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[54] **PROCESS FOR THE SINGLE-BATH DYEING OF UNMODIFIED POLYOLEFIN FIBERS WITH WATER-INSOLUBLE PIGMENT DYESTUFFS**

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[58] **Field of Search** 8/169, 172, 176, 180

[56] **References Cited**

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[57] **ABSTRACT**

Process for the single-bath dyeing or printing of unmodified polyolefin fibers with water-insoluble pigment dyestuffs by reacting under high-temperature dyeing conditions on these textile materials aqueous liquors or printing pastes containing solutions of pigment dyestuffs reversibly solubilized by cationactive compounds and, optionally, strong alkalis, and substances splitting off acid under heat, or dispersions of the salt-like addition products of dyestuffs having anionic character with cationic compounds, in the presence of a dispersion system on the basis of polyglycol ethers.

8 Claims, No Drawings

PROCESS FOR THE SINGLE-BATH DYEING OF UNMODIFIED POLYOLEFIN FIBERS WITH WATER-INSOLUBLE PIGMENT DYESTUFFS

The present invention relates to a process for the single-bath dyeing of unmodified polyolefin fibers with water-insoluble pigment dyestuffs.

It is known that unmodified polyolefin fibers, for example, polypropylene fibers, are, generally, difficult to dye by direct dyeing methods. Besides the immediate dyeing of the spinning mass in the melt with pigment dyestuffs, the dyeing of piece goods made of such fibers with aqueous suspensions of pigment dyestuffs and curable binding systems is described which form a correspondingly coloured film layer fast to washing on the fiber surface when being heated. Disperse dyes used for dyeing polyester fibers and other hydrophobic fibers, however, yield under comparable thermal conditions only very fair dyeings when being fixed the yield of which is unproportioned with respect to the amount of dyestuff used.

Various methods of the modification of the polyolefin material allow to improve the dye receptivity of the fiber considerably. For example, nitrogen-containing copolymers having a basic effect are introduced into the spinning melt of the fibrous ground substance of which the fibers consist and so anchored in the macromolecule. The fibers so modified then have affinity towards the anionic dyestuffs. Polypropylene can also be modified in such a manner that compounds of such metals which can form fast colour lakes with metallizable dyestuffs are incorporated into the mass or fiber. Thus, the fiber properties are influenced either by a metal-containing copolymer or by special aftertreatment operations of the finished, unmodified fibrous material before dyeing, for example, as described in German Auslegeschriften Nos. 1,297,577, 1,469,600 and 1,619,601. But each of these processes for the modification of polyolefins requires additional operational expenditure which makes the fiber more expensive and sometimes inadvertantly affects the physical properties of the fiber, for example, by reducing its stability and elasticity or by increasing its inflammability.

It was now, found, that unmodified polyolefin fibers, preferably polypropylene fibers, can be dyed or printed in a single-bath operation with water-insoluble pigment dyes when allowing to act, under high temperature dyeing conditions, on these textile materials aqueous liquors or printing pastes containing solutions of pigment dyestuffs reversibly solubilized by cation-active compounds and, optionally, strong alkalis, and substances splitting off acid under the action of heat, or dispersions of the salt-like addition products of dyestuffs having anionic character with cationic compounds, in the presence of a dispersion system on the basis of polyglycol ethers.

This invention is based on the observation that the solubilized pigment dyestuffs mentioned above have technically useful affinity towards the highly hydrophobic, unmodified polyolefin fibers when they are present in a special colloidal state of dispersion while concommittently using acid-yielding agents and a determined dispersion system and are applied under suitable thermal conditions. Under these conditions the dyeings or prints can be effected according to the present process using the exhaustion method, the pad-steaming method or a printing method together with steam fixation of the

dyes. The temperatures required for this purpose in the case of the exhaustion method as well as of the pad-steaming or print-steaming method are within the range of from 120° – 135°C, preferably, however, about 130°C. These temperatures comprise a technical safety zone between the range of temperature of 150° – 155°C at which the polypropylene fiber softens. The times of action are with the exhaustion method 50 to 70 minutes, preferably 60 minutes, and with the pad-steaming or print-steaming method from 25 to 45 minutes, preferably 30 minutes.

