Title: PROCESS FOR DYEING POLYAMIDE SUBSTRATES

Abstract

This invention is a method for dyeing polyamides with water soluble, reactive dyes having the reactive substituent (SO₂-Z), wherein "Z" is a fiber reactive group. At least one fiber reactive dye is applied to the polyamide substrate at an acid pH and the dyed substrate is then heated with an alkaline compound and heat to covalent bond the dye to the substrate. The covalently dyed polyamide has superior fastness and overdye properties over polyamide substrates that have been dyed using acid dyes.
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Description

PROCESS FOR DYEING POLYAMIDE SUBSTRATES

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. PatentApplications Serial Nos. 626,807 filed December 13, 1990, and 667,726 filed March 11, 1991; now _________.

FIELD OF THE INVENTION

This invention is directed to the dyeing of polyamide fibers.

BACKGROUND OF THE INVENTION

The dyeing of natural fibers to impart color and styling effects to textile substrates can be traced back to the earliest dates of recorded history. A multitude of natural and synthetic dyes have been developed to accomplish such effects over the years and have been applied to synthetic fibers. One important class of such synthetic dyes are the fiber reactive dyes containing the vinyl sulfone substituent or its chemically reactive analog e.g. the sulfatoethyl sulfonyl substituent. These fiber reactive dyes, hereinafter called vinyl sulfone dyes are capable of forming covalent bonds between the dye molecule and the textile substrate.

The vinyl sulfone dyes are described in the patent, literature as being useful in dyeing practically all known natural and synthetic textile substrates. However, the main commercial application of such dyes has been in the dyeing of cotton. Since the early 1950's, it has been taught that vinyl sulfone type and other reactive dyes can
dye wool and nylon to provide high wash and wet fastness properties see e.g. U.S. Patent No. 3,223,470 to Boedeker et al.

U.S. Patent 3,118,723 discloses dyeing nylon with dyestuff containing at least 2 sulfonic acid groups and 0 to 3 reactive groups (vinyl sulfone or cyanuric chloride groups) in the presence of a condensation product of an "aldone" (aldehydic or ketonic carbonyl compound) and an aryl sulfonic acid to produce a random multi-colored dyeing.

The review article entitled 20 Years of Hoechst Reactive Dyes on Wool, H. U. von der Eltz, Texilveredlung 7 (1972) No 5, 297 discusses the use of fiber reactive dyes in dyeing wool. Similarly, U.S. Patent Nos. 3,802,837 and 4,762,524 disclose the use of the addition products of vinyl sulfone dyes and secondary amines as dyes for wool and synthetic polyamides. These adducts are commercially available under the trademark Hostalan® (Hostalan® is a registered trademark of Hoechst AG, Frankfurt, Germany).

In the referenced review article, the author reports an earlier process for using vinyl sulfone dyes in the coloring of polyamides. In this process, the substrate is introduced into an acidic, aqueous bath to which a previnylized vinyl sulfone dye is added. After holding the acidic bath for a predetermined time, the substrate is treated in an alkaline bath. The review author reports that unlevel dyeing result from this process.

Generally, fiber reactive vinyl sulfone dyes have not
been widely used in dyeing wool and synthetic polyamides because they lack substantivity at high pH values (i.e. 7 or above) where their maximum reactivity is present and because they tend to produce uneven dyeings at such pH values. At present, vinyl sulfone dyes (Hostalan® Dyes) are recommended for use on wool and nylon in straight shades (monochromatic dyeing) or in heavy shades. It is also generally recommended that such dyeings be given a short afterwash with ammonia to improve their wash fastness by stripping unfixed dye.

This invention is directed to the use of vinyl sulfone dyes in the dyeing of polyamides, particularly in multi-colored nylon dyeings. The invention provides a process for producing level polyamide dyeing having superior fastness and overdyed properties.

SUMMARY OF THE INVENTION

This invention comprises a method for dyeing polyamide fibers using vinyl sulfone fiber reactive dyes. Dyeings having superior wet fastness, overdyed fastness and laundry fastness properties are obtained.

The process of the invention may be used to dye natural and synthetic polyamide substrates in the form of fibers such as yarn, stock, knit, carpet or other fabric substrates by either exhaust or continuous dyeing processes.

The essential elements of the invention comprise contacting the polyamide substrate with at least one vinyl
sulfone dye in an aqueous medium at an acidic pH from about 1.5 to about 5. The dyeing is held at this acidic pH for an effective amount of time and temperature to allow the vinyl sulfone dye to migrate into the polyamide substrate; e.g. using an exhaust process, 15 minutes at the boil. The pH of the dyeing is then raised to about 8 to about 12 by the addition of base and heated for an effective amount of time and temperature to covalently bond the vinyl sulfone dye to the polyamide substrate; e.g. using an exhaust process 30-45 minutes at the boil.

