ABSTRACT OF THE DISCLOSURE

Union dyeing or printing of polyester/cellulose blends is carried out by (1) applying to the fabric a padding solution or a printing paste comprising (a) a fiber-reactive dye characterized by the presence therein of a methylo- lated iminobispropionamide group attached to the dye by a defined type of bridging group, (b) a disperse dye having a Hoechst acid catalyst (e.g., ammonium chloride), and (c) water, and (2) drying the fabric at a temperature of 380-435°F, for from 5 seconds to 3 minutes. The dyed fabrics exhibit excellent fastness to washing as well as improved strength, brightness and fastness to light.

This invention relates to and has for its object the provision of an improved process for union dyeing or printing of polyester/cellulose blends and to a dye composition therefor.

More particularly, the invention relates to a process for union dyeing or printing of mixed or blended polyester and cellulose cloth or fabric. Thus, the fabric may be either blended at the yarn stage and subsequently woven into cloth or fabric, or not blended at the yarn stage but woven together into a cloth or fabric.

The process of the present invention makes it possible to produce (1) a solid or union shade or (2) contrast effects on polyester/cellulose fabrics. Thus, the process does not leave one of the mixed fibers undyed, but dyed both fibers simultaneously.

In accordance with the process of the invention, there is used in the pad bath or print paste, a dye reactive with cellulose under acid conditions having at least one imino- bispropionamide radical, an acid catalyst, a disperse dye, water and, optionally, a thickener.

More than one of either type of dye, i.e., disperse or fiber-reactive, may be present in the pad bath or print paste. In accordance with the process the aqueous bath or paste is padded or printed onto the fabric, the fabric is dried and the dry fabric heated at a temperature above 380°F, but below the melting point of the polyester, until maximum fixation of the dyes to the respective fibers has taken place. Any unfixed dye is then removed.

The process of this invention differs from previous methods in providing an improved continuous simultaneous method of union dyeing and printing fabrics composed of both polyester and cellulose. Together the two types of dyes, disperse and reactive, are applied to the cloth, together they are dried and together at the same temperature they are fixed, excess or unixed or unreacted dye being removed. Weakly acid conditions persist as long as there is moisture present. Alkalinity at any point in the process is avoided until union dyeing or printing is complete. Thereafter optionally, the fabric is washed or soaked to remove excess fixed dyes. During the removal of excess dye, mild alkali may be present although even here the use of neutral soaps or surface active agents is the usual practice.

Hertofore, when combinations of disperse and reactive dyes have been used for the union dyeing of polyester/cellulose blends, alkaline conditions have been used at that part of the process where fixation of the reactive dye to cellulose takes place. The fiber-reactive dyes used in the alkaline process of the art differ in structure from the dyes used in the process of this invention. Such prior art dyes may have, for instance, a monochloro or dichlorotriazine moiety (Procion M or A dyes). Such dyes need alkaline conditions for fixation to cellulose. Also, heating in the presence of alkali has an adverse effect on the union shade. Furthermore, disperse dyes tend to be unstable in alkali at high temperature. Also, in the presence of alkali, fiber-reactive dyes can react with a reactive hydrogen if present in the disperse dye. Thus, fixation to the cellulose is substituted by fixation to the disperse dye with resultant loss of color value on the fabric.

The process of this invention is advantageous in that the dyes are not applied with urea. In the mill in the large quantities needed, urea has been found to yellow and dull light shades. It also causes corrosion problems with copper fittings in the drying and heating steps.

The fiber-reactive dyes of the invention are a new class of fiber-reactive dyes characterized by the presence therein of a methyloated iminobispropionamide group which is attached to the dye moiety through a particular type of "bridging group" which has an electron-withdrawing effect by virtue of which the dyes may be applied to cellulose in the presence of an acid catalyst. These new dyes are disclosed and claimed in a copending application of Frank F. Loffelman, Ser. No. 420,448, filed Dec. 22, 1964, now abandoned, and assigned to the assignee of the instant application. They conform to the formula:

\[
D - Y - \text{CH}_{2}\text{CH}_{2}\text{CON} - R' - \text{Y} - \text{CH}_{2}\text{CH}_{2}\text{CON} - R' - \text{CH}_{2}R
\]

where \(D\) is the residue of an organic dye moiety, \(Y\) is a bridging group selected from the group consisting of a covalent bond, sulfonyl, alkylaminoalkyl, alkyleneoxy, alkyleneethio, carbonyl, alkyleneacyononyl and alkylenecarboxylic acid, the alkylened radicals in \(Y\) having 1-2 carbon atoms; \(R\) is a member selected from hydrogen and alkyl carbons; \(R'\) is individually selected from the group consisting of hydrogen and the radical \(\text{CH}_{2}\text{OR}\) and \(n\) is a positive integer less than three.

