United States Patent [19]

Reinhardt et al.

[11] **3,844,710**

[45] **Oct. 29, 1974**

[54] **DYEING POLYESTERS OR CELLULOSIC ESTERS WITH PRINTING PASTE CONTAINING BUTANE DIOL POLYGLYCOL ETHER AND NAPHTHOL POLYGLYCOL ETHER**

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[21] Appl. No.: **293,143**

[30] **Foreign Application Priority Data**

Sept. 30, 1971 Germany 2148867

[52] **U.S. Cl.** **8/62,** 8/169, 8/74, 8/165

[51] **Int. Cl.** **D06p 1/82**

[58] **Field of Search** 8/169, 173, 93

[56] **References Cited**

UNITED STATES PATENTS

3,706,525	12/1972	Blackwell	8/21 C
3,752,649	8/1973	Smerz et al.	8/169

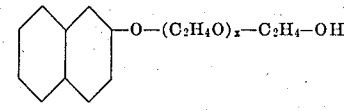
FOREIGN PATENTS OR APPLICATIONS

1,184,730	7/1959	Germany	8/173

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[57] **ABSTRACT**

A process for printing disperse dyes on polyester, cellulose-triacetate or cellulose 2,5 acetate which consists of applying onto the textile material a printing paste of usual composition which contains additionally 2 to 7 percent of a fixing auxiliary mixture of a compound of the formula



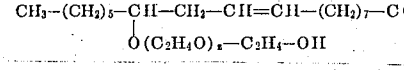
(1)

wherein x is zero or an integer from 1 to 4 and of a compound of the formula

$$HO—C_4H_8—O\,[A]\,—OC—R_1$$

(2)

wherein R_1—CO— is alkanol with 12 to 22 carbon atoms and [A] is a polyethylene oxide and/or a polypropylene oxide chain consisting of from 3 to 20 members, in a ratio of 1:10 to 10:1 by weight and fixing the prints under the conditions used for fixing disperse dyes. The auxiliary mixture may further contain 0.5 to 12 percent by weight of a compound of the formula



(3)

wherein *z* is an integer from 1 to 50 and/or (4) 0.5 to 12 percent by weight of a monoalkyl- or dialkylbenzenesulfonic acid with 3 to 20 carbon atoms in the alkyl chain.

The use of combinations of compound (1) with compound (2) enables brilliant shades and excellent dyestuff yields to be obtained without perceptible deterioration of the fastness to light as has happened with previously used carriers. When adding even slight amounts of compounds (3) and/or (4) the color yield is further improved to an optimum degreee without affecting the shade and fastness to light. The good dispersion effect of the compound (2) on the compound (1) decisively improves the carrier effect of the latter which also allows them to be easily washed out of the fibrous material after the fixation in the following usual after-treatment baths. The favorable effects of the two components acting together prevent the darkening of the shades on the prints and the reduction of the fastness to light practically completely.

2 Claims, No Drawings

DYEING POLYESTERS OR CELLULOSIC ESTERS WITH PRINTING PASTE CONTAINING BUTANE DIOL POLYGLYCOL ETHER AND NAPHTHOL POLYGLYCOL ETHER

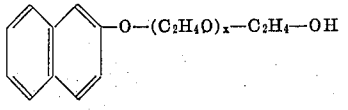
The present invention relates to a process for the continuous fixing of disperse dyestuffs on polyester, cellulose-triacetate and cellulose-2½-acetate and mixtures thereof.

The continuous fixing of disperse dyestuffs on polyester, cellulose-triacetate and cellulose-2½-acetate and mixtures thereof can be carried out either with hot air at from 180° to 200° C or with saturated steam at about 102° to 105° C. It is advantageous to use various accelerating agents, called carriers, during fixation in order to obtain a better dyestuff fixation. These carriers are especially used in thermofixation and steaming at high temperatures. It has become apparent that in the steaming process, especially on cellulose-2½-acetate, higher dyestuff yields can be obtained by the use of carriers. This has the special advantage that the same printing pastes can be used for all the above-mentioned fibrous materials.

