

1457095

PATENT SPECIFICATION

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(54) PROCESS FOR PRINTING OR PAD-DYEING
CELLULOSE/POLYESTER MIXED FABRICS

(71) We, HOECHST ALTIENGESSELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, 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:—

The present invention relates to a process for printing or pad-dyeing textile materials of cellulose and polyester fibres.

Various processes for dyeing and printing polyester and native or regenerated cellulose fibre mixtures are known. In these processes there have been used, for example, pigmented resins, selected vat dyestuffs which have an affinity for both types of fibre, mixtures of fibre-reactive dyestuffs with dispersion dyestuffs, mixtures of dispersion dyestuffs with direct dyestuffs and finally azo dyestuffs which can be developed on the fibre, selected mordant dyestuffs and phthalocyanine dyestuffs which are capable, for example, of forming chromium complexes on the fibre.

Due to the considerable differences in the physical and chemical properties both of the fibres of the material and of the dyestuffs of the dyestuff mixtures used on such fibre mixtures, these processes involve a number of problems and difficulties which do not occur when an individual dyestuff is applied to a homogeneous fibre material.

Thus, for example, the conditions existing in the printing paste or the dyebath which are suitable for achieving fixation of the "cellulose" dyestuff on the cellulose fibre may have detrimental effects on the stability of the "polyester" dyestuff. Furthermore, the conditions may also be favourable for fixation of the "polyester" dyestuff, but they may cause an undesired colouring of the cellulose. Thus, for example, the presence of strongly alkaline substances which are necessary for chemical binding of reactive cellulose dyestuffs may have a very unfavourable effect on the dispersion of dispersion dyestuffs at higher temperatures. This unfavourable effect of the alkaline substances can be avoided if the alkali required for the fixation of the reactive cellulose dyestuff is applied onto the material by impregnation only after fixation of the dispersion dyestuff.

However, if the fibre mixture is subsequently treated with an alkaline impregnation bath, a soiling of the white bottom can easily occur due to contamination of the impregnation bath by dyestuffs which are already on the fibre.

With regard, therefore, to these difficulties the known processes for dyeing or printing mixed fabrics of the abovementioned type involve some undesired limitations compared to what is commercially tolerable.

The present invention provides a process for pad-dyeing or printing a textile material comprising cellulose and polyester fibres, which comprises printing or padding the textile material with a printing paste or padding liquor which contains a reactive dyestuff, a disperse dyestuff, an alkali metal salt of formic acid, and a printing or dyeing auxiliary, carrier, levelling and/or dispersing agent, and subsequently fixing the dyestuffs by subjecting the material to dry heat, preferably at a temperature above 150°C, or hot steam, preferably at a temperature above 140°C. The prints or pad dyeings are then completed in the usual way.

The printing pastes or padding liquors used in the process of the invention may be prepared in usual manner, and generally contain the usual additives, for example thickeners, hydrotropic agents such as urea and *m*-nitrobenzoic acid in the form of the sodium salt, and carriers, levelling and/or dispersing agents. These printing pastes or padding liquors additionally contain, according to the invention, an alkali metal salt

of formic acid, preferably sodium formate, which is generally added to the printing paste or padding liquor in an amount of from 5 to 50 g, preferably from 5 to 30 g, per kg of printing paste or padding liquor.

As examples of suitable carriers there may be mentioned organic esters, for example acetylsuccinic acid dialkylesters, salicylic acid alkyl esters, methyl-salicylic acid alkyl esters, benzoic acid phenyl esters of β -naphthoic acid methyl esters; and the compounds described in German Offenlegungsschrift No. 2 062 287 or in German Patent Specification No. 1,184,730. Particularly suitable substances are mixtures of oxethylated diphenylol propane and oxethylated fatty alcohols, wherein the degree of oxethylation per hydroxyl group is from 2 to 25 units of ethylene oxide (German Offenlegungsschrift No. 2 250 017).

As examples of levelling agents there may be mentioned compounds which can be obtained by esterification of higher molecular polyglycols with carboxylic acids. Such products are described, for example, in German Patent Specification No. 1,133,735. These surface-active esterification products may be used, if desired, together with known water-soluble thickeners as thickening agents.

As examples of dispersing agents there may be mentioned oxethylation products of phenol, alkyl- and/or halogen-substituted phenols, naphthols and fatty alcohols having from 8 to 18 carbon atoms. The degree of oxethylation is on average from 2 to 25 units of ethylene oxide per hydroxyl group.

