PATENT SPECIFICATION (11) 1 568 759

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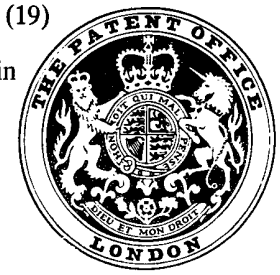
(21) Application No. 52255/77 (22) Filed 15 Dec. 1977
(31) Convention Application No. 2657216 (32) Filed 17 Dec. 1976 in
(33) Fed.Rep of Germany (DE)
(44) Complete Specification Published 4 Jun. 1980
(51) INT. CL.[3] D06P 3/68
(52) Index at Acceptance
D1B 2A2




# (54) PROCESS FOR DYEING CELLULOSE FIBERS

(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a process for dyeing cellulose fibers with insoluble azo dyestuffs produced from their components on the fibers.

The two-bath dyeing of cellulose fibers by the batch exhaustion method with dyestuff components of insoluble azo pigments, in which the coupling component is in the bottoming bath, and the diazo component is in the developing bath, has been known for some years.

In addition, German Auslegeschrift No. 22 13 241 describes a process for dyeing cellulose fibers and mixtures thereof with synthetic fibers, with water-insoluble azo dyestuffs produced on the fibers in a single bath by the batch exhaustion method, in which an aqueous bath is allowed to act upon the textile material at about room temperature, the bath containing, in addition to an alkaline agent, sodium nitrite and an anionic dispersing system, also a solution or dispersion of at least one axo coupling component and of at least one undiazotized primary aromatic amine in a medium based on an organic solvent or solubilizer which is miscible with water and, following the absorption of the coupling component, adding an acid or acid salt to the dye bath at room temperature to cause diazotization of the amine and formation of the dyestuff by coupling, on the fiber.

However, a dyeing process of this type is very time-consuming or requires the use of special apparatus to reduce the dyeing period, for example, by applying different pressures. In order to produce the necessary differences in pressure, the process is carried out at an elevated temperature.

The present invention seeks to provide a quick-dyeing batch exhaustion process for the development of azo pigments on cellulose fibers or mixtures of cellulose fibers with synthetic fibers, which can be carried out without applying a pressure above atmospheric pressure at normal temperature (20° to 40°C) using conventional apparatus, and which can be carried out in less time than conventional dyeing methods of this type.

Surprisingly, it has been found that these objects can be met by impregnating the material with the aromatic amine, the nitride and the coupling component with rapid circulation of the bath and/or the material, and by subsequently diazotizing and coupling the dyestuff by increasing the bath temperature to up to 50°C. Such a process has the advantage that it does not require the application of an elevated pressure.

The present invention therefore provides a process for dyeing a textile material, preferably in the form of a wound package, consisting of or containing cellulose fibers with a water-insoluble azo dyestuff which comprises circulating through the material at a rate of at least 5 times per minute for a period of from 10 to 20 minutes under atmospheric pressure at a temperature of from 10 to 40°C, preferably from 15 to 25°C, an aqueous alkaline liquor which contains sodium nitrite, an anionic dispersing agent and a solution or dispersion of at least one azo coupling component and at least one primary aromatic amine in a water-miscible organic solvent or solubilizer, and then acidifying the liquor with an organic acid and heating the liquor to a temperature of from 30 to 50°C to cause diazotization and

coupling, within a total dyeing period of not more than 30 minutes. Owing to the presence of an anionic dispersing agent in the liquor, no coarse dyestuff pigments are deposited on the fiber surface in spite of using only a single bath, so that after-treatment of the fibers is also made considerably simpler and shorter.

The process of the present invention is a quick-dyeing method for naphthol-based azo developing dyestuffs, which is especially surprising. The advantages of this process are that the use of a simple single bath no longer requires the calculation of factors such as the alkali binding power, which have been common hitherto; and that the considerably shorter time required for dyeing and the good reproducibility of dyeing and fastness properties compete favourably with the ice colour technique and other dyeing processes for cellulose fibers.

In the process of the present invention, the desired naphthol and desired primary aromatic amine are added to the dye liquor containing an anionic dispersing agent, sodium hydroxide solution, optionally from 10 to 30 g/l of salt and the sodium nitrite necessary for the subsequent diazotization, and the textile material is treated with this bottoming liquor at a temperature of from 10 to 40°C, preferably from 15 to 25°C, for a period of from 10 to 20 minutes. Subsequently the liquor is rapidly rendered acid with an organic acid, whereby diazotization and coupling of the azo dyestuff are generally effected at a temperature of from 30 to 50°C. Subsequently, there can be carried out an after-treatment which is convention for azo developing dyestuffs.