Carriers that have been proposed are those on the basis of hydroxy-diphenyl, methylnaphthalene, benzoic acid or salicylic acid alkyl esters and oxethylation products of alkyl phenols. Surface-active esterification products of carboxylic acids with high-molecular polyglycols generally used for synthetic fibers (such as those described in German Auslegeschrift No. 1,138,735) may be used as fixing auxiliary agents, as may alkylation products of fatty acids, fatty acid monoesters or fatty amines (German Pat. No. 1,184,730) the fatty acids having been condensated in a molar ratio of 1:1 with butan-1,4-diol pentaglycol ethers.

These carriers have so far mostly been used as fixing auxiliaries only for dyeings as they have proved inadequate for prints. Other drawbacks are that they can soil the dyeings as they can themselves be washed out of the fibrous material only with difficulty and to a limited extent, and that prints obtained with such auxiliaries generally do not have a good fastness to light. The latter products which do not have the drawbacks mentioned above, are, in general, not satisfactory as carriers.

It was now found that these drawbacks could be overcome when using for the continuous fixing of prints with disperse dyes on fibrous materials of polyester, cellulose-triacetate, cellulose-2½-acetate or a mixture of any two or more thereof or a mixture of any one or more thereof with wool, natural or regenerated cellulose fibers or other synthetic fibers, combinations of fixing auxiliaries of two or more components, the one constituent being an oxethylated naphthol of the general formula (1)



(1)

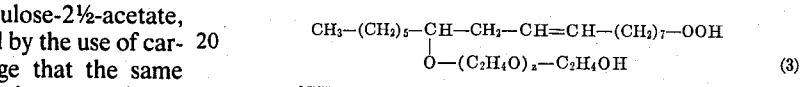
wherein x is zero or an integer from 1 to 4, and the second constituent being a monocarboxylic acid ester of the butan-(1,4)-diol polyglycol ether of the general formula (2)

$$HO—C_4H_8—O[A]—OC-R_1 \qquad (2)$$

wherein R_1—CO— is the acyl radical of a linear or branched alkane or alkene-monocarboxylic acid having from 12 to 22 carbon atoms, preferably from 16 to 22 carbon atoms and [A] is a chain of polyethylene oxide and/or polypropylene oxide having from three to 20, preferably from five to 15 members.

The mixing ratio of these two groups of fixing auxiliaries may vary within wide limits. Even at a weight ratio of 1:10 or 10:1 the poor properties of the individual components can be improved considerably, but the best effects are obtained at a mixing ratio in the range of from 1:3 to 3:1.

It was also found that a much better dyestuff yield could be obtained when adding to the above fixing auxiliaries from 0.5 to 12 percent by weight, preferably, however, from 3 to 6 percent by weight of oxethylated ricinoleic acid of the general formula (3)



(3)

wherein z is an integer from 1 to 50, perferably from 20 to 35, and/or from 0.5 to 12 percent by weight, preferably from 3 to 6 percent by weight of a further product (4) on the basis of mononuclear benzenesulfonic acids which contain at least one linear or branched alkyl group having from three to 20 carbon atoms, preferably from eight to 16, in which case the sulfonic acid group can be present in the form of the free acid, preferably however as an alkali metal or alkaline earth metal salt.

