse dyes for this reason. Polyesters are also undyeable by acid types of dyes. In order to fashion dyeable fibers, yarns and other articles from hydrocarbon or polyester high polymer compositions, it has been found necessary to employ such expedients as the incorporation of quantities of highly polar basic polymeric material in the undyeable polymers. Unfortunately, in order to provide sufficient dye receptor groups to permit the achievement of the desired depth of dyeing, so much of the highly polar polymer must ordinarily be incorporated in the hydrocarbon or polyester polymer that the overall physical properties of the combined polymeric composition are greatly reduced. This is especially detrimental in the case where the polymeric composition is to be used to form fibers.

The copending patent applications Serial No. 375,328, filed June 15, 1964, now Patent No. 3,361,842, and Serial No. 352,317, filed March 16, 1964, both by Robert Miller, Frederick C. Loveless and Milton Farber, describe processes whereby hydrocarbon high polymers and polyesters are rendered deeply dyeable by dyes to which they are normally inert without deleteriously affecting the physical properties of the articles formed from the polymer. Briefly, the processes entail incorporating a minor amount of a highly polar basic polymer in the undyeable hydrocarbon or polyester high polymer and, subsequent to the formation of fibers or other articles from the polymeric composition, treating them by infusing the same with an acidic reagent which reacts with some of the polar groups of the basic polymer at and near the surface of the fibers or articles to form a reaction product of the acidic reagent with the said polar groups.

As is explained in the said copending applications, the incorporation of minor amounts, i.e. from 0.5% to 10%, of highly polar basic polymers such as nitrogen-containing polymers, in a hydrocarbon or polyester high polymer does not render yarns formed from such a polymeric composition substantially dyeable by acid types of dyes. Such dyes will only impart very pale tints to such yarns, so that for all practical purposes the fibers can be said to be substantially undyeable by acid type dyes. Such fibers, however, are substantially susceptible to dyeing by other classes of dyes, such as the disperse dyes.

After the infusion with acidic reagents of fibers made from mixtures of hydrocarbon or polyester high polymers and very small amounts, i.e. between 0.5 to 10% of highly polar basic polymers according to the process of the said copending application, these fibers become highly susceptible to dyeing by acid types of dyes and can readily be dyed to desirable deep shades by them.

Drawn or undrawn fibers and filaments, and yarns

and fabrics and textile articles such as carpet pile made of polymeric compositions comprising hydrocarbon or polyester polymer material containing from 0.5 to 10% of a highly polar basic polymer such as a polymerized nitrogen base can be made highly receptive to the acid types of dyes mentioned above by infusing the filamentous material for a short time with acidic chemical reagents which are capable of dissolving in or diffusing into the hydrocarbon or polyester polymer, where they react with the highly polar basic polymer therein. The material so treated may then be dyed in any conventional manner with the above-named dyes.

The term "hydrocarbon polymer" as used herein refers to polymers having a molecular weight in excess of 600 of compounds of carbon and hydrogen. The preferred material in our invention is a composition which is predominantly isotactic polypropylene, and further discussion will be mainly in terms of this representative hydrocarbon polymer. However, the invention is equally applicable to all fiber-forming hydrocarbon linear high polymers, including poly-(1-alkenes) such as polyethylene, poly-1-butene, poly(4-methyl-1-pentene), copolymers of two or more 1-alkenes, copolymers of non-terminal olefins with 1-alkenes, etc.

The term polyester as used herein refers to polymers having a molecular weight in excess of 600, being condensation polymers of dihydric alcohols with organodibasic acids or their anhydrides, particularly dicarboxylic acids, and self-condensation polymers of omega-hydroxy carboxylic acids. The preferred materials in our invention are poly - (ethylene terephthalate), poly(ethylene terephthalateisophthalate), and poly(1,4 - cyclohexylenedimethylene terephthalate), and further discussion will be mainly in terms of these representative polyesters. It will be understood that the invention is applicable to all fiber-forming polyesters, in which the ester linkage are intralinear, including poly(alkylene alkanedioates), poly(cycloalkylenedimethylene alkanedioates), poly(alkylene arenedioates), poly(cycloalkylenedimethylene arenedioates), and analogous materials. Examples of the above-named polyesters are respectively, poly(ethylene adipate), poly(1,4-cyclohexylenedimethylene adipate), poly(ethylene terephthalate), and poly(1,4-cyclohexylenedimethylene terephthalate).

Examples of the highly polar basic dye receptor polymers which may be incorporated in the hydrocarbon or polyester polymers are basic nitrogen-containing materials of the following types:

(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 containing 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, polyureas, poly(vinylcarbazoles), aniline-formaldehyde resins, etc.

The basic nitrogen polymers employed should not be extractable from admixtures thereof with the hydrocarbon or polyester polymer, under the conditions of treating and dyeing used. Thus, after a one-hour extraction of the fiber with boiling water at a pH of 3, at least 10% of the originally added nitrogen polymer should remain in the hydrocarbon polymer. The amount of the basic nitrogen polymer added to the hydrocarbon polymer should be sufficient so that, after the acid treat-

ment of the invention, it will bind or fix the amount of dye required to produce the shade desired.

