DYING WOOL IN FIBROUS MATERIAL CONTAINING WOOL WITH 1:2 METAL COMPLEX AZO DYES, ACID AND AROMATIC HYDROCARBONS, CARBOXYLIC ACIDS/ESTERS OR PHENOLS

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9 Claims

ABSTRACT OF THE DISCLOSURE

Process for dyeing fibrous materials made of or consisting of wool with 1:2 complex metal compounds of azo dyestuffs insoluble or sparingly soluble in water in which process a dyebath is used that contains, additionally to said dyestuffs and an acid, auxiliaries known as carriers, such as aromatic hydrocarbon, aromatic halohydrocarbons, aromatic carboxylic acids or esters thereof or phenol derivatives. The advantage of the present invention is essentially to be seen in the fact that easily obtainable dyestuffs can be used with good color yield for the dyeing of wool.

The present invention provides a process for dyeing wool or blends consisting of wool and polyester fibres. It has been proposed to dye wool with complex-metal compounds of azo dyestuffs insoluble or sparingly soluble in water. However, the high applicability of said series of dyestuffs is obviously limited with regard to the dyeing of wool by the poor affinity these dyestuffs have to wool leading often to an unsatisfactory color yield. It may, therefore, be assumed that due to this reason no assortment of these dyestuffs has been introduced yet on the market for the dyeing of wool. The use of dyestuffs of the indicated type, however, would offer the particular advantage that, analogously to dispersion dyestuffs usual for the dyeing of polyester fibres, they could be dispersed in the cold in simple manner so that it would not be necessary any more in the preparation of the dyebath to boil the dyestuff in an aqueous medium.

These shortcomings have been remedied to a certain extent by incorporating into the molecule of said insoluble complex-metal dyestuffs suitable substituents, for example sulfoic acid amide groups which enhance the water-solubility of these compounds and at the same time improve their affinity to wool. However, the influence of such solubilizing groups appeared relatively weak, said dyestuffs being generally rather indispensible in the cold even after these groups have been incorporated.

However, the complex metal dyestuffs concerned are often used in practice for dyeing the wool portion of blends of polyester fibres and wool the polyester portion of which is dyed with dispersion dyestuffs. Since the complex metal dyestuffs containing such solubilizing groups are soluble in the heat at a sufficient concentration only, their joint dissolution or dispersion with dispersion dyestuffs, which should be dispersed as cold as possible, is yet causing difficulties. A simultaneous dissolution of these dyestuff mixtures, however, would simplify the dyeing process and at the same time be time saving.

As a make-shift in the dyeing art mixtures of dispersion dyestuffs and 1:2 complex-metal compounds of azo dyestuffs containing solubilizing groups have been stirred into pastes in hot water of about 60° to 80° C.

However, as regards the obtention of deep shades, said procedure implies, especially with large quantities of dyestuffs used, the risk that, on the one hand, the solubility of the hitherto usual wool dyestuffs is insufficient and, on the other hand, the application of elevated temperatures and adjusting the dyeing liquors on the other hand impairs the stability of the dispersion dyestuffs, so that the dyestuff mixtures often yield specky, uneven and unfast dyes.

It has been found that fibrous woolen or wool-containing materials can be dyed with 1:2 complex-metal compounds of azo dyestuffs sparingly soluble or insoluble in water when the dyebath comprises, besides the cited dyestuffs and an acid and/or acid-staining substances or, optionally, other customary auxiliaries, auxiliaries acting as carriers.

The present invention is based on the observation that the above specified auxiliaries, of which it is known that they act with hydrophobic fibre only and that have been employed, recently, as carriers for dyeing polyester fabrics with dispersion dyestuffs, surprisingly, serve in the dyeing of animal fibres, especially wool, with 1:2 complex-metal compounds of azo dyestuffs sparingly soluble in water to improve the affinity of these dyestuffs to textile materials. Thereby very good color yields and deeper shades are obtained.