The compounds that are most preferably used are the following:

1. compounds of the formula (1): two to four times oxethylated β-naphthols or mixtures thereof;
2. compounds of the formula (2): unsymmetrical butan-(1,4)-diol-l-polyglycolether-mono-fatty acid esters having from five to 15 glycol units, the glycol chain being esterified by, preferably, oleic acid, palmitinic acid, stearic acid, lauric acid, nonadecanoic acid, myristinic acid and palmitoleic acid, for example, butan-(1,4)-diol-penta-ethyleneglycol ether-ω-monostearic acid ester or -palmitinic acid ester, butan-(1,4)-diol-l-decaethyleneglycol ether-ω-monostearic acid ester or-palmitinic acid ester, the monooleyl esters of the butan-(1,4)-diol-l-penta, deca, or pentadeca-ethyleneglycol ether and the monoesters of palmitinic acid or stearic acid with the butan-(1,4)-diol-l-ethyleneglycol ether or mixtures thereof;
3. compounds of the formula (3): oxethylating products of the ricinoleic acid which contains from 20 to 35 units of ethylene oxide or mixtures of these products which are prepared, for example, by the action of ethylene oxide or propylene oxide on ricinoleic acid;
4. compounds of the product (4): linear or branched alkane-benzenesulfonic acids, preferably those of the calcium salt, for example, para-pentadecyl-benzenesulfonic acid, para-dodecyl and para-nonyl-benzenesulfonic acid, the ortho-compounds thereof and the 4-dodecyl-2-nonyl-benzenesulfonic acid, the decyl, octyl and hexadecyl-benzenesulfonic acids which may contain a further long-chained alkyl group in para-position, or other closely related compounds which are analogous in their isomeric positions. The compounds (1), (2) and, optionally, (3) and (4) are added to the printing pastes as auxiliary agents in a total amount of from

20 to 70 g per kilogram of printing paste, preferably, however, from 30 to 50 g.

The use of combinations of compounds of formula (1) with compounds of formula (2) enables in the printing process brilliant shades and excellent dyestuff yields to be obtained without perceptible deterioration of the fastness to light as has happened with previously used carriers. When adding even slight amounts of compounds of formula (3) and/or (4) the color yield is further improved to an optimum degree without affecting the shade and fastness to light. The good dispersion effect of the compounds of formula (2) on the compounds of formula (1) decisively improves the carrier effect of the latter which also allows them to be easily washed out of the fibrous material after the fixation in the following usual after-treatment baths. The favourable effects of the two components acting together prevent the darkening of the shades on the prints and the reduction of the fastness to light practically completely.

The material to be printed according to the present process is textile material, for example, woven or knitted fabric or fibre fleeces, consisting of or containing cellulose-2½-acetate, cellulose-triacetate or a high-molecular linear polyester, mixtures of polyethylene terephthalate fibers with wool, natural or regenerated cellulose fibers or other synthetic fibers, such as polyamides or polyacrylonitrile may also be used.

The fibrous material is preferably printed with a product generally known under the name of disperse dyestuffs, for example those selected from the class of the azo or anthraquinone dyestuffs or those of the quinophthalone type. The dyestuff fixation is carried out in the usual manner with hot air at from 170° to 220° C or with saturated steam at from 100° to 110° C or with hot steam at from 140° to 190° C.

The use of combinations of fixing auxiliaries of oxethylated naphthols of the formula (1) with compounds of the formula (2) alone or in combination with slight additives of compounds of formula (3) and/or (4) allows all three types of fibres mentioned to be printed with a single printing paste mixture, which is an operational advantage.

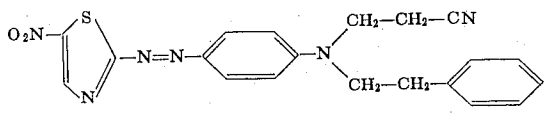
Prints which are prepared according to the process of the invention are distinguished by an excellent dyestuff yield.

Furthermore, the fixing auxiliaries to be used in accordance with the invention facilitate the elimination of the carriers also used by their emulsifying properties in the usual after-treatments of dyeings and prints, so that the shades are protected from being spoiled and, in addition to the usual properties, an optimum fastness to light is obtained.

The following Examples illustrate the invention, the parts and percentages being by weight unless stated otherwise.