Vinyl-substituted monocyclic 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 with 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 monovinylpyridines and monovinylquinolines.

The monovinylpyridines useful in making the above named 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, polypropylene, polystyrene, and polybutadiene. 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 the dyeability of the hydrocarbon polymer.

The polyamides useful as the dye-receptors employed in this process include homopolyamides such as poly(hexamethylene adipamide), poly(hexamethylene sebacamide), polypyrrolidinone, polycaprolactam, polyantholactam, and copolyamides such as Zytel 61 (a trademark of Du Pont de Nemours and Company), an interpolymers 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., N-vinyl-3-alkylpyrrolidinone, and N-substituted polyacrylamides, e.g., N-butylacrylamide. 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, vinyl aryl 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 epihalohydrins or dihaloparaffins with one or more amines, such as those disclosed in Belgian Patent 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 styrene-maleic anhydride copolymer with 3-(dimethylamino)propylamine (the reaction product being a polyamino-polyimide), and styrene-allylamine copolymers such as those disclosed in U.S. Patent No. 2,456,428.

Examples of the introfusible acidic chemical reagents used in the invention are the following:

(1) Mineral acids, such as hydrochloric acid, hydrobromic acid, sulfurous acid, nitric acid, sulfuric acid, phosphoric acid and perchloric acid. The last three acids,

highly ionic materials, are effectively employed at high application temperatures ($>60^{\circ}\text{C}.$).

(2) The anhydrous acid gases corresponding to the mineral acids defined above, whether the undissociated acid or the acid anhydride, illustrated by hydrogen chloride, hydrogen bromide, sulfur dioxide, and nitrogen dioxide. A source of hydrogen ions such as water in or on the hydrocarbon polymer is essential in those cases where the reagent is not a Bronsted acid, i.e. contains no proton which can be donated in the reaction.

(3) Organo-carboxylic acids, including aliphatic and aromatic acids, mono-carboxylic and dicarboxylic acids, saturated and unsaturated acids. Suitable acids are exemplified by formic, acetic, propionic, stearic, and other alkanolic acids in the C_{1-18} range; undecylenic, oleic, benzoic, salicylic, succinic, adipic, phthalic, bromoacetic, chloroacetic and lactic acids. The organic acid may be used in its liquid or molten state (when its melting point is below the temperature selected for the fiber treatment), or in solution in a volatile organic solvent such as benzene or toluene. It may be used in water solution—provided that the solubility of the acid in water is sufficient to provide a solution containing at least 20% (by weight) of the acid solute, and provided that the acid is used at no less than 20% concentration. Greater dilution with water greatly reduces diffusion of the organic acid into polypropylene and results in very low dyeability of the fiber.

(4) Those halide compounds which liberate hydrohalic acid on contact with water at the temperature of the treatment. Examples of such compounds are:

(a) Halogen compounds of non-metallic elements such as phosphorus and sulfur (exemplified by PCl_3 , POCl_3 , S_2Cl_2 , SOCl_2 , SO_2Cl_2);

(b) Metal halides such as the halides of zinc, tin, and aluminum;

(c) Acid halides of organic acids of the class defined in section 3, and organosulfonyl halides, typified by acetyl, benzoyl, adipyl, and p-toluenesulfonyl chlorides;

(d) Activated alkyl halides containing a conjugated grouping which enhances the reactivity of the halogen atom; e.g., allylic and benzylic halides (such as chlorides).

(5) Other acidic and potentially acidic compounds capable of forming complexes or addition compounds with basic nitrogen polymers, e.g. boron trifluoride, borate esters such as n-butyl borate, and phenol.

In all these treatments, hydrogen ions are present either as part of the acid itself, as in nitric or acetic acid, or they may be furnished by water present in or on the fiber, in the amount of at least 1% (o.w.f.).

Representative of those reagents which have the greatest effect in the said process, from the standpoint of increasing the dyeability of hydrocarbon polymers containing up to 10% of polymerized vinylpyridine base dye receptor, are acetic acid, stearic acid, oleic acid, hydrochloric acid, thionyl chloride, sulfurous acid, and p-toluenesulfonyl chloride.

Representative of those reagents which have the greatest effect in the said process, from the standpoint of increasing the dyeability of hydrocarbon polymers containing up to 10% of an amine polymer dye receptor, are acetic acid, hydrochloric acid, adipoyl chloride, and thionyl chloride.

Representative of those reagents which have the greatest effect in the said process, from the standpoint of increasing the dyeability of hydrocarbon polymers containing up to 10% of the polyamide dye receptor, are formic acid, hydrochloric acid, and phosphorus oxychloride.