The vinyl sulfone fiber reactive dyes useful in the invention are known in the textile art. They may be represented by the general formula: \((\text{SO}_3\text{M})_n\text{--D--(SO}_2\text{--Z})_m\) wherein "M" represents hydrogen and water soluble metal atoms, "D" represents a dye chromophore, "Z" represents a fiber reactive moiety and "m" and "n" represent integers of 1-4 and 1-3 respectively. Optionally, one of the moieties -(SO\text{2}-Z) may be replaced by another fiber reactive group such as a mono- or di-halogen-s-triazine.

The covalently bonded dye chromophore produces a dyed polyamide substrate with superior wet fastness, laundry fastness and overdye fastness. Dyeings of the invention may be treated with an anionic resist compound such as the condensation polymer of formaldehyde and an aryl sulfonic acid or salt thereof to prevent stripping and redeposition of the vinyl sulfone dye in subsequent overdyeing or laundering operations.

Illustrative applications of the invention are dyed
entrance carpets which must withstand repeated exposures to water and repeated laundering. Similarly, yarn dyed according to the invention may be tufted into carpeting with grieg yarn and overdyed to achieve a multitude of stylized color effects. Alternately, a substrate may be printed with a pattern of at least one vinyl sulfone dye under acid conditions, treated with base and heat to covalently fix the dye and then overdyed with a standard acid dye such as a level dyeing monosulfonated acid dye to produce a multi-colored polyamide substrate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention is a process for dyeing polyamides to provide superior wet fastness, wash fastness and overdye properties. Polyamides useful in the practice of the invention include both the natural and synthetic fiber-forming polyamides. Examples of such polyamides are wool, silk, nylon-6, nylon-6,6, nylon-11, nylon-12, nylon-6/6,6, nylon-6,12 etc. Particularly preferred polyamides are wool, nylon-6, nylon-6,6 and nylon 6/6,6 copolymers and blends of such synthetic polyamides. The invention is most particularly useful in dyeing of nylon-6 and nylon-6,6. Polyamide substrates dyed in accordance with the invention may be combined with other polyamide substrates or other substrates such as polyurethane, polypropylene, polyethylene, polyester, rayon, wool, silk, etc.

The process of the invention may be used to dye polyamide substrates in the form of yarns, fibers, knit
goods, fabric, stock, carpets etc. Additionally, the process of the invention may be practiced by exhaust and continuous dyeing methods.

The process of the invention comprises:

(a) treating the polyamide substrate with an aqueous dispersion of one or more fiber-reactive, vinyl sulfone dyes at an acid pH;
(b) heating for an effective amount of time and temperature to allow the vinyl sulfone dye to penetrate into the polyamide substrate;
(c) increasing the pH of the dyeing to a pH of about 8 to 12 by contacting the polyamide substrate with an alkaline or basic substance; and
(d) heating the dyed polyamide substrate for an effective amount of time and at an effective temperature to covalently bond the fiber reactive vinyl sulfone dye to the polyamide substrate.

The dyed polyamide may be optionally treated with an anionic, water soluble, fiber-substantive resist chemical in about 1 to about 5 percent (owf - on weight of fiber) to provide a dyed polyamide substrate having superior wet and wash fastness properties as well as superior overdye properties. Overdyeing as used in this description means that a subsequent dyeing is effected after the vinyl sulfone dyed polyamide is incorporated into another article; e.g. vinyl sulfone dyed polyamide yarn is tufted into a carpet with griegre yarn which is then dyed. The vinyl sulfone dyed substrates made in accordance with the
invention exhibit superior resistance to stripping and redeposition on the griege yarn.

The fiber-reactive, vinyl sulfone type dyes useful in the practice of the invention are known. The main use of such fiber-reactive, vinyl sulfone type dyes has been in the dyeing of cotton. However, U.S. Patent No. 3,602,837 and 4,762,524 teach their use in the dyeing of polyamides. These prior art references teach to use the vinyl sulfone dye as a reaction product with a substituted, secondary aliphatic amine such as n-methyltaurine.

The following patents illustrate that the vinyl sulfone type dyes are known in the art:

U.S. Patent No. 4,336,190 (formazon);
U.S. Patent No. 4,492,654 (disazo);
U.S. Patent No. 4,046,754 (monoazo);
U.S. Patent No. 4,577,015 (dioxazine);
U.S. Patent No. 3,359,286; 4,049,656 (anthraquinone);
U.S. Patent No. 3,268,548 (phthalocyanine);
U.S. Patent No. 3,385,843 (pyrazolone); and

The teachings of the above cited patents are hereby incorporated by reference.