All of these auxiliaries mentioned may be used individually or in mixtures with one another. The total amount of auxiliaries in the printing paste or padding liquor is generally from 5 to 75 g, preferably from 5 to 30 g, per kg of printing paste or padding liquor.

After applying the printing paste or padding liquor to the fibre material it is then heated to fix the dyestuffs. It is advantageous to dry the material before the heating operation, for example at room temperature or by a preliminary heating to a temperature below 100°C, at which no fixation occurs. The two dyes of dyestuff are fixed only by a subsequent heat treatment at a higher temperature in hot air or hot steam at atmospheric pressure.

The duration of this heat treatment is generally from 20 to 180 seconds in the case of treatment with hot air, and from 3 to 20 minutes in the case of treatment with hot steam. At lower temperatures longer fixation times are necessary for the fixation than in the case of higher temperatures. The fixation is preferably effected for 6 to 8 minutes at from 180° to 190°C in hot steam, or for 45 to 90 seconds at from 190° to 210°C in hot air.

The printed or impregnated material is finally completed in usual manner by rinsing, soaping, rinsing once more and then drying.

The process of the invention may be applied to textile materials consisting of mixtures of high polymer linear polyesters, for example polyethylene terephthalate, and native or regenerated cellulose. The ratio between the two components may vary within wide limits, for example from 20 to 80% by weight of cellulose or polyester.

The dyestuffs used in the process of the present invention are disperse dyestuffs and water-soluble reactive dyestuffs. As disperse dyestuffs there are considered the dyestuffs which are sufficiently known for dyeing fibre materials of linear polyesters, for example dyestuffs of the azo or anthraquinone series.

As reactive dyestuffs there are considered organic dyestuffs which contain at least one group which reacts with the cellulose fibre, a group which forms such a reactive group under the dyeing conditions, or a substituent which reacts with the cellulose fibre. As basic categories of organic dyestuffs there may be particularly mentioned dyestuffs of the anthraquinone, azo and phthalocyanine series, where the azo and phthalocyanine dyestuffs may be free from or may contain metal. As examples of reactive groups, or groups which form such reactive groups in the alkaline medium, there may be mentioned the epoxy group, the ethyleneimide group, the vinyl group in a vinylsulphone group or in the acrylic acid radical, and the β -sulphatoethyl-sulphone group. As reactive substituents there are considered substituents which can be easily split off and leave an electrophilic radical; as examples there may be mentioned halogen atoms in the following ring systems; quinoxaline, pyridazine, triazine, pyrimidine, phthalazine and pyridazine.

The combination of alkali metal formate and one or more of the textile dyeing or printing auxiliaries described above provides on polyester/cellulose mixed fabrics dyeings and prints which show a pure and brilliant shade, good colour intensity, are fast to rubbing, and have an excellent fastness to laundering and to perspiration. They generally do not possess the turbidity and etiolating effects which appear when carrying

out heat treatments at elevated temperatures in the present of urea and alkali and which cause a dulling of the dyeing.

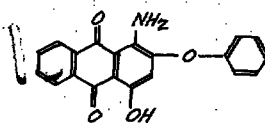
A further advantage of the process of the invention is that the padding liquors and printing pastes are stable and, therefore, may be prepared for stock before required for the printing or padding process. It is also possible to dwell the padded or printed material before continuing the process. It may also subsequently be over-printed and the dyed bottom and the overprint may be developed simultaneously.

The following Examples illustrate the invention. Parts and percentages are by weight unless stated otherwise.

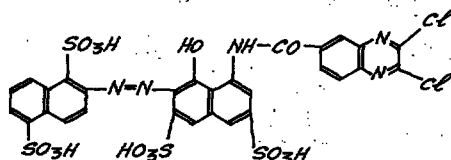
EXAMPLE 1

A mixed fabric containing 67 parts of polyester fibres and 33 parts of cotton was printed with a printing paste having the following composition:

30 Parts of the disperse dyestuff of the formula



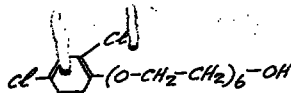
30 Parts of the reactive dyestuff of the formula



20 Parts of sodium formate

5 Parts of the compound of the formula $C_8H_{17}-(O-CH_2-CH_2)_{15}-OH$

15 Parts of the compound of the formula



5 Parts of butane-diol-(1,4)-pentaglycol ether-stearic acid ester
600 Parts of alginate thickening (4% in water)
295 Parts of water
1000 Parts of printing paste.