The temperature range within which our chemical treatment of the fibers is carried out is not critical but is of course below the softening temperature of the particular hydrocarbon polymer employed. For isotactic polypropylene this would be below $160^{\circ}\text{C}.$, its melting point. In practice, however, with drawn fibers of polypropylene, for instance, which shrink greatly at temperatures

above $140^{\circ}\text{C}.$, temperatures not greater than $140^{\circ}\text{C}.$ will of course be used to avoid such shrinkage. There is likewise no critical lower limit, but the lowest useful temperature will simply be dictated by rates of diffusion and reaction, and in many cases $0^{\circ}\text{C}.$ represents a practical lower value.

The duration of the acid treatment may vary from less than 1 second up to 3 hours, depending on the reagent and the temperature selected. Usually a time of from 5 seconds to 30 minutes, using temperatures in the range from about 20° to about $140^{\circ}\text{C}.$, is satisfactory and sufficient for most reagents and solutions.

The physical form of the fibers on which these treatments is carried out may vary widely. It may be monofilament or multifilament; plain, bulked, or texturized; staple; tow, or stock. The treatment may be done batchwise or in any convenient continuous fashion. A number of efficient and practical techniques will readily suggest themselves to those skilled in the art.

Although the process is applicable in the range of 0.5 to 10% content of nitrogen base polymer in the fiber, we prefer to employ the range of 0.5–5%, the particular value depending upon the nitrogen content and relative basicity of the additive. This lower range is advantageous because of the high cost of the nitrogen base polymers and because it minimizes any undesirable effects on the physical properties of the fiber. The presence of 0.5 to 5% of nitrogen base polymer is usually sufficient to exhaust a 1% (o.w.f.) dye bath, which gives deep colors with many dyes.

The vinylpyridine polymers used in the examples herein include suspension polymers and solution polymers, the polymerization initiator used having been azobisisobutyronitrile. The polymers had an intrinsic viscosity in the range from 0.2 to 2.0 measured in pyridine at $30^{\circ}\text{C}.$ The polyamines used in the examples were made by conventional means, e.g., by procedures similar to those described in Belgian Patent No. 606,306 or by treatment of a styrene-maleic anhydride copolymer with 3-dimethylaminopropylamine, as described, for instance, by Cohen and Minsk (J. Org. Chem. 24, 1404 (1959)). The polyamide high polymers used were obtained from commercial sources. The hydrocarbon polymers used were polyethylene, polypropylene, and poly(4-methylpentene-1). The mixtures of hydrocarbon polymer and the dye acceptor polymers were made by blending, tumbling or any convenient method, and they were then spun into yarns by conventional melt-spinning.

The acid treatment step may be effected either before or after the yarn has been drawn—most conveniently after the drawing. Hanks, coils, and packages of the resulting filaments were variously subjected to treatments with acidic reagents according to the above-described process, and were thereafter processed as described in the detailed examples which follow. The abbreviation o.w.f. used herein means "on the weight of the fiber," in the parlance of the dyer's trade.

The dyes suitable for use in this invention fall into two categories. One category is the broad group of acid type dyes, which includes the so-called strong acid dyes, direct dyes, and the metallized dyes which includes the so-called acid metallized dyes and the so-called neutral metallized dyes. Only the fibers activated by the above-described process entailing infusion with an acid reagent are substantially dyeable by the aforesaid types of dyes. That is, only the activated yarns will have any substantial degree of color imparted to them which will remain fast in subsequent washing upon exposure to acid type dyes. On the other hand, the disperse type dyes will dye the above-described fibers to a substantial degree whether or not they have been subjected to the above-described activation process entailing infusion with an acid reagent.

Among the acid types of dyes suitable for use in this invention to dye the classes of yarns which have

been pretreated with the described acid infusion process are the following strong acid dyes:

Dimacide Light Yellow JRL
Dimacide Light Red 2B
Carbolan Brilliant Blue 2GS
Carbolan Brilliant Green 5GS
Anthraquinone Blue Sky (Color Index No. 62105)
Kiton Fast Orange 2R (Color Index No. Acid Orange 10)

The following acid metallized dyes are also examples of acid type dyes useful in this invention in that they dye only those classes of the above-described fibers which have been pre-treated by the acid infusion process:

Pharmalan Red GB (Color Index No. Acid Red 183)
Pharmalan Blue 2G (Color Index No. 14880)
Palatine Yellow ELNA-CF (Color Index No. 19010)
Neolan Green B (Color Index No. Acid Green 12)
Neolan Orange R (Color Index No. Acid Orange 76)
Chromacyl Bordeaux R (Color Index No. Acid Red 194)

The following neutral metallized dyes are also examples of dyes useful as acid type dyes in this invention, in that they will dye only those above-described classes of yarns which have been pre-treated by acid infusion:

Irgalan Yellow GL (Color Index No. Acid Yellow 114)
Capracyl Orange R (the half-chrome complex of 1-phenyl-3-methyl-4-(2-hydroxy-5-sulfamoyl phenylazo)-5-pyrazolone)
Lanasyl Brown (Color Index No. Acid Brown 19)
Isolan Red B
Cibalan Blue BL
Lanasyn Green 2GL