Suitable dyes of the vinyl sulfone type are represented by the following general formula:

\[(SO_3M)_n-D-(SO_2-Z)_n\]

In the above formula, "D" represents a dye chromophore selected from the anthraquinone, dioxazine, formazon,
phthalocyanine, mono- and disazo series and their metal complexes wherein the metal is selected from copper, chromium, iron, cobalt and nickel; preferably copper or nickel. Particularly preferred are those chromophores of the formazone series, the mono- and disazo series and their metal complexes. "Z" represents the fiber reactive group: \(-\text{CH}_2\text{-CH}_2\text{-Y}\) wherein "Y" is a substituent capable of being split off by an alkaline reagent: e.g., chlorine, bromine, thiosulfate, sulfato, phosphato, a carboxylic acyloxy of one to four carbon; or by an acidic reagent: e.g., dimethylamino, diethylamino, N-alkyl (C₁ to C₄) acids. The sulfato group is most preferred. The term "n" represents an integer from 1 to 3; preferably 2-3 and most preferably 2. The term "m" represents an integer from 1 to 4, preferably 1 to 3 and most preferably 1 to 2. The term "M" represents hydrogen and the water soluble metals; e.g. sodium, potassium, lithium or calcium; preferably sodium. The dye chromophore may contain in addition to the vinyl sulfone group an additional fiber reactive groups: e.g. a mono- or di-halogen-s-triazine, a mono cyanamido-s-triazine, a mono-, di- or tri- halogen pyrimidine, a mono or dichloroquinoxaline, a dichlorophthalazine, a dichloropyridazine or the bromine or fluorine derivatives thereof. Of course, the vinyl sulfone dyes may be employed in their water soluble salt form e.g. as sodium, potassium and lithium salts. One particularly preferred class of vinyl sulfone dyes are termed mixed anchor dyes: i.e. a vinyl sulfone group and a mono-, or di-halogen-s-triazine
group.

Not all fiber reactive, vinyl sulfone dyes can be effectively used in the practice of the invention. It has been found that the number of solubilizing groups does not appear to have a significant affect in the process beyond the normal wet fastness, solubility and substantivity properties that a comparable acid dye would have. In continuous dyeing processes, a vinyl sulfone dye having at least two fiber reactive groups perform best. In continuous dyeing processes, dyes with a single fiber reactive group provides improved wet fastness but they do not appear to be particularly suited to use in the continuous processes.

In exhaust dyeing processes, a vinyl sulfone dye having only one fiber reactive group will work in the process of the invention. However, fiber reactive, vinyl sulfone dyes with at least two fiber reactive groups are still preferred.

It is believed, without being bound to any particular theory, that the greater number of available reactive groups, increases the odds of forming a covalent bond with the terminal amine groups on the polyamide substrate within the constraints of normal processing times found in continuous applications. Whereas, in exhaust processes, the fixation cycle is 5 to 10 times longer thus allowing greater opportunity for forming covalent bonds. The preferred fiber reactive vinyl sulfone dyes useful in the invention are those with two or more fiber reactive groups,
e.g. two vinyl sulfone groups (-SO₂-Z), a vinyl sulfone and a monochloro-s-triazine or two vinyl sulfone groups and a monochlorotriazine group etc. Additional illustrative fiber reactive groups are the triazine, pyrimide, haloquinoxaline, or halophthalazine types previously described; most preferred are the monochloro-s-triazines.

The selection of the vinyl sulfone dye or dyes may be determined by simple experimentation within the above parameters. The addition of auxiliary agents such as ethoxylated aliphatic amines; may be added to the dye mixture to compatibilize the strike rates of the dyes. Various cationic leveling agents can be employed depending on the dyeing conditions. The amounts used can be from 2.0 to 6.0 g/l of a 30% active tallow amine with 15 moles of ethylene oxide, or a 30% active tallow diamine with 105 moles ethylene oxide, or a tallow diamine with 28 moles ethylene oxide that has been quaternized. Sequesterants such as ethylenediamine tetra-acetic acid and nitrilotriacetic acid should not be used. In the covalent bonding fixing step, no auxiliary chemicals (other than water or steam) are required only an alkaline reagent such as trisodium phosphate.

In order to maximize the affinity and build-up of the vinyl sulfone dyes in a continuous process, the application pH should be between 1.5 - 4.0, with 2.0 to 2.5 being preferred. Sulfamic acid (1-4 g/l) has been found to be the best pH control agent. Commercially available acid buffers give inconsistent results. When covalently fixing
the dyes, the pH should be between 8-12. Alkaline reagents useful in the practice of the invention are well known in the art. They are those substances capable of converting the sulfonyl moiety to its fiber reactive form, i.e. \(-\text{SO}_2\text{-CH}_2\text{-CH}_2\). Alkali metal salts and hydroxide such as trisodium phosphate or soda ash or potassium phosphate, potash ash, caustic etc. can be used in amounts between 10 - 50 g/l. ammonia is not useful for this purpose. It is known in the art that ammonia will strip an unfixed vinyl sulfone dye from the textile substrate. In exhaust dyeing situations, the dyebath containing vinyl sulfone dyes should be at pH 3.0 - 5.0 at the beginning of the cycle and held there until the bath has reached the boil for 15 minutes. At this point the pH is raised to the alkaline side and the bath is boiled an additional 30-45 minutes. In continuous or print applications, the vinyl sulfone dye should be steamed on the acid side for 6 - 10 minutes and on the alkaline side for 4 - 8 min. For good results using thermofixing methods, the dyed substrate must be above 300°F for 30 seconds to 30 minutes. Alternatively, fixing may be achieved using saturated steam at temperatures as low as 270°F with dwell times as little as 45-65 seconds when the substrate used is yarn. The proper time and temperature to effect fixation of the vinyl sulfone dye by covalent bonding will depend on the process (exhaust or continuous), the equipment employed and the amount of moisture present. It that been found that water accelerates the fixing process of high and shorter as
evidenced by the achievement of high fixation at lower temperatures and shorter treatment time when the process is conducted in the presence of water versus the use of dry heat alone. Appropriate conditions for the process and equipment can be determined by simple experimentation and will be apparent to the worker in the field.