In carrying out the process of the invention the material to be dyed is treated in known manner for about 10 minutes on a winch, an X-shaped bobbin dyeing apparatus or another convenient dyeing machine, at about 40° to 60° C, in a dyebath not yet containing the dyestuff with an acid, for example acetic acid and/or an acid-staining substance, e.g., ammonium acetate or sulfate and an auxiliary acting as carrier. The pH of the pretreatment bath should be maintained in the neutral to acid range, preferably between 4 and 6. The sparingly soluble or insoluble complex-metal dyestuff is subsequently stirred with 10--40 times the amount of cold to warm water having a temperature of 20° to 50° C and added to the dyebath through a filter, whereupon the liquor is allowed to act on the material at said temperatures for another 10 minutes. Then the temperature is raised to the boil within, generally, 45 to 60 minutes or to about 106° C, the material being subsequently dyed at said temperatures for another one or two hours and finally rinsed.

The same dyeing effects are achieved when the auxiliary acting as the carrier is added to the bath simultaneously with the dyestuff. For final cleaning the so-obtained dyings are treated for 20 minutes in a fresh bath containing a non-ionic detergent of, for example, the type of a highly-ethoxylated fatty acid polyglycol ether and acetic acid at temperatures ranging from 60° to 80° C and the goods are, subsequently, rinsed. The final cleaning may also consist in treating for 20 minutes at 40° to 50° C in a fresh bath containing hydroxalkaline, ammonia and a non-ionic detergent, for example an oxyethylated alkylphenol, acidifying, subsequently, the dyed material and rinsing it.

As dyestuffs for dyeing wool according to the process of the invention 1:2 complex-metal compounds of azo dyestuffs sparingly soluble or insoluble in water are suitable that contain in the o,o'-position to the azo bridge metalalizable groupings and above all do not comprise in their molecule solubilizing groups or substrates improving the solubility of concerned compounds such, for example as sulfonic acid amide groups or carboxy groups that are not part of the complex. As complex-bound atoms of trivalent metals of said dyestuffs, for example cobalt and chromium may be mentioned. The complex metal compounds of this type are
known products easy to obtain by known methods which in the process of the invention are used in finely divided form as powders or liquid suspensions. The concentrations at which these dyestuffs are applied depend on the desired depth of shade.

As auxiliaries for carrying out the process of the invention for the dyeing of wool essentially all products which, generally act as carriers in the dyeing of polyester fibres with dispersion dyestuffs may serve such, for example, as aromatic hydrocarbons, halogenated aromatic hydrocarbons, aromatic carboxylic acids or their esters, derivatives of phenols and other substances or, optionally, mixtures thereof. For dyeing wool, particularly, o-phenylphenol, p-phenylphenol, diphenyl, o-dichlorobenzene, terephthalic acid dialkyl esters and hydroxyalkyl ethers of phenols (cf. German patent specification No. 1,001,966) are suitable. The carrier substances mentioned are mostly compounds sparingly soluble or insoluble in water which, when applied in aqueous preparations should, advantageously, be used in conjunction with a convenient emulsifier such as the oxalkylation products of phenols or phenol derivatives or an emulsifier mixture as disclosed, for example, in Belgian patent No. 703,716, should be employed. The auxiliaries intended to act in the present dyeing process as carriers are used in concentrations of 0.5 to 10, preferably 2 to 5 g. per litre of dye bath. Besides the additives mentioned the dye bath may, if required, contain a levelling agent, for example a condensation product of 1 mol of 2-heptadecyl-oxazoline-4-hydroxymethyl ether with 70 mols of ethylene oxide, a dispersing agent, e.g., a condensation product of sulfonated naphthalene and formaldehyde and/or a sequestering auxiliary, such, for example, as a polyphosphate.

The present process can be applied to wool textiles in all stages of manufacture without difference.

