COLOURING OF POLYESTER FIBRES

The present invention concerns improvements in the colouring of polyester fibres. It is known that it is possible to dye polyester fibres by means of the so-called "plastosoluble" dyestuffs, which are used for dyeing cellulose acetate fibres. These dyestuffs can be applied either at ordinary pressure in the presence of carriers, the most common of which are o-phenylphenol and the chlorinated derivatives of benzene, or under superatmospheric pressure and consequently in the absence of carriers and in a shorter time. The shades obtained are generally rather bright; in many cases, however, they lackfastness, especially to light, to wet tests and to sublimation.

It is further known that it is possible to dye polyester fibres under the conditions used for the so-called "plastosoluble" dyestuffs, by means of mixtures of diazotisable bases and coupling compounds belonging to the series of arylaldehydes of \( \beta \)-hydroxynapthalic acid. The corresponding pigments are formed on the fibre by simultaneous diazotisation and coupling. Provided that the choice of base and arylide and the relation between the amounts of these substances fixed on the fibre are correct, the colours obtained are capable of satisfying to a high degree the requirements so far as fastness to light and wet tests are concerned. Although from the absolute point of view the resistance to sublimation is satisfactory, in numerous cases, however, variations in shades which can be considered are observed at the time of preforming. In addition, this method of dyeing has the disadvantage of being lengthy since two successive treatments of the fibre are necessary.

It has already been proposed to dye, by conventional processes, certain textile fibres by means of very finely dispersed pigmental dyestuffs like those which are quite commonly used for the coloration of viscose or cellulose acetate in bulk. In most cases, however, the tinctorial yield is low and, in addition, the shades obtained are not sufficiently fast to rubbing for this solution to be capable of being applied in practice.

We have now found that dyestuffs of the general formula:

\[
\begin{align*}
\text{R} - \text{N}=\text{N} \rightarrow \text{O} \xrightarrow{\text{CONR}} \text{OX}
\end{align*}
\]

in which \( \text{R} \) represents the residue of a benzene amine and \( \text{X} \) represents an alkyl group possess, at high temperature, an excellent affinity for polyester fibres. By the expression "polyester fibres" we mean quite generally the fibres obtained by the poly-condensation of di-acids with di-alcohols, and in particular those obtained by the poly-condensation of terephthalic acid with ethylene glycol. Such fibres are on the market under the names "Terylene," "Dacron" and "Tergal."

The dyestuffs of the above general formula 1 can be applied to these fibres at a high temperature by any of the processes already used for the coloration of the latter by means of other pigments. Dyeing can be carried out, for example, under superatmospheric pressure and at temperatures above 100°C, preferentially at temperatures between 101°C and 150°C, by means of aqueous dispersions of the dyestuffs of general formula 1. Another process comprises fouling the fibres by means of aqueous dispersions of these dyestuffs and then subjecting them to a treatment at high temperature, preferably between 150°C and 200°C. Also, after fouling by means of these aqueous dispersions, the impregnated fibres can be subjected to steaming under superatmospheric pressure. Fabrics based on polyester fibres can also be printed by means of pastes containing aqueous dispersions of the said dyestuffs and then the printed fibres subjected to steaming under superatmospheric pressure.

Alkylaryl sulphonates and the products resulting from the condensation of sulphonated aromatic derivatives with aldehydes, such as the methylene-dinaphthylsulphonates, are particularly valuable auxiliary substances since they allow the preparation of a good dispersion of the dyestuffs and facilitate the taking up of the latter on the polyester fibres. On the other hand, "carriers," such as monoor poly-chlorinated derivatives of the benzene series or diphenyl, can be added to the dye bath or to the printing pastes. These substances exert a swelling action on the polyester fibres and are capable of improving the tinctorial yield. In addition, it is useful, and particularly so in the case of dyeing on bobbins, to add to the dye bath anti-static agents, such as the products of condensation of compounds containing an active hydrogen with ethylene oxide and quaternary ammonium salts containing a fatty chain. This addition allows lack of uniformity to be remedied which in all probability is due to the accumulation of electrical charges as a result of the circulation of the bath around hydrophobic fibres.

The dyestuffs of general Formula I give, with excellent yields, bright shades characterised by very good fastness. These shades are not in general comparable with those obtained on cotton or obtained by coloration of viscose in bulk. It is necessary to consider that the fact of operating at high temperature has the effect of giving to the pigment its definitive physical form, a result which is certainly not attained when the pigment is formed on the polyester fibre by diazotisation and coupling.

The invention will be more clearly understood by reference to the following examples which are purely illustrative.