It will be readily apparent that when the invention is carried by the continuous method, many process variations can be employed to effect fixation of the vinyl sulfone. Exemplary fixing processes follow. In all cases, the vinyl sulfone dye is applied by continuous means (padding, printing, flooding, spraying etc.) at low pH and then steamed for about 5 - 8 minutes, preferably about 6 minutes.

In the first example, the vinyl sulfone dyed polyamide is washed and then passed through a washbox containing an alkaline solution. The substrate is then dried with heat and partial covalent bonding occurs. The substrate can be then given an additional heat treatment to complete the covalent fixing process. If the substrate is yarn, then subsequent twist-heat setting operations such as autoclaving, Suessen setting or Superba setting will thermofix the dye giving almost complete covalent bonding. Superba setting accomplishes thermofixing with saturated steam at temperatures as low as 270°F and dwell times between 45-65 seconds. Suessen thermofixing uses dry heat at temperatures above 390°F and dwell times of 55-65 seconds. Autoclaving, although technically a batch
process, uses saturated steam at a temperature up to 280°F using alternating cycles of 12-18 minutes. Alternatively after the alkali is applied the substrate may be simply steamed for 6 - 8 minutes. A third variation is to give the substrate a short steaming cycle after alkali application and dried in the normal manner. The dried substrate can then be heated to 300 - 340°F for 15 - 20 minutes to complete the fixing step; e.g. when a washable rug is made, the dyed carpet is bonded to a rubber or vinyl backing at 320°F for 15 - 20 minutes. These methods as well as many others will be readily apparent to the skilled worker.

When greige carpet containing vinyl sulfone dyed yarn is overdyed by either exhaust or continuous process, the normal dyebath chemicals employed in dyeing monosulfonated acid dyes can be used such as sodium dodecyl diphenyloxide disulfonate. If there is some unreacted vinyl sulfone dyes present during an overdye cycle, the addition of 1 - 5 % owf of a anionic chemical will prevent stripping and redeposition on the greige resist carpet and the same also holds true in laundering operations. The results achieved by the addition of anionic resist is not readily explained since they are normally applied at pH's of 2.0 - 4.5 and in the above cases the bath pH's are between about 6.0 and about 10.0., e.g. acid dyes are normally applied from about pH 6.0 to about 7.5 and in laundering the pH is normally between about 7.0 to about 10.0.

The anionic, water-soluble, fiber-substantive resist
chemicals useful in the invention include sulfonated phenol-aldehyde condensation products, a sulfonated naphthol condensation product, polymethacrylic acid polymers, acrylic acid polymers, copolymers of acrylic acid or methacrylic acid with ethylenically unsaturated comonomers, the polymerization reaction product of an alpha-substituted acrylic acid or ester prepared in the presence of one of the above described sulfonation condensation products, the water soluble salts of said condensation products and said polymerization products and mixtures thereof. The anionic, water-soluble, fiber substantive resist chemical useful in the invention contain \(-\text{SO}_3\text{X}\) and \(-\text{COOX}\) substituents wherein \(\text{X}\) is hydrogen or a cation of the alkali earth metals e.g. sodium, potassium, lithium, or an ammonium ion. The resist chemicals useful in this invention are characterized in that they may be applied in combination with an acid or direct dye and the acid or direct dye may be fixed to the fiber area.

The following U.S. Patents describe the preparation of anionic resist compounds useful in the practice of this invention: U.S. 3,293,214; U.S. 3,663,157, U.S. 3,790,344; U.S. 4,592,940; U.S. 4,619,853; U.S. 4,680,212; U.S. 4,839,212; U.S. 4,879,180; U.S. 4,822,373; U.S. 4,937,123 and U.S. 4,940,757; the teaching of which are hereby incorporated by reference.

Illustrative anionic resist compounds and their preparation are described for example in U.S. Patent No. 4,592,940 (col 3 & 4) which is incorporated herein by
reference. This patent discloses mixed condensation compounds prepared from formaldehyde and a mixture of diphenolsulfone, diphenolsulfone sulfonic acid, phenolsulfonic acid and salts thereof wherein at least 40 percent of the monomeric units contain a sulfonic acid (or salt) radical (-SO₃X) and at least 40 percent of the units contain the -SO₂⁻ radical. In the formula SO₃X, X is hydrogen or a cation. Other useful anionic resists are mixed condensation products of naphthalene monosulfonic acid with diphenylsulfone and formaldehyde.