The dyestuffs to be used for carrying out the dyeings according to the new method are derived from water-insoluble organic pigment dyestuffs, for example, azo, anthraquinone, phthalocyanine or similar pigments. According to the processes described in German Patents Nos. 1,265,700, 1,269,587, 1,297,071 and 1,297,073 they are made reversibly water-soluble by means of highly cationactive components, for example, quaternary ammonium compounds, especially those of the type of alkyldimethyl-benzyl-ammonium chloride, optionally in the presence of strong alkalis. The dyestuffs hereinbefore mentioned have a marked affinity towards the surface of the fiber already at the beginning of the dyeing process because of their cationactive component. The dyestuff is thus concentrated at the surface where the diffusion of the pigment into the fiber occurs under high-temperature dyeing conditions.

To carry out the process of the invention it is essential that the dissolved dyestuff, when being reprecipitated, is suitably distributed under the action of acid-yielding agents. The dyestuff can so diffuse into and be absorbed by the fiber which is, at best, achieved by means of a mixture of auxiliaries. This dispersion system mainly consists of a non-ionic auxiliary on the basis of alkyl- or alkylaryl-polyglycol ethers or oxethylated fatty acid polyglycol esters, preferably a reaction product of 1 mol of isotridecyl alcohol with 8 mols of ethylene oxide, which is combined in the case of the exhaustion method optionally with anionic protective colloids having a dispersing effect, preferably those on the basis of lignin-sulfonic acid, and in the case of the pad-steaming or print-steaming method with non-ionic protective colloids having a thickening effect, preferably of the type of a completely etherified locust bean flour.

When performing the process of the invention it could not be expected that the use of acid-yielding agents which are only active at higher temperatures, for example, of the type of monohalogenated acetates of alkali metals, preferably sodium monochloro-acetate, increases the color yield to such a considerable degree that it can be considered as a prerequisite for an economic operation of the process of the invention. By lowering the pH under the action of the acidyielding agent the cationic compound which is only loosely bound is split off and the dyestuff is converted from the dissolved into the dispersed form.

When performing the process of the invention it was also found that dyeings could also be obtained on unmodified polyolefin fibers (under analogous dyeing conditions in the high temperature range) also with combinations of any anionic, water-soluble or dispersed dyestuff, for example, acid dyestuffs, with strongly cationic auxiliaries, for example, of the type of alkyl-dimethyl-benzyl-ammonium chloride, its deriva-

tives, mixtures or other surface-active quaternary fatty amines.

Those cationic products produce with anionic dyestuffs precipitations. When using suitable dispersing agents, for example, oxethylated fatty alcohols, it is possible to maintain these salt-like addition compounds in such a finely colloidal state of dispersion that a diffusion in the fiber under high-temperature dyeing conditions and thus, staining of the material is possible. The cationic precipitating agent can develop, when being in excess, such a dispersing effect.

The following Examples illustrate the invention. The Colour-Index numbers indicated in the Examples to characterize the dyestuffs have been taken from the second edition 1956 and from the supplement volume 1963.

EXAMPLE 1

Loose material of unmodified polypropylene fibers was dyed in a high-temperature dyeing apparatus, with a goods-to-liquor ratio of 1:20 for 60 minutes with an aqueous liquid of 130°C which contained, calculated on the weight of the dry material, the following constituents:

2 percent of the azo dyestuff Pigment Yellow 12 - C.I. No. 21,090, dissolved according to the process described in German Patent No. 1,265,700,
2 percent of sodium monochloroacetate and
1 percent of the reaction product of 1 mol of isotridecyl alcohol with 8 mols of ethylene oxide.

Then, the material so treated was rinsed with warm and cold water and finished in the usual manner.

A brilliant, fast yellow dyeing was obtained the colour intensity of which corresponded to the amount of dyestuff used.

EXAMPLE 2

Dyeing was carried out in an analogous manner as described in Example 1 while using, however,

2 percent of the dyestuff copper-phthalocyanine-trisulfonic acid anilide dissolved according to the process described in German Patent No. 1,269,587.

A brilliant, blue dyeing fast to light and to washing was obtained.