**Example 1**

3.5 parts of monochlorotoluene are emulsified in 10 parts of water by means of about 1.5 parts of the butyl ester of sulphonated ricinoleic acid. This emulsion is
poured into 1000 parts of tepid water and 1 part of dye stuff of the following formula:

\[
\text{OH} \quad \text{CO-NH} \quad \text{OH} \\
\text{N=N} \quad \text{OCH}_3 \\
\text{Cl}
\]

(Previously dispersed with 2 parts of the sodium salt of methylene-dinaphthyl sulphonic acid) is mixed therewith. 100 parts of polyester fibres, previously degreased by treatment in an alkaline medium in the hot, are introduced. The dyeing is carried out in an apparatus which enables it to be effected under slight superatmospheric pressure, while the temperature is kept at 105°C for one hour. The treatment is finished by subjecting the fibres to cleaning by alkaline reduction in a bath containing one to two grams per litre of an alkyl phenol ethylene oxide condensate. The polyester fibres are dyed a bright orange shade, which is fast to light, to wet tests, rubbing and sublimation.

**Example 2**

3.5 parts of orthodichlorobenzene are emulsified in 10 parts of water by means of about 1.5 parts of the butyl ester of sulphonated ricinoleic acid. This emulsion is poured into 1000 parts of tepid water and one part of the dye stuff of the formula:

\[
\text{OH} \quad \text{CO-NH} \quad \text{OH} \\
\text{N=N} \quad \text{OCH}_3 \\
\text{Cl}
\]

(Previously dispersed by means of 2 parts of the sodium salt of methylene-dinaphthyl sulphonic acid) is mixed therewith. 100 parts of a mixed material made up of polyester/wool fibres, previously degreased in the hot in a bath containing 1 to 2 g. per litre of an alkyl phenol ethylene oxide condensate, are introduced. Dyeing is effected under superatmospheric pressure while keeping the temperature at 105°C for one hour. The polyester fibres are dyed a bluish red shade, fast to light, wet tests, rubbing and sublimation, while the wool is only very slightly coloured. This light shade is not of such nature that it diminishes the quality of the acid dye stuff which must be applied simultaneously or subsequently to the wool; moreover, it readily disappears if the dyeing is followed by a slightly reducing cleaning treatment by means of a bath containing 1 to 2 g. per litre of an alkyl phenol ethylene oxide condensate.

**Example 3**

3 parts of diphenyl are emulsified in 10 parts of water at 85°C by means of about 1.5 parts of the butyl ester of sulphonated ricinoleic acid. This emulsion is poured into 1000 parts of water previously heated to 85°C and the operation is continued according to the process described in Example 2, using 0.5 parts of each of the dyestuffs of the following formulae:

**Example 4**

A printing paste is prepared comprising the following constituents:

<table>
<thead>
<tr>
<th>Dyestuff of the formula:</th>
<th>Parts</th>
</tr>
</thead>
</table>
| \[
\text{OH} \quad \text{CO-NH} \quad \text{OH} \\
\text{N=N} \quad \text{OCH}_3 \\
\text{NO}_3
\] | 3 |
| \[
\text{OH} \quad \text{CO-NH} \quad \text{OH} \\
\text{N=N} \quad \text{OCH}_3 \\
\text{OCH}_3
\] | 3 |
| Sodium methylene-dinaphthyl sulphonate | 14 |
| Monoethyl glycol | 60 |
| Water | 300 |
| 1:2 aqueous solution of sodium chloride (containing 1 part of chloride to 2 parts of water) | 80 |
| Thicker | 600 |
The paste is applied to a fabric based on polyester by the frame or roller process. There then follows a steaming process under atmospheric pressure at 120–130°C, for the purposes of fixing the dye, and finally there is an alkaline reducing treatment in the hot in a bath containing 1 to 2 g. per litre of an alkylphenol-ethylene oxide condensate.

On the polyester fabric there is obtained a bluish red shade which has the fastness characteristic of the dyes obtained by the processes of the preceding examples.

**Example 5**

A "Tergal" fabric which has been previously desized is foularded at about 50°C. in a suspension containing 6 grams per litre of the dyestuff of the formula:

![Dyestuff formula](image)

(Previously dispersed by means of twice its weight of sodium methylene-dinaphthylsulphonate) and 50 grams per litre of a condensation product of ethylene oxide with stearic acid. The fabric thus foularded is passed on a tenter for 30 seconds at 200°C. and subjected to a stripping of 5 minutes at the boil in an alkaline reducing bath containing a non-ionic detergent.

A bright orange shade is obtained having the same qualities of fastness as those obtained in Example 1.

**Example 6**

A "Tergal" fabric, previously desized, is foularded at about 50°C. in a bath containing 6 grams per litre of the dyestuff of the formula:

![Dyestuff formula](image)

(Previously dispersed by means of twice its weight of sodium methylene-dinaphthylsulphonate) and 50 grams per litre of a condensation product of ethylene oxide with stearic acid. The fabric thus foularded is subjected to steaming for 30 minutes under 1.8 to 2 kg. pressure and washed for 5 minutes at the boil in an alkaline reducing bath containing a non-ionic detergent.