In comparison with the known state of the art it is a considerable advantage of the present process that the easily obtainable, simply applicable 1:2 complex-metal compounds of azo-dyestuffs that are sparingly soluble or insoluble in water can now be used with good color yield also for dyeing wool. Hence derives a further advantage of the present process which enables preparation of mixtures of dispersion dyestuffs and the complex-metal dyestuffs defined hereinbefore which are simply dispersible together and may serve for the dyeing of blends of polyester fibres and wood. Moreover, said dyestuff mixtures may also be adjusted for the purpose into the so-called paste form recently practised in trade with dispersion dyestuffs only, without the risk that the wool dyestuff in the mixture crystallizes as may occur with hydro-soluble dyestuffs. In view of the automation of the dyeing apparatus it must be considered a major improvement that it is now possible to prepare pasty mixtures of dispersion dyestuffs, 1:2 complex-metal compounds of azo-dyestuffs sparingly soluble or insoluble in water, and auxiliaries used according to the invention, for the production rate and safety of operation of continuous dyeing processes are thus enhanced, a double or triple dosing of the individual dyestuff mixtures components having become unnecessary and a sole dosing device being required for the addition of the dyestuff mixture (instead of the components individually added) with adequately equipped dyeing machines.

As dispersion dyestuffs for the dyeing of the polyester portion of blends of polyester fibres and wool according to the present process dyestuffs usual for the purpose may be employed, for example those of the azo or anthraquinone series or of the type of quinaphthalone, the azo dyestuffs, if required, applied in their metalized form.

The following examples are to illustrate the invention but they are not intended to limit it thereto. The percentages of the dyestuffs, auxiliaries and acids in the examples refer to the dry weight of the material to be dyed.

**EXAMPLE 1**

10 g. of a wool flannel were treated for 10 minutes at a goods to liquor ratio 1:40 with an aqueous liquor of 40° C. containing

2% of acetic acid (of 30% strength)
5% of ammonium acetate and
3 g./l. of o-phenylenol.

To the dyebath there were added 3% of a dyestuff paste having about 10% strength that had been stirred with cold water and contained the 1:2 chromium complex compound of the dyestuff of formula

![Formula](image)

in commercial form and condition; whereupon the goods were treated in said liquor for another ten minutes. The dye bath was, subsequently, heated within 45 minutes to the boil and the goods were dyed at that temperature for another one and a half hours, whereupon the dyeing was finished in usual manner. A uniform grey dyeing was obtained, substantially deeper in shade than that produced without auxiliaries.

**EXAMPLE 2**

Dyeing was affected as disclosed in Example 1 using instead of the dyestuff specified in said example a combination of

0.7% of a 1:2 cobalt-complex compound of the dyestuff of formula

![Formula](image)

0.7% of the 1:2 chromium-complex compound of the dyestuff of formula

![Formula](image)

and

0.7% of the 1:2 chromium complex compound of the dyestuff of formula

![Formula](image)

as a pulverulent mixture in commercial form and condition.

A brown uniform dyeing was obtained substantially deeper in shade than produced without auxiliaries.

**EXAMPLE 3**

Dyeing was effected analogously as disclosed in Example 1 using instead of the dyestuff specified therein
2% of the 1:2 chromium complex compound of the dye-stuff of formula

the whole as a pulverulent mixture in commercial form and condition. A uniform red dyeing was obtained distinctly deeper in shade than produced without the use of auxiliaries.

EXAMPLE 4

The dyeings were produced as described in the Examples 1-3; however, instead of wool flannel as textile material 5 g. of a worsted yarn and a polyester fibre yarn were used.

While the polyester yarn remained undyed, the wool yarn showed analogous dyeings as in Examples 1-3 but distinctly deeper in shade than obtained without the use of auxiliaries. Hence it was also obvious that the presence of the polyester material in the dyebath did not interfere with the action of the auxiliary on wool.

EXAMPLE 5

10 g. of a mixed tissue consisting of polyester fibres and wool of the mixing ratio 55:45 were treated for about 10 minutes at a goods to liquor ratio 1:40 with an aqueous liquor having a temperature of 50° C. and containing

2% of acetic acid (of 30% strength)
5% of ammonium acetate and
3 g./l. of o-phenylphenol.

Into this dyebath a pulverulent jointly dosed mixture consisting of 0.5% of the dispersion dyestuff of formula

and 1% of the 1:2 chromium complex compound of the dyestuff of formula

dispersed in warm water at 40°-50° C., was introduced and the goods were treated in said liquor for another 10 minutes. Subsequently, the dyebath was heated to boiling temperature within 45 minutes and the goods dyed at the boil for another one and a half hours, whereupon they were rinsed, finally cleaned in an aqueous washing liquor to which a non-ionic detergent of the type of a highly ethoxylated fatty acid polyglycol ether and acetic acid had been added, at 70° C., rinsed again and dried.