The following are examples of disperse dyes which are useful in this invention to dye all of the above-described classes of fibers and thereby impart another color to the multi-color pattern to which the fabrics of this invention may be dyed:

Latyl Yellow 4RL (Color Index No. 26070)
Latyl Orange 3R
Cibacete Pink FG
Cibacete Orange DNA (Color Index No. Disp. Orange 21)
Interchem Blue RLF 40

The filaments and yarns which have been subjected to the acid treatment to render them dyeable by acid dyes differ from the untreated filaments and fibers only in that some of the basic polymer at and near the surface of the filaments and fibers have reacted with, and are now in the form of a reaction product thereof with, the acid reagent used in the activation treatment. The fundamental polymeric structure, and therefore important physical properties such as tensile strength, degree of shrinking, modulus, luster, etc. of the activated and unactivated yarns and filaments are the same.

When a fabric or a textile article such as a carpet pile is assembled, whether by weaving, tufting, knitting, felting, hooking or other means from various classes of yarns of the type described, some of which classes of yarns have been activated by a treatment such as the one described for dyeing by acid dyes and other classes of yarns have not, only those portions of the fabric made of activated yarn will be dyed by the acid dyes. This portion of the fabric or textile article will also be dyed by other dyes to which those yarns are susceptible when the fabric is exposed to them, such as disperse dyes. That portion of the fabric composed of unactivated yarns or fibers will remain essentially undyed by the acid dyes, and therefore will only be dyed by disperse dyes present in the dyeing step. By judicious choice of acid dyes of certain colors and disperse dyes of other colors, which acid and disperse dyes are mutually compatible in a dye bath, the fabric of this invention can be dyed to a multiple color pattern, convenient-

ly in a single dyeing step in which the fabric is exposed to this mixture of dyes.

Thus, for instance upholstery fabric or carpets woven with some of the pattern elements selected from classes of activated yarns and other of the pattern elements selected from classes of unactivated yarns can be piece-dyed to the predetermined pattern by exposure to acid and dispersed dyes. This can be accomplished in a single dyeing step where the acid and disperse dyes are mutually compatible. Similarly, carpets tufted with alternate rows of activated and unactivated yarns can be dyed to a two-color pattern in similar fashion.

A multiple color pattern involving more than two colors can be achieved by this invention by interspersing with the classes of yarn already described totally undyeable yarns, such as those of pure hydrocarbon, as for instance pure polypropylene, or of pure polyester, which has been pigmented to various colors or which has been left in its natural color, off-white.

Carpets of more intricate multi-colored designs than alternate rows can be achieved by suitably weaving the carpet with the classes of yarns as described. The carpet piles of this invention can be tufted or otherwise assembled upon any type of carpet backing, such as jute, hemp, polypropylene, etc.

Other variations of this invention include the achievement of a tweed effect in fabrics by plying yarns from classes of activated yarn piles with classes of inactivated yarn plies and then using ends of such compositely plied yarns to tuft carpets, weave fabrics, etc.

The following examples, in which all percentages are o.w.f. (on weight of fiber), will further illustrate this invention:

Example 1

An intimate mixture of 97.1% isotactic polypropylene and 2.9% of poly(2-vinylpyridine) was melt spun and drawn into a 35 filament, 524 denier yarn. Three ends of this yarn were plied together and texturized. One portion of this plied yarn was activated by immersion in glacial acetic acid at 60° C. for 1.5 minutes, and was subsequently washed thoroughly with water. Ordinary carpet backing was tufted with alternate rows of activated and unactivated yarn. The tufted carpet was then dyed by the following procedure: Prescour with an aqueous solution containing 1.0% o.w.f. Triton X-100 (a nonylphenol-ethylene oxide condensate) and 1.0% soda ash for 20 minutes at 180° F. Immerse for 45 minutes in an aqueous dye bath at 200° F. containing 3.0% acetic acid and 0.15% of Triton X-100 and 1% of Coomassie Turquoise 2GS, an acid dye, and 0.2% of Latyl Yellow 4RL, a disperse dye, all percentages being o.w.f. Then post-scour for 15 minutes with a 160° F. aqueous solution of 0.5% Triton X-100 and 0.25% soda ash. A carpet having alternate rows of bright yellow and bright green tufts resulted.

Example 2

A mixture of 98% isotactic polypropylene and 2% poly(2-ethyl-5-vinylpyridine) was melt spun and drawn to a 3500 denier, 210 filament yarn, and then texturized. A portion of this yarn containing 10% o.w.f. water, was activated by holding it in an atmosphere of SO₂ for a period of ten minutes at room temperature. A carpet tufted with alternate rows of activated and unactivated yarn was dyed in the piece for a period of 45 minutes in a dye bath maintained at 200° F. containing 1% Carbolan Green 5GS and 1% Interchemical Blue RLF-40, dyeing conditions being the same as in Example 1. A carpet containing alternate rows of deep green and light blue tufts resulted.