The temperature is raised to 125–130°C. and kept at this for an hour. The polyester fibres are dyed a bright orange shade endowed with good general fastness; the bobbin having been completely penetrated, the fibre is evenly dyed.

**Example 7**

On replacing the dyestuff used in Example 5 by the mixture of dyestuffs used in Example 3, a scarlet shade possessing good fastness is obtained.

**Example 8**

On replacing the dyestuff used in Example 6 by the mixture of dyestuffs used in Example 4, a bluish red shade possessing excellent fastness is obtained.

**Example 9**

6 parts of a condensation product of oleyl alcohol with ethylene oxide is dissolved in 881 parts of water at 30–35°C. and into this are introduced 100 parts of previously degreased polyester fibre yarn on a bobbin. The bath is circulated for some minutes and the fluid paste prepared with the following constituents is poured in:

<table>
<thead>
<tr>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
</tr>
<tr>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>10</td>
</tr>
</tbody>
</table>

The temperature is raised to 125–130°C. and kept at this for an hour. The polyester fibres are dyed a bright orange shade endowed with good general fastness; the bobbin having been completely penetrated, the fibre is evenly dyed.

**Example 10**

The dyestuffs used in Example 9 are replaced by a mixture of the dyestuff of formula:

![Dyestuff formula](image)

2 parts, previously dispersed, and of the dyestuff of formula:

![Dyestuff formula](image)

2 parts, previously dispersed.

The polyester fibre is dyed a dark navy blue shade endowed with good general fastness, more particularly to sublimation.

**Example 11**

A dye bath is prepared with 881 parts of water at 30–35°C. and 6 parts of cetyl-trimethyl ammonium bromide, and 100 parts of polyester fibre yarn are introduced in the form of a crossed bobbin, previously degreased.
The bath is circulated for some minutes and a paste obtained by mixing the following components is added:

<table>
<thead>
<tr>
<th>dyestuff of the formula:</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="" alt="Chemical Structure" /></td>
<td>0.4</td>
</tr>
<tr>
<td>and the dyestuff of the formula:</td>
<td>0.5</td>
</tr>
<tr>
<td><img src="" alt="Chemical Structure" /></td>
<td></td>
</tr>
<tr>
<td>previously dispersed with: sodium methylene-naphthylsulphonate</td>
<td>2</td>
</tr>
<tr>
<td>mixture of water and denatured alcohol</td>
<td>10</td>
</tr>
</tbody>
</table>

The dyeing is effected as in Example 10; the polyester fiber is coloured a bluish red of great brilliance possessing good general fastness.

**Example 12**

On replacing the two dyestuffs used in Example 11 by the same quantities of the following dyestuffs, previously dispersed:

| ![Chemical Structure](attachment:image3.png) | 35 |
| ![Chemical Structure](attachment:image4.png) | 40 |

a very bright reddish violet possessing good general fastness is obtained on polyester fiber.

**Example 13**

A printing paste is prepared with the following dyestuffs:

| ![Chemical Structure](attachment:image5.png) | 50 |
| ![Chemical Structure](attachment:image6.png) |     |

under the same conditions, a red brown shade, having good general fastness, is obtained on polyester fabric.

We claim:

1. Process for the colouration of polyethylene terephthalate textile material which comprises printing a fabric made from the fibres with a printing paste containing an aqueous dispersion of a dyestuff on the general formula:

| ![Chemical Structure](attachment:image7.png) | |

in which R represents a phenyl radical substituted by at least one member selected from the group consisting of hydrogen, halogen, alkoxy, nitro, cyano, phenyl amino, alkoxy phenyl amino, and benzene azo group, and X represents an alkyl group, and subjecting the treated fibres to steaming under superatmospheric pressure at a temperature between 101° C. and 150° C.

2. Process for the coloration of polyethylene terephthalate textile material which comprises dyeing the fibres under super atmospheric pressure and at a temperature...
about 100° C. with an aqueous dispersion of a dyestuff of the general formula:

\[
\begin{align*}
\text{R-} & \text{N=}=\text{N} \\
\text{OH} & \text{C}-\text{NH}- \\
\text{O} & \text{X}
\end{align*}
\]

in which \( R \) represents a phenyl radical substituted by at least one member selected from the group consisting of hydrogen, halogen, alkoxy, nitro, cyano, phenyl amino, alkoxy phenyl amino, and benzene azo group and \( X \) represents an alkyl group.

3. Process as claimed in claim 2 in which the temperature is between 101° C. and 150° C.

4. Process for the coloration of polyethylene terephthalate textile material which comprises foullarding the fibres with an aqueous dispersion of a dyestuff of the general formula:

\[
\begin{align*}
\text{R-} & \text{N=}=\text{N} \\
\text{OH} & \text{C}-\text{NH}- \\
\text{O} & \text{X}
\end{align*}
\]

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