For use in this process, there may be used the coupling components conventionally used in the ice colour technique; according to the present invention, there are used those coupling components which have a substantive and/or highly substantive character towards the fibrous material. These are compounds which are coupled in a neighboring position to a hydroxy group and which do not have any solubilizing group, especially arylamides of aromatic or heterocyclic *o*-hydroxy-carboxylic acids or of acylacetic acids, as well as other aromatic or heterocyclic hydroxy compounds and compounds containing an enolizable or enolized ketomethylene group which is present in a heterocyclic ring. Substances of this type are, for example arylamides of 2,3-hydroxynaphthoic acid, of 2-hydroxy-anthracene-3-carboxylic acid, of 4-hydroxy-diphenyl-3-carboxylic acid, of 2-hydroxy-carbazole-3-carboxylic acid, of 3-hydroxy-diphenyloxide-2-carboxylic acid, of 3-hydroxydiphenylene sulfide-2-carboxylic acid, of acetoacetic acid, and of benzoylacetic acid. In addition hydroxybenzenes, polyhydroxybenzenes, hydroxynaphthalenes and pyrazolones which are optionally substituted by non-ionic radicals, have also proved suitable.

For the development of the azo dyestuffs there may be used according to the present invention any primary aromatic amine which yields with the above-mentioned coupling components water-insoluble mono-, dis- or polyazo dyestuffs, that is, mono- or di-amines. These amines, which include also aminoazo dyestuffs, do not possess any ionic substitutents and are conventional diazo components in the ice colour technique.

The process of the present invention may be used for dyeing known cellulosic fibers and mixtures thereof with synthetic fibers, for example polyester fibers, and cellulose fibers. The cellulose fibers may be natural fibers, for example flax, hemp, linen and cotton, or regenerated fibers, for example viscose, spun rayon and modal fibers.

The anionic dispersing system for the dyestuff-forming components and for azo pigment formed before and after the addition of the acid may be, for example based on sodium 2,2'-dinaphthylmethane-6,6'-disulfonate or lignosulfonate, optionally in admixture with oleylmethyltaurine.

As organic acids there may be used, for example monochloroacetic acid, lactic acid, formic acid and acetic acid.

In order to accelerate bottoming, the material may be thoroughly wetted, and may also be subjected to pre-steaming for eliminating the air within the wound package. Any required cooling of the textile material may be achieved by the application of a reduced pressure.

The following Examples illustrate the invention.

*Example 1*:

Wound packages of cotton are treated in a cross-wound bobbin dyeing apparatus, with a bath circulation of 6 times per minute, for 15 minutes at 30°C with an aqueous liquor (goods-to-liquor ratio of 1:10) containing

3 g/l of the dissolved coupling component Azoic Coupling Component 8 - C.I. No. 37 525,

5 g/l of a 50% amine dispersion of Azoic Diazo Component 5 - C.I. No. 37 125 dispersed with polyethyleneglycol having a molecular weight of 600 and ethylene glycol,

3 g/l of an anionic protective colloid on the basis of an oleic acid-protein hydrolysate condensation product,

6 $cm^3$/l of sodium hydroxide solution of 32.5 % strength (= total amount including the amount required for dissolving the above coupling component),

3 g/l of sodium nitrite and

20 g/l of sodium chloride.

Following this bottoming phase of the wound packages,
10 $cm^3/l$ of 80% lactic acid and
10 $cm^3/l$ of 85% formic acid are added to this bath to reduce the pH value, and the goods are continued to be treated for 10 minutes at a temperature of from 40 to 45°C under the acid conditions established, during which process the diazotization of the amine as well as the development of the dyestuff are effected. The after treatment of the textile goods thus dyed shows the following operating steps:

5 minutes of rinsing the dyeing with water at 40°C, 10 minutes of soaping at 60°C with an aqueous bath, while adding
1 g/l of the reaction product of 1 mole of nonlyphenol with 10 moles of ethylene oxide,
1 g/l of calc. sodium carbonate and
1 g/l of a high-molecular-weight polyphosphate;
5 minutes of soaping at the boil with an aqueous bath, while adding
1 g/l of oleylmethyltaurine (sodium salt)
1 g/l of calc. sodium carbonate and
1 g/l of a high-molecular-weight phosphate;
5 minutes of rinsing with warm water and 5 minutes of rinsing with cold water.

An even red dyeing of the wound package is obtained which shows good fastness properties.

*Example 2*:

The dyeing of a cotton fabric is carried out, while using a jet dyeing apparatus "System Thies" with a goods-to-liquor ratio of 1:10. The material rate is 5 circulations per minute.