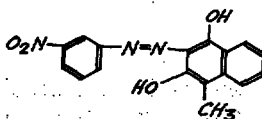
To fix the dyestuffs the fabric was subsequently treated for 90 seconds in hot air at $195^{\circ}C$. Then the material was hot rinsed, soaped with a solution which contained 1.5 g of a non-ionic detergent per litre, rinsed again and dried.

Brilliant even red prints were obtained on both types of fibre.

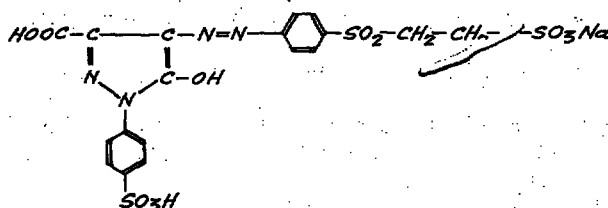
EXAMPLE 2

A mixed fabric containing polyester and spun rayon (mixture ratio 70:30) was printed with a printing paste having the following composition:

30 Parts of the disperse dyestuff of the formula



30 parts of the reactive dyestuff of the formula



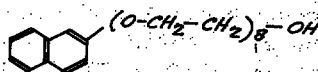
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- 20 Parts of sodium formate
10 Parts of *p*-phenylphenol
10 Parts of the compound of the formula



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- 10 Parts of acetyl-succinic acid diethyl ester
600 Parts of aliginate thickening (4% in water)
290 Parts of water
1000 Parts of printing paste.

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To fix the dyestuffs the material was steamed for 8 minutes in hot steam at 180°C. Then the material was hot rinsed hot, soaped with a solution which contained 1.5 g of an anion-active detergent per litre, rinsed again and dried. Yellow prints were obtained on both types of fibre.

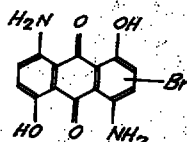
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EXAMPLE 3

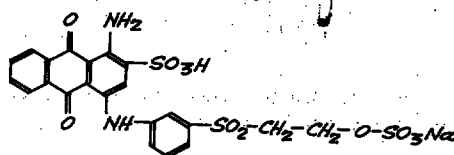
A mixed fabric containing polyester and spun rayon (mixture ratio 70:30) was printed with a printing paste having the following composition:

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- 40 Parts of the disperse dyestuff of the formula



- 50 Parts of the reactive dyestuff of the formula



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- 30 Parts of sodium formate
20 Parts of nonyl phenol oxethylate having 12 ethylene oxide units
10 Parts of salicylic acid ethyl ester
600 Parts of starch ether thickening (10% in water)
250 Parts of water
1000 Parts of printing paste.

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Then the material was dried and treated for 60 seconds with hot air at 200°C. The material was hot rinsed, soaped with a solution which contained 1 g of a non-ionic detergent per litre, soaped again and dried. Blue prints were obtained on both types of fibre.

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WHAT WE CLAIM IS:—

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1. A process for pad-dyeing or printing a material comprising cellulose and polyester fibres, which comprises printing or padding the material with a printing paste or padding liquor which contains a reactive dyestuff, a disperse dyestuff, an alkali metal salt of formic acid, and a printing or dyeing auxiliary, carrier, levelling agent and/or dispersing agent, and subsequently fixing the dyestuff by subjecting the material to dry heat or hot steam.

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2. A process as claimed in claim 1, wherein the alkali metal salt of formic acid is sodium formate.

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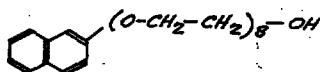
3. A process as claimed in claim 1 or claim 2, wherein the alkali metal salt of formic acid is present in an amount of from 5 to 50 grams per kilogram of printing paste or padding liquor.

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4. A process as claimed in claim 3, wherein the alkali metal salt of formic acid is



- 20 Parts of sodium formate
10 Parts of *p*-phenylphenol
10 Parts of the compound of the formula



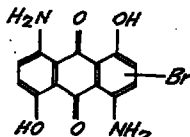
- 10 Parts of acetyl-succinic acid diethyl ester
600 Parts of aliginate thickening (4% in water)
290 Parts of water
1000 Parts of printing paste.