The preparation of anionic resist chemicals from methacrylic acid and copolymers thereof is described in U.S. Patent 4,937,123, Column 3 and 4 thereof and the Examples of said patent, the teaching thereof are incorporated herein by reference.

The preparation of anionic resist chemicals prepared by polymerizing an alpha substituted acrylic acid or ester in the presence of a sulfonated aromatic - aldehyde condensation polymer is described in U.S. Patent 4,940,757 at Column 3-6 thereof and the Examples of said patent; the teachings thereof are hereby incorporated by reference.

Illustrative commercially available anionic resist are Erional®PA and Erional®NW from Ciba Geigy; Intratex®N from Crompton and Knowles, Stainfree® from Sybron and Karafix®NA from Lyndal. These resists are sulfonated condensation products of aldehydes and phenols or naphthols and they are the preferred type of anionic resist chemical for the practice of the invention. Another anionic resist
commercially available is 3M Company's stainblocker FX 661, a mixed sulfonated condensation product of a phenol and aldehyde with a methacrylic polymer. Leukotan® 970, 1027, 1028 and QR 1083 from Rohm and Haas Co. are examples of commercially available methacrylic polymer anionic resist chemicals. These chemicals are used presently in the textile dyeing industry as stainblockers, leveling agents and wet fastness additives.

The acid dyes which can be used in this invention to overdye substrates containing vinyl sulfone dyed substrate are those dyes containing one or more anionic functional groups. The acid dyes useful in the practice of the invention are classified in the "Color Index" under the classifications "Acid" and "Direct". "Mordant" dyes and "Reactive" dyes under the "Color Index" classification are not within the scope of the term acid dyes as used in this disclosure, nor are those dyes having fiber reactive substituents. Acid dyes have large molecules containing one or more functional sulfonic or carboxylic acid salt groups. Direct dyes are a special class of dyes which have a long, narrow, flat molecule and one or more carboxylic or sulfonic acid salt functional groups which allow these dyes to function in the same manner as an "Acid" dyes. The "acid" dyes useful in the invention are termed "anionic dyes" in U.S. Patent 4,218,217 and described at Column 4, lines 29-59 thereof; the disclosure thereof is hereby incorporated by reference.

The preferred acid dyes useful in the invention are
the monosulfated acid dyes and 2:1 metal complexed acid dyes (2 moles of acid dye to 1 mole of metal).

Conventional methods of applying dyes to a substrate can be used in producing multi-colored dyeing by overdyeing according to the invention. These methods of application include padding, printing, spraying, dropping etc. Illustrative machines or apparatus known in the art for application of dyes and useful in the practice of the invention are rotary screen printers, TAK machines, jet printers, pad rolls, spray nozzles etc. The application methods vary widely in continuous dyeing depending upon the type and placement of application equipment on the line and are obvious to the skilled artisan. Similarly, various exhaust dyeing methods can be used to apply the overdye; e.g. skein, beck, jig, beam, stock kettle, package machine etc.

The vinyl sulfone dyes used in the following examples are illustrative of the vinyl sulfone dyes that may be used in this invention. The structures of these dyes are shown in Table 1 in their free acid form wherein the dyes are designated Yellow 1, Yellow 2, Yellow 3, Red 1, Blue 1, Blue 2, Orange 1 and Black 1 for reference purposes.

The acid dyes used in the following examples are acid dyes and are referenced by their Color Index (CI) number. Illustrative dyes useful in the invention are Acid Yellow 49, Acid Yellow 151 (2:1 premetallized), Acid Blue 277, Acid Orange 156, Acid Red 266, Acid Red 337, Acid Red 361, Acid Blue 277, Acid Blue 324, Acid Blue 158 (a pre-
metallized acid dye) Acid Blue 78, Direct Red 185, and Acid Orange 156.
TABLE 1

VINYL SULFONE DYES

YELLOW 1

YELLOW 2

YELLOW 3

RED 1

SUBSTITUTE SHEET
TABLE 1

VINYL SULFONE DYES

**ORANGE I**

![Orange I Structure](image)

**BLACK 1**

![Black 1 Structure](image)

**BLUE 1**

![Blue 1 Structure](image)

**BLUE 2**

![Blue 2 Structure](image)
The following examples illustrate the invention:

**EXAMPLE 1**

A 20 gram piece of nylon 6 carpet was dyed in an aqueous dye bath containing:

- 0.60 % owf Yellow 2 (owf = on weight of fabric)
- 0.30 % owf Red 1
- 0.10 % owf Blue 2
- 1.00 % owf Remol® GES (cationic leveling agent)

*Remol® is a registered trademark of Hoechst A.G., Frankfurt, Germany.*

The bath was set at a pH of 3 at 80°F. The bath was raised at a rate of 3°F/minute until it reached the boil. After boiling for 15 minutes, trisodium phosphate was added to attain a pH of 12 and boiling continued for another 45 minutes. The bath was dropped and the carpet was rinsed in cold water and dried. The dyeing was a rust color which was uniform in shade throughout.