As shown in the copending application, the radical "\(D\)" can be the moiety of any organic dye, the novel and characterizing feature of the new dyes being the group. Numerous examples of the new class of dyes and their outstanding acid-fixing properties on cellulose are disclosed in the application Ser. No. 420,448.

The dyes fix over a wide range of temperatures, i.e., 300°F to 435°F, which coincides with the range needed for the dyeing of polyes ters, i.e., 380-450°F. They react well under slightly acid conditions which are also good for the Thermosol dyeing polyes ters. They do not react with the fiber under alkaline conditions and thus are distinct from known reactive dyes used in conjunction with disperse dyes in dyeing polyester/cotton blends.

The disperse dyes used in the present invention should be chosen especially for their fastness to sublimation and
3,413,074

stability of hue to heat and pH. They should also have good fastness to light, washing and gas-fading. Examples of disperse dyes are azo dyes of the phenylazo-
razozone series, as disclosed in U.S. 3,019,217 and 3,198-783, anthraquinone dyes containing a 2-(2-cyanoethoxy)
ethoxy group, as disclosed in U.S. 3,264,325, substituted
quinazinines, indandiones, substituted quinolines and the
like. Suitable disperse dyes are those having a rating of
4–5 or 5 in Hot Pressing as shown in vol. I of the Colour
Index, 2nd edition, pages 1655–1742. Under the acid fixation
conditions of the process of this invention a stronger,
brighter result is obtained in dyeing the disperse dye than
under alkaline conditions of fixation.

The concentration of the acid catalyst, which fixes
the fiber-reactive dye to the cellulose is important. It is,
however, geared to the temperature and time of fixation
rather than the concentration of the dye. The amount
used is varied inversely to the temperature range of
380° F. to 435° F. Suitable acid catalysts are ammonium
salts, such as the chloride, sulfate, phosphate and gluc-
ionate, hydrochlorides of mono-, di- and triethanolamines
and chlorides of magnesium. Also, Lewis acids, dilute
mineral acids, organic acids, such as oxalic, malonic,
adipic, acetic or lactic acids, and inorganic acids, such
as fluoroboric or fluorosulfonic acid are suitable for the
practice of this invention. The optimum catalyst concen-
tration of ammonium chloride, a preferred acid catalyst,
for example, is 4 grams per liter where the padded ar-
dried fabric is heated in hot air at 350° F. for 1.5 minutes.
When the temperature is 410° F., and the time 1.5 minutes,
a concentration of 0.5 gram of ammonium chloride
per liter is preferred.

A thicken may be used to adjust the viscosity and
facilitate application of the pad bath or printing paste.
Natural gums or resins or sodium alginates, about 2 g. per
liter at pH 6–7, are preferred. The thicken also helps to
prevent migration of the dyes on drying and sub-
sequent heat treatment. In printing the thicken is in-
creased or the water content reduced, or both.

The padded fabric or print is then dried. Infrared pre-
drying may be used followed by hot cylinder drying.
After drying, the fabric is heated (subjected to the
action of heat) at 380–435° F. Either hot air may be
used or actual contact with a hot roll or cylinder. Contact
heat is faster and may even halve the amount of time
needed for the heat treatment. In hot air, at 350° F.,
fixation of the fiber reactive dye is complete at 1.5 min-
utes, but at 380° F. it is needed for the polyester part
of the union dying. At 410° F. the maximum fixation
of the reactive dye takes place within 1.0 minute. This is
an optimal temperature for dyeing of a disperse dye on
polyester. The preferred temperature and time for hot air
union dyeing in the process of this invention is 410° F.
for 90 seconds. Excessive times such as five minutes cause
appreciable tensile strength loss in the cellulose fiber.