On both the polyester and the wool portion of the mixed tissue a uniform red dyeing was obtained.

EXAMPLE 6

Dyeing was performed as described in Example 5 using instead of the dyestuff indicated therein 5% of a dyestuff suspension (a paste) consisting of 10 parts of the 1:2 chromium complex compound of the dyestuff of formula

in commercial form and condition and 55 parts of water and a dispersing agent of the type of a sulfonated condensation product of naphthalene and formaldehyde. A uniform dyeing was obtained showing on the portion of the polyesters a yellow and on the portion of wool a grey shade.

EXAMPLE 7

10 g. of a mixed yarn consisting of polyester fibres and wool (mixing ratio 55:45) were treated for about 10 minutes at a goods to liquor ratio 1:20 with an aqueous liquor having a temperature of 40° C. and containing

2% of acetic acid (of 30% strength) and
5% ammonium acetate.

Then 15% of a liquid suspension consisting of

10 parts of the 1:2 chromium complex compound of the dyestuff of formula

in commercial form and condition were added, moreover

30 parts of o-phenylphenol and
47 parts of water and a dispersing agent of the type of a sulfonated condensation product of naphthalene and formaldehyde, whereupon the goods were treated in said liquor for 10 minutes. Subsequently, the dyebath was heated within 45 minutes to 106° C. and the yarn dyed for one and a half hours at said temperature and rinsed.

Then, the goods were rinsed once more for 20 minutes, finally cleaned at 80° C. in an aqueous washing liquor to which acetic acid and a non-ionic detergent of the type of a highly ethoxylated fatty acid polyglycol ether had been added, rinsed once more and dried.
A uniform grey dyeing was obtained on both the polyester and the wool portion of the mixed yarn.

**EXAMPLE 8**

The dyeing was produced as described in Example 1, however using instead of the o-phenylenephonol indicated in said example as auxiliary the products given below:

<table>
<thead>
<tr>
<th>Auxiliary</th>
<th>Quantity used (gram/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Dichlorobenzene</td>
<td>4</td>
</tr>
<tr>
<td>Terephthalic acid dimethyl ester</td>
<td>10</td>
</tr>
<tr>
<td>Diphenyl</td>
<td>3</td>
</tr>
<tr>
<td>p-Hydroxyethyl-p-chlorophenyl ether</td>
<td>4</td>
</tr>
</tbody>
</table>

Using the above mentioned auxiliaries according to Example 1 there were likewise obtained distinctly deeper shades than produced in the absence thereof.

We claim:

1. In a process for dyeing wool fibers in a fibrous material containing wool with a complex metal azo dyestuff in a dye bath containing an acid or an acid-yielding agent, the improvement which comprises dyeing the wool fibers in said fibrous material containing wool in a dye bath containing a water-insoluble or water-sparingly soluble 1:2 metal complex azo dyestuff, an acid or an acid-yielding agent and, as a carrier auxiliary, o-phenylenephonol, p-phenylenephonol, diphenyl, o-dichlorobenzene, terephthalic acid dialkyl ester or hydroxyalkyl-phenol ether.

2. The improvement according to claim 1 wherein the metal of said metal complex azo dyestuff is chromium or cobalt.

3. The improvement according to claim 1 wherein said metal complex azo dyestuff is substantially free from groups imparting water solubility.

4. The improvement according to claim 1 wherein said carrier auxiliary is o-phenylenephonol.

5. The improvement according to claim 1 wherein said carrier auxiliary is p-phenylenephonol.

6. The improvement according to claim 1 wherein said carrier auxiliary is diphenyl.

7. The improvement according to claim 1 wherein said carrier auxiliary is o-dichlorobenzene.

8. The improvement according to claim 1 wherein said carrier is terephthalic acid dimethyl ester.

9. The improvement according to claim 1 wherein said carrier auxiliary is p-hydroxyethyl-p-chlorophenyl ether.

**References Cited**

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