To determine if all the vinyl sulfone dyes were covalently bonded to the nylon a test dyebath was prepared using:

- 1.00 % owf sodium dodecyl diphenyloxide disulfonate (SDDDD)
- xx % owf monosodium phosphate and trisodium phosphate to a pH of 7.0

A 10 g swatch of dyed carpet was placed in the dyebath along with 10 g of greige carpet. A dye cycle was run for 30 minutes at the boil, after which the pieces were
removed, rinsed, and dried.

There was no apparent change in the dyed piece of carpet after being subjected to the test dye cycle. The greige piece was dyed very slightly to a pale cream shade, equivalent to a 3 on the AATCC Grey Scale for evaluating staining.

EXAMPLE 2

A 20 gram piece of nylon 6 carpet was dyed with the formula:

0.30 % owf Yellow 2
0.10 % owf Red 1
0.60 % owf Blue 2
1.00 % owf Sandogen® NH - Sandoz (cationic leveling agent)

[Sandogen® is a registered trademark of Sandoz Ltd., Basel, Switzerland.]

The bath was set at a pH of 3 at 80°F and then the same dyeing cycle as used in Example 1 was followed. The resultant shade was greyish blue which was uniform in shade throughout.

As in Example 1, a dye cycle was run in a test bath containing dyed and undyed carpet. There was no apparent change in the dyed piece of carpet and the greige piece was dyed a pale blue shade, equivalent to a 3 on the AATCC Grey Scale for evaluating staining.

Another test dye bath was prepared with:

1.0 % owf SDDD
1.0 % owf anionic resist chemical (HT-3908 - Hoechst Celanese Corporation,
Somerville, NJ)

X.X % owf monosodium phosphate / trisodium phosphate to a pH of 7.0

After running another test dye cycle, there was again no change in the dyed piece. However, the greige piece was dyed an almost undetectable blue shade, equivalent to 4-5 on the Grey Scale for evaluating staining.

**EXAMPLE 3**

A 20 gram piece of nylon 6 carpet was dyed in an aqueous dye bath containing:

- 0.10 % owf Yellow 2
- 0.60 % owf Red 1
- 0.30 % owf Blue 2
- 1.00 % owf Remol® GES

The bath was set at a pH of 3 at 80°F and then the same dyeing cycle as used in Example 1 was followed. The resultant shade is a deep lavender which is uniform in color.

Next, 4 grams of the dyed lavender carpet was placed in a dyebath along with 16 grams of greige carpet and a standard dye cycle was run for 30 minutes at the boil with the formula:

- 0.030 % owf Tectilon® Orange 3G 200% (CI Acid Orange 156)
- 0.030 % owf Tectilon® Red 2B 200% (CI Acid Red 361)
- 0.033 % owf Tectilon® Blue 4R 200% (CI Acid Blue 277)
1.00 % owf SSSD

X.X % owf monosodium phosphate/trisodium phosphate to a pH of 6.5

[Tectilon® is a registered trademark of Ciba Geigy Ltd., Basel, Switzerland.]

The greige piece was slightly dyed a beige shade and the lavender piece was dulled and cast to the yellow side. A dyeing was then made using the above Tectilon® dye formula on 20 grams of greige carpet without the lavender piece being present. The resultant beige shade was the same as the beige shade obtained when the lavender piece of vinyl sulfone dyed carpet was present. This showed that the vinyl sulfone dyes do not interfere with a subsequent overdyeing cycle and that the vinyl sulfone lavender sample was only slightly affected by the acid dyes.

EXAMPLE 4

A 30 gram piece of nylon 6,6 carpet was wetted out with 1.0 g/l Hostapur® CX (nonionic wetting agent) and then flooded with dye solution of the formula:

3.0 g/l Orange 1

2.0 g/l Guar thickener

4.0 g/l Sulfamic acid pH 2, viscosity 20 cps

[Hostapur® is a registered trademark of Hoechst A.G., Frankfurt, Germany.]

The carpet was steamed 6 minutes and then removed and dipped in a 50 g/l solution of trisodium phosphate and steamed again for 6 minutes. The carpet was rinsed and dried.

To check the amount of reactive bonding, 10 grams of the dyed carpet was placed in an exhaust dye bath with 10 grams of greige carpet. As in Example 1, a blank dye cycle
was run for 45 minutes at the boil at a pH of 7.0 with no chemicals present. The result was that the greige carpet was dyed a pale orange shade, equivalent to a 2 on the Grey Scale for evaluating staining.

Another test bath was prepared as above except that 1 % owf resist chemical (Sybron Stainfree) was added. The result this time was that the greige piece was undyed or a 5 on the Grey Scale for evaluating staining.