EXAMPLE 3

Dyeing was carried out in an analogous manner as described in Example 1 while using, however,

1 percent of the azo pigment indicated in Example 1
1 percent of the copper phthalocyanine dyestuff indicated in Example 2

both dyestuffs being dissolved according to the methods described in the literature indicated above.

A brilliant, fast green dyeing was obtained.

EXAMPLE 4

Dyeing was carried out in an analogous manner as described in Example 1 while using, howver,

2 percent of an azo dyestuff obtained by coupling 2 mols of a-phenyl-3-methyl-5-pyrazolone with the diazo compounds of 0.3 mol of dianisidine and 0.7 mol of dichlorobenzidine, which was made soluble according to the process described in German Patent No. 1,265,700.

A brilliant, fast red dyeing was obtained.

EXAMPLE 5

Piece-goods of unmodified polypropylene fibers were padded, with a liquor-pick-up of 70 % by weight, with a cold liquid which contained per liter of water the following constituents:

16 g of the dyestuff indicated in Example 1 and dissolved as described hereinbefore,
5 g of the reaction product of 1 mol of isotridecyl alcohol with 8 mols of ethylene oxide,
10 g of a 2 % aqueous solution of a completely etherified locust bean flour and
10 g of sodium monochloroacetate.

After having applied the dyestuff the material so treated was dried at 100°C, steamed at 130°C for 30 minutes in a pressure steamer and rinsed and finished in the usual manner.

A brilliant, fast yellow dyeing was obtained the colour depth of which corresponded to the amount of dyestuff used.

When proceding by this method prints can also be effected on the material.

EXAMPLE 6

Dyeing was carried out, in an analogous manner as described in Example 5 while using, however, a padding liquor which contained instead of the dyestuff mentioned in this Example

10 g/l of the dyestuff indicated in Example 1 and
10 g/l of the dyestuff indicated in Example 2.

A brilliant fast green dyeing was obtained.

EXAMPLE 7

Dyeing was carried out as described in Example 5 while using, however, a padding liquor which contained in addition to the auxiliaries mentioned therein

4 g/l of the dyestuff indicated in Example 1,
5 g/l of the dyestuff indicated in Example 2 and
8 g/l of the dyestuff indicated in Example 4.

A fast brown dyeing was obtained.

We claim:

1. A process for the single-bath dyeing or printing of unmodified polypropylene fibers with water-insoluble pigment dyestuffs, which comprises: treating said fibers, under high temperature dyeing conditions above 120°C, with aqueous liquors or printing pastes containing,

1. a pigment dyestuff which is reversibly solubilized by a cation-active quaternary ammonium compound and strong alkali,
2. a compound which yields acid at temperatures above 100°C, and
3. a dispersion system based upon polyglycol ethers or esters.

2. A process as claimed in claim **1**, wherein the dyestuffs are applied on the fibers according to the exhaustion method for 50 to 70 minutes at a temperature from 120°C to 135°C.

3. A process as claimed in claim **1**, wherein the dyestuffs are padded or printed onto the fibers and these paddings or prints are steamed in a pressure steamer at 120° - 135°C for 20 to 45 minutes.

4. A process as claimed in claim **1**, wherein dyestuffs of the azo, anthraquinone or phthalocyanine series are used.

5. A process as claimed in claim 1, wherein as acid-yielding agent monohaloacetates of alkali metals are used.

6. A process as claimed in claim 1, wherein as cationic quaternary compound, an alkyl-dimethyl-benzyl-ammonium chloride is used.

7. A process as claimed in claim 2, wherein as dispersion system for the exhaustion method, anionic protective colloids having a dispersing effect based upon lignin-sulfonic acid are used in combination with a non-ionic auxiliary based upon the reaction product of 1 mol of isotridecyl alcohol with 8 mols of ethylene oxide.

8. A process as claimed in claim 3, wherein as dispersion system for the pad-steaming or print-steaming method, nonionic auxiliaries based upon the reaction product of 1 mol of isotridecyl alcohol with 8 mols of ethylene oxide are used in combination with non-ionic protective colloids having a thickening effect of the type of a completely etherified locust bean flour.

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