Example 3

An intimate mixture of 97.1% linear polyethylene and 2.9% of a copolymer of equal parts of 2-methyl-5-vinylpyridine and 2-vinylpyridine was melt spun into an 8

filament, 500 denier yarn and then drawn 4:1. A portion of this yarn was activated by soaking in POCl_3 for two minutes at 50°C . and was subsequently rinsed in acetone and then in water. A fabric woven in part with activated yarn and in part with the same yarn which had not been activated was immersed for 45 minutes in a dye bath maintained at 200°F . containing 0.5% Celanthrene Blue GSS, a dispersed dye and 0.5% of Irgalan Yellow GL (Color Index Number Acid Yellow 114), an acid type dye dyeing conditions being the same as in Example 1. The portions of the fabric formed of the activated fiber dyed a dark green whereas the portions of the fabric formed from the unactivated fiber dyed a very light shade of green.

Example 4

Carpet tufted as that in Example 1 was subjected to dyeing according to the method of Example 1, but with dye baths of the following compositions with the following resultant colors:

Dye	Combination Shades
(a) 0.5% Dimacide Blue JL (an acid type dye) 1.0% Latyl Yellow YL (a disperse dye)	Yellow/green.
(b) 2.0% Irgalan Gray BL (an acid type dye) 0.5% Celanthrene Blue GSS (a disperse dye)	Lt. Blue/Gray Blue
(c) 3.0% Irgalan Olive BL (an acid type dye) 1.0% Latyl Yellow YL (a disperse dye)	Yellow/Brt. Olive.
(d) 3.0% Capracyl Red B (an acid type dye) 1.5% Celanthrene Blue GSS (a disperse dye)	Gray/Blue.
(e) 1.5% Dimacide Red 2 BL (an acid type dye) 0.5% Celanthrene Blue GSS (a disperse dye)	Navy/Tan.
(f) 0.4% Latyl Yellow YL (a disperse dye) 0.1% Latyl Crise B (a disperse dye) 2.0% Carbolan Green 5 GS (an acid type dye)	Lt. Gray/Dk. Gray.
(g) 0.5% Latyl Cerise B (a disperse dye) 0.1% Latyl Yellow 4 RL (a disperse dye) 3.0% Vialon Copper R (an acid type dye)	Brown/Yellow.
(h) 3.0% Latyl Yellow YL (a disperse dye) 0.5% Dimacide Red 2B (an acid type dye) 1.0% Latyl Yellow YL (a disperse dye)	Red/Tan.
(i) 3.0% Vialon Brown R (an acid type dye) 0.1% Celanthrene Blue GSS (a disperse dye)	Lt. Gray/Dk. Gray.
(j) 3.0% Irgalan Gray BL (an acid type dye) 1.5% Cibacete Pink FG (a disperse dye)	Lavender/Cerise.
(k) 3.0% Vialon Black R (an acid type dye) 0.1% Latyl Cerise B (a disperse dye)	Charcoal/Pink.
(l) 0.5% Cibalan Red 2 GL (an acid type dye) 1.0% Latyl Yellow YL (a disperse dye)	Orange/Yellow.

Example 5

A mixture of 97.1% poly(4-methylpentene-1) and 2.9% of a copolymer of equal parts of 2-methyl-5-vinylpyridine and 2-vinylpyridine was melt spun and drawn to a 105 filament, 1750 denier yarn. A portion of this yarn was activated by soaking it for 1 minute at room temperature in PCl_3 , and then washing it with acetone and then with water. Activated and unactivated portions of this yarn were plied together and twisted $1\frac{1}{2}$ "Z" turns per inch and texturized.

This plied yarn was tufted on ordinary jute carpet backing to produce a tufted carpet. The carpet was then piece-dyed for 45 minutes in a dye bath maintained at 200°F . and containing 1.3% Pharmalan Navy, 0.3% Irgalan Orange RL, 0.2% Latyl Yellow 4RL and 3% formic acid. A carpet with a tweed effect of black and mustard resulted.

Example 6

A drawn, 40-filament, 441 denier poly(ethylene terephthalate) yarn containing 3.0% by weight of poly(2-vinylpyridine) was soaked in acetic acid for 4 minutes at 110°C . and then rinsed in water and woven into a fabric by combining it with yarn identical thereto except that it had not been acid-treated. After scouring the fabric as in Example 1, it was dyed to deep colors with the two dyes used in Example 2. A fabric with a deep green and light blue pattern resulted.