EXAMPLE 1

30 g of the disperse dyestuff of formula



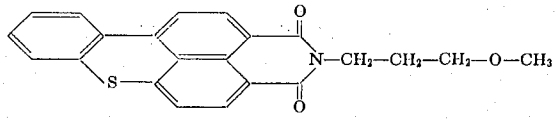
in commercial form and standard, were first pasted with 100 g of cold water and then dispersed with 330 g of boiling water. This dispersion was introduced via a sieve into 500 g of a stock thickening which consisted of a mixture of 750 g of a 13 percent aqueous locust-flour thickening. 200 g of a 10 percent aqueous sodium alginate thickening. 48 g of an aqueous solution of 15 g of m-nitrobenzene-sulphonic acid sodium and 3 g of monosodium phosphate, and 40 g of a mixture of 10 g of butan-1,4-diol-pentaglycolether-mono-stearic acid ester and 30 g of an addition product of 4 moles of ethylene oxide and 1 mole of β-naphthol were then introduced while stirring and the printing paste was then filled up to 1 kg with water.

With the above-mentioned printing paste, a knitted fabric from textured polyethylene terephthalate fibers was printed, dried and steamed at 180° C for 8 minutes in a high-temperature steaming apparatus for the fixation of the dyestuff. Finally, the material was rinsed and soaped in the usual manner.

A brilliant violet print was obtained in a high yield having good fastness properties.

EXAMPLE 2

40 g of a powdery disperse dyestuff of the formula



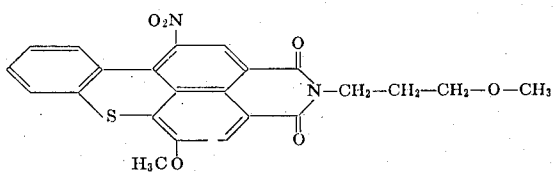
in commercial form and standard were first pasted with 100 g of cold water and then dispersed with 300 g of hot water and introduced via a sieve in 550 g of a thickening while stirring, which consisted of a mixture of equal parts of a 25 percent crystal gum thickening and a 10 percent aqueous solution of a commercial starch ether. Then there were also introduced, while stirring, 25 g of an aqueous solution of 8 g of m-nitrobenzene-sulphonic acid sodium and 2 g of monosodium phosphate, as well as 30 g of a mixture of 18 parts of a two times oxethylated β-naphthols, 9 parts of butan-1,4-diol pentaglycolether monostearic acid ester, 1.5 parts of the calcium salt of the tetrapropylene-benzensulfonic acid and 1.5 parts of the addition product of 32 moles of ethylene oxide and 1 mole of ricinoleic acid.

With the above-mentioned printing paste, a fabric of cellulose-2½-acetate was printed, dried and steamed at a temperature of 100° to 102° C for 8 minutes in a continuous steamer for the fixation of the dyestuff and then finished in the usual manner.

A brilliant, yellow print was obtained in a high yield having excellent fastness properties.

EXAMPLE 3

40 g of the disperse dyestuff of the formula

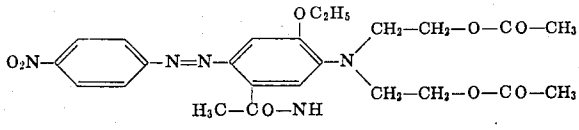


in commercial form and standard were first pasted with 100 g of cold water and then dispersed with 300 g of boiling water and introduced via a sieve into 500 g of an aqueous thickening while stirring which consisted of a mixture of equal parts of a 25 percent crystal gum thickening and a 10 percent aqueous solution of the esterification product of polyglycol (molar weight 2,000) and of stearic acid. Then, there was also added 25 g of an aqueous solution consisting of 8 g of m-nitrobenzenesulphonic acid sodium and 2 g of monosodium phosphate as well as 40 g of a mixture of equal parts of butan-1,4-diol pentaglycolether monopalmitic acid ester and the addition compound of 4 moles of ethylene oxide and 1 mole of β-naphthol.