To fix the dyestuffs the material was steamed for 8 minutes in hot steam at 180°C. Then the material was hot rinsed hot, soaped with a solution which contained 1.5 g of an anion-active detergent per litre, rinsed again and dried. Yellow prints were obtained on both types of fibre.

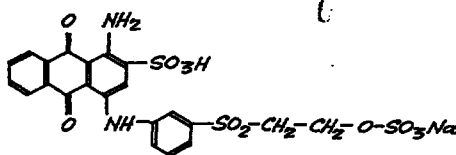
EXAMPLE 3

A mixed fabric containing polyester and spun rayon (mixture ratio 70:30) was printed with a printing paste having the following composition:

- 40 Parts of the disperse dyestuff of the formula



- 50 Parts of the reactive dyestuff of the formula



- 30 Parts of sodium formate
20 Parts of nonyl phenol oxethylate having 12 ethylene oxide units
10 Parts of salicylic acid ethyl ester
600 Parts of starch ether thickening (10% in water)
250 Parts of water
1000 Parts of printing paste.

Then the material was dried and treated for 60 seconds with hot air at 200°C. The material was hot rinsed, soaped with a solution which contained 1 g of a non-ionic detergent per litre, soaped again and dried. Blue prints were obtained on both types of fibre.

WHAT WE CLAIM IS:—

1. A process for pad-dyeing or printing a material comprising cellulose and polyester fibres, which comprises printing or padding the material with a printing paste or padding liquor which contains a reactive dyestuff, a disperse dyestuff, an alkali metal salt of formic acid, and a printing or dyeing auxiliary, carrier, levelling agent and/or dispersing agent, and subsequently fixing the dyestuff by subjecting the material to dry heat or hot steam.

2. A process as claimed in claim 1, wherein the alkali metal salt of formic acid is sodium formate.

3. A process as claimed in claim 1 or claim 2, wherein the alkali metal salt of formic acid is present in an amount of from 5 to 50 grams per kilogram of printing paste or padding liquor.

4. A process as claimed in claim 3, wherein the alkali metal salt of formic acid is



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present in an amount of from 5 to 30 grams per kilogram of printing paste or padding liquor.

5. A process as claimed in any one of claims 1 to 4, wherein the printing paste or padding liquor contains a total amount of from 5 to 75 grams of dyeing or printing auxiliary, carrier, levelling agent and dispersing agent per kilogram.

6. A process as claimed in claim 5, wherein from 5 to 30 grams of auxiliary, carrier, levelling agent and dispersing agent is used per kilogram.

7. A process as claimed in any one of claims 1 to 6, wherein the printed or padded material is dried at room temperature or at an elevated temperature below 100°C before the dyestuff fixation.

8. A process as claimed in any one of claims 1 to 7, wherein the printed or padded material is overprinted before the the dyestuff fixation.

9. A process as claimed in any one of claims 1 to 8, wherein the dyestuffs are fixed by subjecting the material to hot air at a temperature above 150°C.

10. A process as claimed in claim 9, wherein the fixation is carried out for a period of from 20 to 180 seconds.

11. A process as claimed in claim 10, wherein the hot air fixation is carried out for 45 to 90 seconds at from 190°C to 210°C.

12. A process as claimed in any one of claims 1 to 8, wherein the dyestuffs are fixed by subjecting the material to hot steam at a temperature above 140°C.

13. A process as claimed in claim 12, wherein the fixation is carried out for a period of from 3 to 20 minutes.

14. A process as claimed in claim 13, wherein the hot steam fixation is carried out for 6 to 8 minutes at from 180° to 190°C.

15. A process as claimed in claim 1, conducted substantially as described herein.

16. A process as claimed in claim 1, conducted substantially as described in any one of the Examples.

17. A material comprising cellulose and polyester fibres, whenever dyed or printed by a process as claimed in any one of claims 1 to 16.

18. A printing paste or padding liquor which contains a reactive dyestuff, a disperse dyestuff, an alkali metal salt of formic acid and a printing or dyeing auxiliary, carrier, levelling and/or dispersing agent.

19. A printing paste or padding liquor as claimed in claim 18, wherein the alkali metal salt of formic acid is sodium formate.

20. A printing paste or padding liquor as claimed in claim 18 or claim 19, which contains from 5 to 50 grams of the alkali metal salt of formic acid per kilogram.

22. A printing paste or padding liquor as claimed in claim 18 and described herein.

23. A printing paste or padding liquor as described in any one of the Examples.

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