Example 7

Three plies, each comprising a 70 filament, 1230 denier textured yarn, were twisted together. The first ply was a polypropylene yarn pigmented to a light shade of beige. The second and third plies were extruded from an unpigmented polymeric mixture containing 97% polypropylene and 3% of a copolymer prepared from 50 parts by weight of 2-vinylpyridine and 50 parts by weight of 2-methyl-5-vinylpyridine. The second ply was not subjected to an after-treatment with acid, but the third ply was subjected, after texturing, to a treatment with SO_2 like that described in Example 2. The composite yarn was tufted onto an ordinary carpet backing. The resultant carpet was then subjected to dyeing in a dye bath containing (all percentages are expressed on weight of fiber):

	Percent
Latyl Yellow 4RL (a disperse dye)	0.5
Neolan Brown GR (an acid pre-metallized dye)	1.5
20 Formic Acid	3
Triton X-100	1

As a result, the first ply, made of pigmented polypropylene, became a yellowish shade of beige, the second ply, made of the polymeric mixture but not subjected to activation, was dyed to a rich shade of gold, and the third ply, made of the polymeric composition and subjected to the acid activation treatment, was dyed to a deep brown. The carpet gave the appearance of a combination of these shades. Although the hue of the first ply was altered slightly by the disperse dye in the dye bath, it must nevertheless be considered to have been left substantially undyed by both the disperse and the acid-type dyes.

Example 8

A carpet backing was tufted alternately with ends of each of the three following types of yarns:

(a) A 3500 denier, 210 filament textured yarn extruded from a polypropylene melt which contained a light beige pigment.

(b) A 3500 denier, 210 filament textured yarn extruded from a polymeric composition comprising 97% polypropylene and 3% of a copolymer prepared from 50 parts by weight of 2-methyl-5-vinylpyridine and 50 parts by weight of 2-vinylpyridine.

(c) A 3500 denier, 210 filament yarn extruded from the same polymeric composition as that in (b) above and subsequently subjected to the same activation treatment with SO_2 as that described in Example 2. This carpet was piece-dyed with a dye solution having the following composition (all percentages are on weight of fiber):

	Percent
55 Terasil Orange 3RL (a disperse dye)	1.0
Neolan Red BRE (an acid-metallized dye)	0.5
Formic Acid	3
Triton X-100	1

After dyeing, the ends of yarn (a) were yellowish beige, the ends of yarn B were light orange and the ends of yarn C were red orange.

Example 9

A circular knit fabric was prepared by knitting a three inch wide strip of yarn (a) as described in Example 8, followed by a three inch wide strip of yarn (b) of Example 8, followed by a three inch wide strip of yarn (c) of Example 8. This fabric was piece dyed in the following dye bath (all percentages are on weight of fiber):

	Percent
65 Latyl Yellow 4RL (a disperse dye)	1.5
Dimacide Blue JL (a strong acid dye)	0.3
Formic Acid	3
75 Triton X-100	1

11

After dyeing, the section knitted with type A yarn was yellowish beige, the section knitted with type B yarn was gold and the section knitted with type C yarn was green.

Although a slight hue was imparted to the beige pigmented polypropylene yarn by the disperse dye used in each of Examples 7, 8 and 9, each of these yarns must be considered to be substantially undyed by both the disperse and the acid-type dye used.

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

1. A fabric suitable for dyeing in the piece to a multi-color pattern through exposure to a mixture of acid type dyes and other types of dyes, said fabric containing a plurality of synthetic yarns, all of which are formed from a polymeric mixture comprising at least 90% of a polyolefin or polyester which is inert to acid type dyes, and up to 10% of a thermoplastic highly polar basic nitrogen-containing polymer, said polymeric mixture being substantially undyeable by said acid type dyes but dyeable by said other types of dyes, at least one, but less than all of said yarns having been rendered, subsequent to forming, dyeable with acid type dyes by an infusion with an acidic reagent which reacts with some of the polar groups of said basic polymer to form a reaction product capable of fixing acid type dyes.

2. A fabric suitable for dyeing in the piece to a multi-color pattern through exposure to acid and disperse dyes, said fabric containing a plurality of synthetic yarns extruded from a polymeric mixture comprising from 90 to 99.5% of an alpha-olefin polymer and from 10 to 0.5% of a thermoplastic highly polar basic nitrogenous polymer, said polymeric mixture being substantially undyeable by acid type dyes but dyeable by said disperse dyes, at least one but less than all of said yarns having been rendered dyeable with acid type dyes by an infusion with an acidic reagent which reacts with some of the polar groups of said basic polymer to form a reaction product capable of fixing acid type dyes, such infusion occurring after extrusion but before assembly of said yarns into said fabric.

3. A fabric suitable for dyeing in the piece to a multi-color pattern through exposure to acid type and disperse dyes, said fabric containing a plurality of classes of synthetic yarns extruded from a polymeric mixture comprising from 90 to 99.5% of a polyester high polymer and from 10 to 0.5% of a highly polar thermoplastic basic nitrogenous polymer, said polymeric mixture being substantially undyeable by acid type dyes but dyeable by said disperse dyes, at least one but less than all of said yarns having been rendered dyeable with acid type dyes by an infusion with an acidic reagent which reacts with some of the polar groups of said basic polymer to form a reaction product capable of fixing acid type dyes, such infusion occurring after extrusion but before assembly of said yarns into said fabric.