For the preparation of the dye liquor
2.2 g/l of the coupling component Azoic Coupling Component 32 - C.I. No. 36 580 and
2.9 g/l of the amine Azoic Diazo Component 3 - C.I. No. 37 010 are stirred into a paste in 5.7 cm/- of denatured ethanol, then a mixture of 2.2 $cm^3/l$ of water of 70°C and 1.1 $cm^3/l$ of 32.5 % sodium hydroxide solution is added, and the mixture obtained is dissolved, while stirring. This solution is now introduced into an aqueous bath prepared which contains the following auxiliary agents and chemical substances:
2 g/l of the condensation product of sodium-2,2'-dinaphthyl-methane-6,6'-disulfonic acid with m-cresol,
6 $cm^3/l$ of 32.5 % sodium hydroxide solution (= total amount including the amount used to dissolve the coupling component),
10 g/l of sodium chloride, and
2 g/l of sodium nitrite.

The textile goods are impregnated with the liquor thus prepared for 20 minutes at 30°C. Subsequently, 8.5 $cm^3/l$ of monochloroacetic acid are introduced into the liquor circulation via the overflow, whereupon the amine is diazotized within 10 minutes at a temperature rising from 30° to 45°C, and the dyestuff is developed. For the after-treatment, the goods dyed in this manner are rinsed for 5 minutes with warm water and soaped for 10 minutes at 60°C with an aqueous bath, while adding
1 g/l of calc, sodium carbonate and
1 g/l of a high-molecular-weight phosphate; then rinsed for 5 minutes with warm water and soaped at the boil for 10 minutes with an aqueous bath, while adding
1 g/l of oleylmethyltaurine (Na-salt)
1 g/l of calc. sodium carbonate and
1 g/l of a high-molecular-weight phosphate; and thereafter rinsed for 5 minutes with warm and cold water.

An even red dyeing of the cotton fabric is obtained which shows good fastness properties.

*Example 3*

The dyeing of terry cloth goods is effected on a dyeing apparatus for material ropes with a bath circulation at a goods-to-liquor ratio of 1:20. The circulation of the bath is 5 times per minute.

The liquor to be used is prepared in the following manner:
2.2 g/l of Azoic Coupling Component 28 - C.I. No. 37 541 and
2.7 g/l of Azoic Diazo Component 32 - C.I. No. 37 090 are stirred into a paste together with 7.2 $cm^3/l$ of denatured ethanol, and 1.1 $cm^3/l$ of 32.5% sodium hydroxide solution are added to this paste. Upon diluting with 4.4 $cm^3/l$ of water of 40°C, the mixture is dissolved, while stirring. The solution thus obtained is then introduced into an aqueous bath mixture having the following composition:
2 g/l of the condensation product of sodium 2,2'-dinaphthylmethane-6,6'-disulfonic acid with m-cresol,
6 $cm^3/l$ of 32.5% sodum hydroxide solution (= total amount including the amount used to dissolve the coupling component),
20 g/l of sodium chloride and
2 g/l of sodium nitrite.

The goods are impregnated with the dye liquor prepared in the described manner for 15 minutes at 30°C, and thereafter 10 $cm^3/l$ of acetic acid of 60% strength are added to this bath, whereupon the amine is diazotized and the dyestuff is developed in the course of 15 minutes at a temperature rising up to 46°C.

For the after-treatment of the dyed goods, the following operating steps are carried out:
5 Minutes of rinsing with cold water and 10 minutes of soaping at 60°C with an aqueous bath containing

1 g/l of the reaction product of 1 mole of nonylphenol with 10 moles of ethylene oxide,
1 g/l of calc. sodium carbonate and
1 g/l of a high-molecular-weight phosphate;
5 minutes of rinsing with warm water and 10 minutes of soaping at 95°C with an aqueous bath, while adding
1 g/l of oleylmethyltaurine (sodium salt),
1 g/l of calc. sodium carbonate and
1 g/l of a high-molecular-weight phosphate;
5 minutes of rinsing with warm and cold water.

An even red dyeing is obtained on the terry cloth which shows good fastness properties.

WHAT WE CLAIM IS:

1. A process for dyeing a textile material consisting of or containing cellulose fibers with a water-insoluble azo dyestuff which comprises circulating through the material at a rate of at least 5 times per minute for a period of from 10 to 20 minutes under atmospheric pressure at a temperature of from 10 to 40°C, an aqueous alkaline liquor which contains sodium nitrite, an anionic dispersing agent and a solution or dispersion of at least one azo coupling component and at least one primary aromatic amine in a water-miscible organic solvent or solubilizer, and then acidifying the liquor with an organic acid and heating the liquor to a temperature of from 30 to 50°C to cause diazotization and coupling, within a total dyeing period of not more than 30 minutes.

2. A process as claimed in claim 1, wherein alkaline liquor has a temperature of from 15 to 25°C.

3. A process as claimed in claim 1 or claim 2, wherein the textile material is in the form of a wound package.

4. A process as claimed in claim 1 carried out substantially as described in any one of Examples 1, 2 and 3 herein.

5. A textile material consisting of or containing cellulose fibers which has been dyed by a process as claimed in any one of claims 1 to 4.

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Printed for Her Majesty's Stationery Office,
by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings,
London, WC2A 1AY, from which copies may be obtained.