With this printing paste, a fabric of polyethylene terephthalate fibers was printed, dried and thermofixed at 195° C for 45 seconds on a stenter frame for the fixation of the dyestuff, and then finished in the usual manner. A brilliant pink printing design was obtained in an excellent yield having good fastness to light and to wet processing.

EXAMPLE 4

70 g of a powdery disperse dyestuff of the formula



in commercial form and standard were first pasted with 100 g of cold water and then dispersed with 290 g of hot water and then introduced via a sieve into 500 g of a stock-thickening (having the constitution described in Example 1) while stirring. Then, there were also added 35 g of a mixture of 60 parts of the addition product of 2 moles of ethylene oxide and 1 mole of β-naphthol, 30 parts of butan-1,4-diol decaglycolether monostearic acid ester and 10 parts of pentapropylenebenzenesulfonic acid calcium.

With this printing paste, a fabric of cellulose-triacetate was printed, dried and thermofixed at 185° C for 60 seconds on a stenter frame for the fixation of the dyestuff and then aftertreated in usual manner by rinsing and soaping.

A deep, navy-blue print was obtained in a very good yield having good fastness to use and light.

EXAMPLE 5

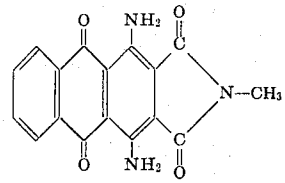
40 g of the dyestuff of the formula given in Example 3 were first pasted with 100 g of cold water and then dispersed with 295 g of hot water and then intorudced via a sieve in 500 g of a 10 percent aqueous thickening of a commercial starch ether while stirring. Then, there were also introduced 25 g of an aqueous solution of 8 g of m-nitrobenzensulfonic acid sodium and 2 g of monosodium phosphate as well as 40 g of a mixture of 3 parts of butan-1,4-diol pentaglycolether-monostearic acid ester and 1 part of the addition product of 2 moles of ethylene glycol and 1 mole of β-naphthol.

With the printing paste so prepared, a fabric of polyethylene terephthalate fibers was printed, dried and steamed at 180° C for 6 minutes in a high-temperature steaming apparatus for the fixation of the dyestuff. After the usual after-treatment a brilliant pink print was obtained in an optimum yield and with an excellent fastness to light and to wet processing.

The color yield was similarly good when the fabric was thermofixed on a stenter frame at 185° C for 60 seconds instead of being steamed.

EXAMPLE 6

40 g of the disperse dyestuff of formula



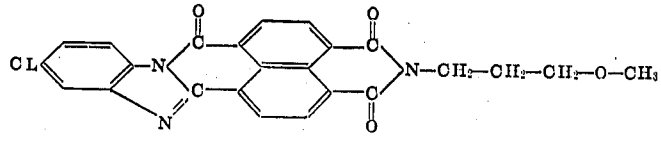
in commercial form and standard were first pasted with 85 g of cold water and then dispersed with 250 g of boiling water and introduced via a sieve in 600 g of a thickening while stirring, which consisted of a mixture of equal parts of a 25 percent crystal gum thickening and a 12 percent aqueous solution of the addition compound of 10,000 moles of ethylene oxide and 1 mole of stearic acid. Then, there were also added 25 g of an aqueous solution of 8 g of m-nitrobenzenesulfonic acid sodium and 2 g of monosodium phosphate and 35 g of a mixture of 60 parts of the addition product of 4 moles of ethylene oxide and 1 mole of β-naphthol, 30 parts of butan-1,4-diol pentadecaglycolether monooleyl ester and 10 parts of the addition product of 25 moles of ethylene oxide and 1 mole of ricinoleic acid.

A fabric of cellulose-triacetate was printed with the printing paste described above on a roller printing machine, dried and steamed at 180° C for 5 minutes on a high-temperature steaming apparatus for the fixation of the dyestuff and then finished in the usual manner.