4. A fabric suitable for dyeing in the piece to a multi-color pattern through exposure to a mixture of acid type and disperse dyes in a single dyeing step, said fabric containing a plurality of synthetic yarns extruded from a polymeric mixture comprising from 90% to 99.5% of an alpha olefin polymer which is predominantly isotactic polypropylene and, correspondingly, from 10 to 0.5% of a thermoplastic highly polar basic nitrogen-containing polymer selected from the class consisting of polymers of at least one vinylpyridine compound, polymeric amines or polymeric amides, said polymeric mixture being substantially undyeable by acid type dyes but dyeable by said disperse dyes, at least one but less than all of said yarns having been rendered dyeable with acid type dyes by an infusion with an acidic reagent which reacts with said basic polymer to form a reaction product capable of fixing acid type dyes, said infusion occurring after extrusion but before assembly of said yarns into said fabric.

12

5. The fabric of claim 4 wherein said acidic reagent is selected from the group of acidic reagents consisting of

- (I) mineral acids,
- (II) anhydrous acid gases of said mineral acids,
- (III) organo-carboxylic acids,
- (IV) halides which liberate hydrohalic acid on contact with water,
- (V) boron trifluoride,
- (VI) borate esters, and
- (VII) phenol.

6. A fabric suitable for dyeing in the piece to a multi-color pattern through exposure to acid type and other types of dyes, said fabric containing a plurality of synthetic high polymer yarns, said high polymer comprising a blend of at least 90% of a polyolefin or polyester inert to acid type dyes and up to 10% of a highly polar thermoplastic basic nitrogen-containing polymer, some of the highly polar groups in said basic nitrogen polymer of at least one but less than all of said yarns having been reacted with an acidic reagent infused therein to form a reaction product capable of fixing acid type dyes.

7. A fabric suitable for dyeing in the piece to a multi-color pattern through exposure to acid type and disperse dyes, said fabric containing a plurality of synthetic high polymer yarns, said high polymer comprising a mixture of from 90 to 99.5% of an alpha olefin polymer which is predominantly isotactic polypropylene and from 10 to 0.5% of a thermoplastic highly polar basic nitrogenous polymer selected from the class consisting of polymers of at least one vinylpyridine compound, polymeric amines and polymeric amides, some of the highly polar groups in said basic nitrogen polymer of at least one but less than all of said yarns having been reacted with an acidic reagent infused therein to form a reaction product capable of fixing acid type dyes.

8. A fabric suitable for dyeing in the piece to a multi-color pattern through exposure to a mixture of acid type and disperse dyes in a single dyeing step, said fabric containing yarns formed from a polymeric mixture of from 90 to 99.5% of an alpha olefin polymer which is predominantly isotactic polypropylene and, correspondingly from 10 to 0.5% of a thermoplastic highly polar basic nitrogenous polymer selected from the class consisting of polymers of at least one vinylpyridine compound, polymeric amines and polymeric amides, some of the polar groups of the nitrogenous polymer of at least one but less than all of said yarns having been reacted with an acidic reagent infused therein to form a reaction product capable of fixing acid type dyes.

9. The fabric of claim 3 wherein said acidic reagent is selected from the group of acidic reagents consisting of

- (I) mineral acids,
- (II) anhydrous acid gases of said mineral acids,
- (III) organo-carboxylic acids,
- (IV) halides which liberate hydrohalic acid on contact with water,
- (V) boron trifluoride,
- (VI) borate esters, and
- (VII) phenol.

10. A synthetic carpet pile suitable for dyeing in the piece to a multi-color pattern through exposure to acid type and other types of dyes, said pile comprising a plurality of synthetic high polymer yarns, said high polymer comprising a blend of at least 90% of a polyolefin or polyester which are substantially undyeable by acid type dyes and up to 10% of a highly polar thermoplastic basic nitrogen-containing polymer, some of said highly polar groups of said nitrogen-containing polymer of at least one but less than all of said yarns having been reacted with an acidic reagent infused therein to form a reaction product capable of fixing acid type dyes.

11. A synthetic carpet pile suitable for dyeing in the piece to a multi-color pattern through exposure to acid

type and disperse dyes, said pile comprising a plurality of synthetic high polymer yarns, said high polymer comprising a blend of from 90 to 99.5% of an alpha olefin polymer which is predominantly isotactic polypropylene and from 10 to 0.5% of a thermoplastic highly polar basic nitrogen-containing polymer selected from the class consisting of polymers of at least one vinylpyridine compound, polymeric amides or polymeric amines, some of said highly polar groups of said nitrogen-containing polymer of at least one but less than all of said yarns having been reacted with an acidic reagent infused therein to form a reaction product capable of fixing acid type dyes.