After the heat treatment any excess dye not attached
to the fabric is removed by washing or soaping. Soap-
ing is done in neutral soap or detergent solution at the
boil. The fabric is rinsed, soaped and dried. The rinsing
and soaping steps may be eliminated prior to resin finish-
ing if this is done. However, the resin-finished fabric
should then be soaped. Resin after-treatment may be de-
sirable to improve fastness to perspiration and to dry-
cleaning.

The resulting union-dyed fabric is characterized by
excellent fastness to washing as well as improved strength,
brightness and fastness to light.

When a fabric of polyester/cellulose blended yarn is
union dyed using the process of this invention, it has no
significant shade differences from face to back or sides to
center.

When a fabric is woven with separate polyester and
cellulose yarns, either union or patterned effects are pos-
sible, depending upon weave and the choice of hue of
fiber-reactive and disperse dyes.

The components of the pad bath of the present
invention may be present within the following concentra-
tion ranges.

<table>
<thead>
<tr>
<th>Grams/liter</th>
<th>Preferred</th>
<th>Operable</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Fiber reactive dye</td>
<td>0.1–0.5</td>
<td>0.001–0.20</td>
</tr>
<tr>
<td>(b) Dispersive dye</td>
<td>0.1–0.5</td>
<td>0.001–0.20</td>
</tr>
<tr>
<td>(c) Acid catalyst</td>
<td>0.25–1.0</td>
<td>0.1–0.35</td>
</tr>
<tr>
<td>(d) Thicken</td>
<td>2–5</td>
<td>0–1.0</td>
</tr>
</tbody>
</table>

The following examples illustrate this invention.

EXAMPLE 1
Union pad dyeing of polyester/cotton
A pad bath is prepared by mixing, per liter, 2 g. Dye I,
0.5 g. Dye II and 5 g. Dye III with 10 g. ammonium
chloride, 15 g. refined solution of natural gums as thicken-
ner and water.

The Dyes I, II and III are identified as follows:
I. Fiber Reactive Dye (Example 25, Ser. No. 420,448)
II. Fiber Reactive Dye (Example 2, Ser. No. 420,448)
III. Disperse Dye (U.S. 3,264,325)

The solution is padded on a 50/50 polyester/cotton
blend fabric, dried and cured at 410° F. for 90 seconds
in hot air. The union dyed fabric is then soaped off at
160° F. for 3 minutes in a bath containing 0.06% tetra-
sodium pyrophosphate and 0.03% nonionic detergent
which is a condensate of ethylene oxide with nonyl alco-
hol 9.5/1. The fabric is washed and dried. It is dyed a uni-
form pink shade.

If 5 g. ammonium chloride is used with contact heat at
Continuous-union pad dying of polyester/cotton

A bath pad is prepared by mixing, diluting and dissolving with hot water in a pail, Dyes I, II and III (of Example 1) in amounts of 1.5 lb, 0.375 lb. and 4.5 lb. paste, respectively. The solution of dye is added to a tank containing fifty gallons water at 110°F; 9.0 lb. solution of natural gums and 3.0 lb. ammonium chloride are added. The whole is diluted to 75 gal. with water. Five hundred yards of 50/50 polyester/cotton are padded with this solution at a rate of 70 yards per minute, skyed, predried by infrared and dried by four hot roll cylinders at 180°, 250°, 250° and 350° F., respectively. The fabric is heat-treated for nine seconds by contact with ten rolls at 400–435° F. Following this, the yardage is rinsed, soaked at 180° F., in water containing 1 lb./100 gallons of an anionic detergent, sodium N-methyl-N-olyl taurate, rinsed and dried. The union-dyed fabric obtained is a medium pink shade. It is uniformly dyed with no shade differences from face to back or sides to center.