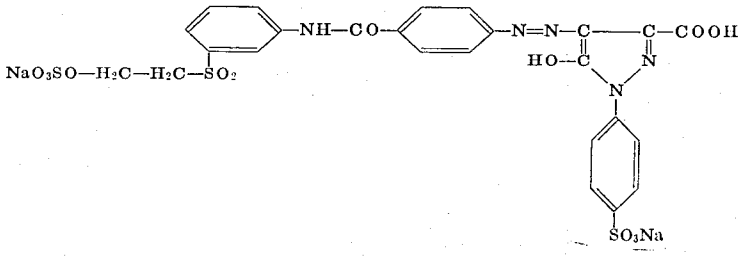
A limpid blue print was obtained in an excellent yield having very good properties.

EXAMPLE 7

A mixture of 24 g of the disperse dyestuff of formula



in commercial form and standard and 16 g of the reactive dyestuff of formula



in commercial form and standard were first pasted with 105 g of cold water and then dissolved or dispersed with 250 g of boiling water. This dispersion was then introduced in a mixture of 350 g of an aqueous sodium alginate thickening and 200 g of a 10 percent aqueous solution of the esterification product of polyethylene glycol (molecular weight: about 2,000) with stearic acid while stirring and then, 25 g of an aqueous solution of 8 g of m-nitrobenzenesulfonic acid sodium and 2 g of monosodium phosphate as well as 30 g of a mixture of 55 parts of the addition product of 2 moles of ethylene oxide and 1 mole of β-naphthol, 35 g of butan-1,4-diol pentaglycolether monostearic acid ester, 5 parts of tetrapropylenebenzenesulfonic acid calcium and 5 parts of 32 times oxyethylated ricinoleic acid were added.

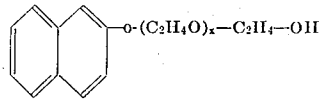
With this printing paste, a mixed fabric of polyethylene terephthalate fibers and mercerized cotton, in a ratio of 67:33, was printed and dried. Then, the material was thermofixed at 200° C for 40 seconds on a stenter frame for the fixation of the disperse dyestuff and then padded with an alkaline solution containing electrolytes according to the two-phase-cold-dwell process for the fixation of the reactive dyestuff, which solution had the following composition:

180 g of calcined sodium sulfate, 50 g of anhydrous potassium carbonate, 150 g of anhydrous sodium carbonate, and 100 g of sodium hydroxide solution at 38° Be(32.5 percent), and, after a short passage in the air for about 20 seconds, it was stored for 4 hours when plaited down and batched up.

After the usual after-treatment, a limpid yellow print was obtained in an optimum color yield and with excellent shades having very good fastness properties as to light and to wet processing.

What we claim is:

1. A process for printing disperse dyes on polyester, cellulose-triacetate or cellulose-2,5-acetate which consists of applying onto the textile material a printing paste of usual composition which contains additionally 2 to 7 percent of a fixing auxiliary mixture of a compound of the formula



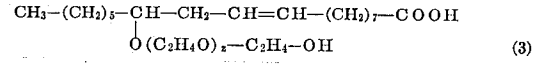
(1)

wherein x is zero or an integer from 1 to 4 and of a compound of the formula

$$HO\text{-}C_4H_8\text{-}O[A]\text{-}OC\text{-}R_1 \qquad (2)$$

wherein R_1—CO— is alkanoyl with 12 to 22 carbon atoms and [A] is a polyethylene oxide and/or a polypropylene oxide chain consisting of from three to 20 members, in a ratio of 1:10 to 10:1 by weight, and fixing the prints under the conditions used for fixing disperse dyes.

2. A process as claimed in claim **1**, wherein the fixing auxiliary mixture contains additionally 0.5 – 12 percent by weight of a compound of the formula



(3)

wherein z is an integer from 1 to 50 and/or 0.5 to 12 percent by weight of a monoalkyl- or dialkylbenzenesulfonic acid with three to 20 carbon atoms in the alkyl chain.

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