12. A synthetic carpet pile suitable for dyeing in the piece to a multi-color pattern through exposure to acid type and disperse dyes, said pile comprising a plurality of synthetic high polymer yarns, said high polymer comprising a blend of from 90 to 99.5% of a polyester which is predominantly poly(ethylene terephthalate) and from 10 to 0.5% of a thermoplastic highly polar basic nitrogen-containing polymer selected from the class consisting of polymers of at least one vinylpyridine compound, polymeric amides or polymeric amines, some of said highly polar groups of said nitrogen-containing polymer of at least one but less than all of said yarns having been reacted with an acidic reagent infused therein to form a reaction product capable of fixing acid type dyes.

13. A carpet pile suitable for dyeing in the piece to a multi-color pattern through exposure to a mixture of acid type and disperse dyes in a single dyeing step, said pile comprising a plurality of synthetic yarn extruded from a polymeric composition comprising a mixture of from 90 to 99.5% of a hydrocarbon high polymer which is predominantly isotactic polypropylene and, correspondingly from 10 to 0.5% of a thermoplastic highly polar basic nitrogen-containing polymer selected from the class consisting of polymers of at least one vinylpyridine compound, polymeric amines or polymeric amides, at least one but less than all of said yarns having been rendered dyeable with acid type dyes by infusing therein an acidic reagent capable of reacting with some of the polar groups in said nitrogen-containing polymer to form a reaction product capable of fixing acid type dyes, said treatment occurring after extrusion but before assembly of said yarns into said fabric.

14. The carpet pile of claim 13 wherein said acidic reagent is selected from the group consisting of

- (I) mineral acids,
- (II) anhydrous acid gases of said mineral acids,
- (III) organo-carboxylic acids,
- (IV) halides which liberate hydrohalic acid on contact with water,
- (V) boron trifluoride,
- (VI) borate esters, and
- (VII) phenol.

15. A textile article suitable for dyeing in the piece to a multi-color pattern through exposure to acid type and disperse type dyes, said fabric containing a plurality of synthetic yarns extruded from polymeric compositions comprising at least 90% of a polyolefin or polyester polymer which are substantially undyeable by said acid and said disperse dyes, at least one but less than all of said yarns being substantially undyeable by said acid type dyes and said disperse type dyes, and at least another two of said yarns being extruded from polymeric compositions comprising, in addition to said polyolefin or polyester polymer, from 10 to 0.5% of a thermoplastic highly polar basic nitrogenous polymer, the last-mentioned said compositions being substantially undyeable by acid type dyes but substantially dyeable by disperse dyes, the yarns of at least one but less than all of the last-mentioned said yarns having been rendered dyeable with acid dyes by infusing therein an acidic reagent capable of reacting with the polar groups in said nitrogenous polymer to form a reaction product capable of fixing acid type dyes, such

treatment occurring after extrusion but before assembly of said yarns into said textile article.

16. The textile article of claim 15 wherein the yarn of at least one of the yarn classes substantially undyeable by said acid type and said disperse dyes is pigmented prior to assembly of said yarns into said textile article.

17. The process of assembling a textile article suitable for dyeing in the piece to a multi-color pattern through exposure to a plurality of types of dyes comprising infusing synthetic high polymer yarns formed from a polymeric composition comprising a mixture of at least 90% of a polyolefin or polyester inert to acid type dyes and up to 10% of thermoplastic highly polar basic nitrogen-containing polymer with an acidic reagent capable of reacting with the polar groups of nitrogen-containing polymer after said yarns are formed and combining these yarns with other yarns formed from a polymeric composition comprising at least 90% of a polyolefin or polyester inert to acid type dyes and up to 10% of a highly polar basic nitrogen polymer but not so infused into said fabric.

18. The process of producing a textile article suitable for dyeing to a multi-color pattern by exposure to a mixture of acid type and disperse dyes in a single dyeing step, comprising forming synthetic yarns from a polymeric mixture comprising from 90% to 99.5% of a hydrocarbon high polymer which is predominantly isotactic polypropylene and, correspondingly from 10 to 0.5% of a thermoplastic highly polar basic nitrogen-containing polymer selected from the class consisting of polymers of at least one vinyl pyridine compound, polymeric amines or polymeric amides, dividing the yarns thus formed into classes, and infusing at least one but less than all of said classes of yarns with an acidic reagent capable of reacting with the polar groups of said nitrogen-containing polymer and combining yarns from classes so treated with yarns from classes not so treated into said textile article, whereby those portions of said textile article containing the yarn so treated will be dyeable by acid type as well as disperse dyes but portions of the textile article containing yarn from the classes not so treated will be dyeable only by said disperse dyes.

19. The process of claim 18 wherein said acidic reagent is selected from the group of acidic reagents consisting of

- (I) mineral acids,
- (II) anhydrous acid gases of said mineral acids,
- (III) organo-carboxylic acids,
- (IV) halides which liberate hydrohalic acid on contact with water,
- (V) boron trifluoride,
- (VI) borate esters, and
- (VII) phenol.

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