EXAMPLE 3

Red union dyeing of polyester/cotton fabric
A pad bath is made up having a concentration per liter of

<table>
<thead>
<tr>
<th>Fiber reactive dye</th>
<th>Disperse dye</th>
<th>30% NH₄Cl solution in ml.</th>
<th>Union shade on polyester/cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>II</td>
<td>III</td>
<td>V</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>0.00</td>
<td>2.15</td>
</tr>
<tr>
<td>2.00</td>
<td>2.00</td>
<td>0.00</td>
<td>1.50</td>
</tr>
<tr>
<td>3.00</td>
<td>3.00</td>
<td>0.00</td>
<td>2.20</td>
</tr>
<tr>
<td>4.00</td>
<td>4.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>5.00</td>
<td>5.00</td>
<td>0.00</td>
<td>0.85</td>
</tr>
<tr>
<td>6.00</td>
<td>6.00</td>
<td>0.00</td>
<td>0.60</td>
</tr>
<tr>
<td>7.00</td>
<td>7.00</td>
<td>0.00</td>
<td>0.75</td>
</tr>
<tr>
<td>8.00</td>
<td>8.00</td>
<td>0.00</td>
<td>0.65</td>
</tr>
</tbody>
</table>

The prints obtained have good fastness to AATCC Tests Wash No. 2A, Acid Perspiration, Alkaline Perspiration, Dry Crocking and Dry Cleaning. The dyes of Table I are identified as follows: Dyes I and II are Dyes I and II of Example 1. Dye IV is a copper phthalocyanine dye of the structure:

![Dye IV structure](image)

Dye III is Dye III of Example 1.

Dye V is:

![Dye V structure](image)

Dye VI is a substituted quinizarine. We claim:

1. Process for union dyeing or printing of fabric composed of cellulose and polyester which comprises

   (1) applying to the fabric a padding solution or a printing paste composed of:

   (a) a fiber-reactive dye of the formula

   ![Dye V formula](image)

   (b) a disperse dye of the formula

   ![Disperse dye formula](image)

   (c) a 30% NH₄Cl solution in ml.

   (d) a union shade on polyester/cotton.
wherein D is the residue of an organic dye moiety, Y is a bridging group selected from the group consisting of a covalent bond, sulfonyl, alkylsulfonfyl, alkyleneoxy, alkylenethio, carbonyl, alkylene carbonyl and alkyleno, the alkyleno radicals in Y having 1–2 carbon atoms; R is a member selected from hydrogen and alkyl of 1–4 carbons; R' is individually selected from the group consisting of hydrogen and the radical —CH₃OR and n is a positive integer less than three;

(b) a disperse dye having a rating of 4–5 or 5 in Hot Pressing as shown in the Colour Index, 2nd edition, vol. I, page 1655–1742;

(c) an acid catalyst, and

d) water, and

(2) drying the fabric at a temperature of 380–435°F for from 5 seconds to 3 minutes.

2. A process according to claim 1 in which the acid catalyst is ammonium chloride present in an amount of from 0.25 to 4.0 g. per liter.

3. A dye composition comprising:

(a) a fiber-reactive dye of the formula

\[
\begin{align*}
D & \quad Y = \text{N} \\
\text{CH₂CH₂CON} & \quad \text{CH₃OR} \\
\text{CH₂CH₂CON} & \quad \text{R'} \\
\end{align*}
\]

wherein D is the residue of an organic dye moiety, Y is a bridging group selected from the group consisting of a covalent bond, sulfonyl, alkylsulfonfyl, alkyleneoxy, alkylenethio, carbonyl, alkylene carbonyl and alkyleno, the alkyleno radicals in Y having 1–2 carbon atoms; R is a member selected from hydrogen and alkyl of 1–4 carbons; R' is individually selected from the group consisting of hydrogen and the radical —CH₃OR and n is a positive integer less than three;

(b) a disperse dye having a rating of 4–5 or 5 in Hot Pressing as shown in the Colour Index, 2nd edition, vol. I, page 1655–1742;

(c) an acid catalyst; and

d) water.

4. A dye composition according to claim 3, in which the acid catalyst is ammonium chloride present in an amount of from 0.25 to 4.0 g. per liter.

References Cited

UNITED STATES PATENTS

2,346,013 4/1944 Dickey ——— 260—199 XR

3,066,005 11/1962 Wedemeyer ——— 8—17 XR

FOREIGN PATENTS

805,562 12/1958 Great Britain.

OTHER REFERENCES


NORMAN G. TORCHIN, Primary Examiner.

D. LEVY, Assistant Examiner.