**EXAMPLE 5**

Two 10 gram pieces of nylon 6 carpet were wetted out with 1.0 g/l Hostapur CX and then printed with the formula:

- 3.0 g/l Yellow 1
- 4.5 g/l Guar thickener
- 4.0 g/l Sulfamic acid pH 2, viscosity 300 cps

The pieces were steamed 6 minutes, washed, and then one piece was dried only and one piece was dipped in a 50 g/l TSP solution before drying.

For the two pieces, a blank dyebath was prepared which contained 8 grams of dyed carpet and 27 grams of greige carpet. The cycle was 45 minutes at the boil with the formula:

- 1.0 % owf SSSD
- 1.0 % owf anionic resist chemical

The above process was repeated with a second set containing 3.0 g/l Yellow 2 and a third set with 3.0 g/l Yellow 3. The results or the blank dyeings were as follows:
<table>
<thead>
<tr>
<th>Dye</th>
<th>No Alkali aftertreat</th>
<th>Alkali aftertreat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow 1</td>
<td>90% loss of shade</td>
<td>50% loss of shade</td>
</tr>
<tr>
<td>Yellow 2</td>
<td>50% loss of shade</td>
<td>20% loss of shade</td>
</tr>
<tr>
<td>Yellow 3</td>
<td>95% loss of shade</td>
<td>80% loss of shade</td>
</tr>
</tbody>
</table>

Thus, in this example, a dye having one vinyl sulfone and one SO₃ substituent (Yellow 3) had the least overdye fastness; followed by the dye having one vinyl sulfone and two SO₃ substituents (Yellow 1). The best dye was the Yellow 2 dye having two vinyl sulfone and one SO₃ substituents.

**EXAMPLE 6**

A 20 gram piece of nylon 6 was wetted out as in above examples and then printed with repeating stripes of the following four colors:

Print 1 - 3.0 g/l Orange 1

Chemical:

4.5 g/l Guar thickener
4.0 g/l Sulfamic acid

pH 2, viscosity 300 cps

Print 2 - 2.5 g/l Red 1

same chemicals

Print 3 - 3.0 g/l Black 1

same chemicals except pH 2.5

Print 4 - 3.0 g/l Orange 1

0.3 g/l Red 1
1.7 g/l Black 1

same chemicals
The prints were steamed 6 minutes, washed, dripped in 50 g/l trisodium phosphate, and dried. Next two dyebaths were prepared which contained 8 grams of dyed carpet and 27 grams of greige carpet:

**Dyebath 1** - 1.0% owf SSSD (Chemcogen® AC - Lyndal)

1.0% owf anionic resist chemical

monosodium phosphate/trisodium phosphate to pH 7.0

**Dyebath 2** - .0570 g/l CI Acid Yellow

10 .0315 g/l CI Acid Red 361

10 .0265 g/l CI Acid Blue 277

same chemicals as bath 1

[Chemcogen® is a registered trademark of Lyndal Corp.]

After a dye cycle of 45 minutes at the boil, the greige piece in the test dyebath 1 was totally undyed. In the other one the greige carpet was dyed a beige shade and the printed areas were only slightly dulled.

**EXAMPLE 7**

Two 20 gram pieces of nylon 6-6 carpet were pad dyed a dark brown shade with the formula:

2.7 g/l Yellow 1

1.1 g/l Red 1

1.3 g/l Blue 1

25 3.5 g/l thickening agent (EM-40 - Lyndal)

2.0 g/l Hostapur® CX (nonionic wetting agent)

4.0 g/l Sulfamic acid pH 2.0

The processing sequence was:
pad dye
steam 6 minutes
wash
pad 50 g/l trisodium phosphate
steam 4 minutes
wash
dry

In addition one of the pieces was thermofixed at a temperature of 325°F for 20 minutes, which simulates the curing cycle when the rubber backing is bonded to the carpet in the manufacture of the washable mats.

A laundry cycle was carried out on each of the two dyed pieces along with a greige blank. The bath was held at 160°F for 2 hours and contained 1.0 g/l of a commercial detergent which gave the bath a pH of 9.4.

The sample which had been dried only lost 30-40% of the dye and the shade went extremely red. No redeposition on the griège sample was observed. However, the sample which had been thermofixed only lost 10-20% of the dye and went slightly redder. Again, there was no redeposition on the greige sample.

This example shows the improvement in wash fastness which a thermofix cycle gives to the vinyl sulfone dyed carpet. It also shows that single vinyl sulfone substituted dyes still do not give the maximum was fastness properties.
EXAMPLE 8

Two 20 gram pieces of nylon 6-6 were dyed a dark brown shade with the formula:

- 2.7 g/l Yellow 2
- 1.0 g/l Red 1
- 1.3 g/l Blue 2

Chemicals the same as in Example 7

The same processing sequence was followed as in Example 7 and the same wash tests were performed. In the case of the sample which had been dried only, there was only a slight loss of color after the wash cycle. The sample which had been thermofixed showed no loss of color. This example shows that multiple anchor dyes (i.e. dyes with at least 2 fiber reactive groups) give the best wash fastness.

EXAMPLE 9

A piece of nylon 6-6 carpet was printed with dark red and dark maroon dots and then flooded with a heavy red shade using the following formula:

Print 1 -

- 0.3 g/l Yellow 2
- 4.0 g/l Red 1
- 0.1 g/l Blue 2

Chemicals:

- 10.0 g/l thickening agent (EM-40 - Lyndal)
- 2.0 g/l Hostapur® CX (nonionic wetting agent)
- 4.0 g/l Sulfamic acid

SUBSTITUTE SHEET
Print 2 - 1.0 g/l Yellow 1
   3.0 g/l Red 1
   2.0 g/l Blue 2
   Chemicals same as Print 1
Flood - 2.5 g/l Yellow 1
   2.5 g/l Red 1
   .1 g/l Blue 2
   3.5 g/l thickening agent
   2.0 g/l nonionic wetting agent
   4.0 g/l Sulfamic acid

The above sample of carpet was fixed following the procedure in Example 7, including the thermofixation cycle. Also as in Example 7, a wash cycle was carried out on the carpet and no loss of shade or deposition was observed.
I claim:

1. A method of dyeing a polyamide substrate comprising:

(a) contacting said polyamide substrate with a fiber reactive, vinyl sulfone dye at a pH of about 1.5 to about 5;
(b) heating said substrate to fix said vinyl sulfone dye to said substrate to provide a vinyl sulfone dyed polyamide substrate;
(c) treating said vinyl sulfone dyed polyamide substrate with an alkaline reagent at a pH of about 8 to 12 to convert said dye to its fiber reactive form; and
(d) heating said alkaline reagent treated, vinyl sulfone dyed polyamide substrate to covalently bond said vinyl sulfone dye to said polyamide substrate.

2. A process according to Claim 1 wherein said vinyl sulfone dye has at least two fiber reactive substituents capable of forming covalent bonds with a polyamide substrate.

3. A process according to Claim 2 wherein said vinyl sulfone dyed polyamide is treated with an anionic resist chemical.
4. A process according to Claim 2 wherein said vinyl sulfone dyed polyamide is overdyed with at least one acid dye.

5. A process according to Claim 1 wherein said alkaline treated vinyl sulfone dyed polyamide substrate is heated to a temperature of at least 300°F to covalently bond said vinyl sulfone dye to said polyamide substrate.

6. A process according to Claim 1 wherein said alkaline treated vinyl sulfone dyed polyamide substrate is heated to a temperature of at least 270°F in the presence of water vapor to covalently bond said sulfone dye to said polyamide substrate.

7. A process according to Claim 1 wherein said alkaline treated vinyl sulfone dyed polyamide substrate is heated to a temperature of at least 270°F in a substantially water saturated atmosphere.

8. A process according to Claim 7 wherein substrate is heated to at least 270°F using steam.
## INTERNATIONAL SEARCH REPORT

### I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

**U.S. CL.:** 8/449,924, Dig. 2  
**IPC(5) CL.:** D06P 5/12; D06P 3/24

### II. FIELDS SEARCHED

<table>
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<tr>
<th>Classification System</th>
<th>Classification Symbols</th>
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<tbody>
<tr>
<td>US</td>
<td>8/449,924, Dig. 2</td>
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</tbody>
</table>

Documented searched other than minimum documentation to the extent that such documents are included in the fields searched:

### III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
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<tbody>
<tr>
<td>X</td>
<td>US, A, 3,775,045 (BUEHLER et al.), 27 November 1973</td>
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<td>Y</td>
<td>See Example 1.</td>
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<tr>
<td>Y</td>
<td>US, A, 4,878,920 (RUSSELL et al.), 07 November 1989</td>
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<td>See column 3, lines 9-13.</td>
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<tr>
<td>A</td>
<td>US, A, 4,911,735 (VONDER ELTZ et al.) 27 March 1990, See Abstract and examples.</td>
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<tr>
<td>A</td>
<td>US, A, 4,680,033 (PURL et al.) 14 July 1987</td>
<td>1-8</td>
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<tr>
<td>A</td>
<td>US, A, 4,218,217 (REDD, JR.) 19 August 1980</td>
<td>1-8</td>
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<tr>
<td></td>
<td>See Abstract.</td>
<td></td>
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</tbody>
</table>

* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier document but published on or after the international filing date
  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "O" document referring to an oral disclosure, use, exhibition or other means
  - "P" document published prior to the international filing date but later than the priority date claimed
  - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
  - "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
  - "A" document member of the same patent family

### IV. CERTIFICATION

**Date of the Actual Completion of the International Search:** 22 May 1992  
**Date of Mailing of this International Search Report:** 11 Jun 1992

**International Searching Authority:** ISA/US  
**Signature of Authorized Officer:** [Signature]

Form: PCT/ISA/210 (second sheet) (Rev.11-97)