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54 **Dyeing and printing fibres.**

57 In the pretreatment of textile fibres, prior to dyeing or printing, with a compound comprising the reaction product of an amine with cyanamide, dicyandiamide, guanidine or bisguanidine, operation at pH values greater than 11 and temperatures less than 50°C gives improved fixation of pretreatment agent and superior fastness properties of the finished dyeing or printing.

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Description

Dyeing and Printing Fibres

This invention relates to the dyeing and printing of textile fibres.

European published Patent Application 151,370A describes a process for improving the dyeing properties of textile fibres by pretreating the fibres prior to dyeing with an agent based on the reaction product of an amine with cyanamide, dicyandiamide, guanidine or bisguanidine. By using this pretreatment agent and colour yields and wet fastness of the dyed fibres can be improved. The pretreated fibres may be dyed with a variety of anionic dyes including direct and acid dyes, but the use of the pretreatment agent is especially advantageous for reactive dyes as it enables cellulosic fibres to be dyed with reactive dyes under neutral and acid conditions as well as the conventional alkaline conditions. Under acid conditions the dyeing process is more efficient and economical because there is, for example, reduced dye hydrolysis, which allows greater dye uptake, and also a reduction in dyeing time.

A method described in EP 151,370A for treating the fibres with the pretreatment agent is an exhaust process whereby the textile fibres are immersed in an initially weakly acidic bath which is then heated from room temperature to 50-100°C and made alkaline (pH 9-11) by the addition of 0.5-5 per cent w/wf sodium carbonate. The fibres are subsequently washed to remove any unfixed agent and may then be dyed. According to this process the maximum amount of agent that can be fixed to the fibres is between 0.6 and 2% w/wf, although for most cottons it is no more than 0.9% w/wf. Whilst this level of fixation is high enough to enable many good quality colour shades to be produced, it has been found that it is not possible to produce satisfactory dyed fabrics with particularly deep or dark colour shades such as deep reds, navy blues and blacks when using a reactive dye under acid conditions.

A process has now been discovered which enables a higher level of the pretreatment agent to become fixed to the textile fibres.

Accordingly the present invention provides a process for the dyeing or printing of textile fibres which comprises pretreating the fibres before the dyeing or printing step with a solution of a compound (hereinafter referred to as Compound A) comprising the reaction product of a mono- or polyfunctional amine having one or more primary and/or secondary and/or tertiary amino groups with cyanamide, dicyandiamide, guanidine or bisguanidine, or with a solution of a labile salt of Compound A, characterised in that the temperature of the solution is less than 50°C and the pH of the solution is greater than 11.

By "labile salt" is meant a salt that dissociates under the pretreatment conditions to generate Compound A in free base form, examples being the sulphate and phosphate salts.

The pH of the solution is preferred to be greater than 12. The required pH value is obtained by the inclusion in the solution of a suitable alkali such as sodium or potassium hydroxide. The use of caustic alkali is disclosed in the above-mentioned European application EP-A-151,370 although it is stated therein that "excessive alkalinity causes deactivation of the groups available for dyeing, probably as a result of cross-linking of the compound and therefore it is preferred to avoid the use of caustic alkali." However, it has now been discovered that, provided the temperature of the solution is maintained below 50°C while the textile fibres are being treated, this problem does not arise, at least not to any noticeable extent, and furthermore a larger amount of Compound A can be fixed to the fibres than has previously been possible. Preferably the temperature of the solution is between ambient temperature and less than 50°C, more preferably less than 45°C. Where Compound A is applied to the fibres by an exhaustion process this temperature is more preferably between 35 and 45°C and especially about 40°C. Where the compound is applied by a padding process, ambient temperature is usually used, although where the padding apparatus is capable of being operated at higher temperature, a temperature between ambient and less than 50°C preferably less than 45°C may be used.

It has also been found that the amount of Compound A that is fixed to the fibres depends upon the concentration of alkali in the solution, too little or too much alkali reducing the fixation of the compound. The preferred amount in weight of alkali included in the solution is between 0.05x and 0.30x, more preferably between 0.10x and 0.2x, and especially about 0.12x, where x is the amount in weight of Compound A present in the solution, provided that the concentration of alkali in the solution does not exceed 20g/l. It has been found that if the concentration exceeds this value then the solution becomes unstable.

Although the process according to the invention can be used to apply lower levels of Compound A to textile fibres, typically Compound A is applied in a concentration which allows at least 1.0 per cent by weight of the compound to become fixed onto the fibres, based on the dry weight of the fibres. If this material contains fibres which do not take up the compound or take it up only minimally, then either these fibres are excluded from the fibre weight in calculating the concentration of the compound, or an adjustment is made to account for any compound they take up.

Usually Compound A is applied in concentrations so that at least 2.0 per cent w/wf is fixed to the material, often 2.2 per cent w/wf. Higher levels, for example, 2.5 per cent w/wf or more, can be applied if desired.

Preferably Compound A is distributed evenly over the fibres in order to achieve even dyeing. This requires a sufficient concentration of Compound A in the aqueous solution. In exhaustion processes too low a concentration of compound leads to premature exhaustion of the bath and hence uneven take-up. In continuous processes such as padding too low a concentration of compound can lead to a reduction of that concentration during processing; this is known as tailing. This and other factors lead to uneven application.

Even take-up is promoted if the concentration of the compound applied is sufficiently high to allow the take-up of fixed compound to reach or approach the saturation value for the fibres concerned. In commercial practice it is better to provide a safety margin by applying the compound at a higher concentration than the saturation value and subsequently washing off unfixed compound. Solution concentrations usually will be higher than the concentration which it is intended to apply to the fibres to take account of the fact that percentage exhaustion or percentage expression is usually considerably less than 100. On the other hand, solution concentrations usually may be reduced by an appropriate amount if the fibres to be pretreated are blended with fibres which are unaffected or minimally affected by the pretreatment. Where 100 per cent of the fibres accept the pretreatment, suitable solution concentrations will usually be in the range 1.5 to 20 per cent w/wf, preferably 2.5 to 10%. If, as is preferred, excess Compound A is applied to the fibres, then the fibres are subsequently washed to remove any unfixed compound.

Any suitable method may be used to apply Compound A to the textile fibres according to the process of the invention, for example by exhaustion padding, spraying, injection, printing or foam application. Exhaustion or padding is preferred.

Where padding is used it has been found that a subsequent batching or steaming treatment aids fixation.

Preferably Compound A is the reaction product of dicyandiamide with a polyamine, especially diethylenetriamine.

Compound A may be prepared in its free base form or as a salt and suitable methods are described in U.K. Patent 657,753 and U.S. Patents 2,649,354 and 4,410,652. Suitably the amine, in free base or salt form, is reacted with the other starting material in the absence of water at elevated temperatures optionally in the presence of a non-aqueous solvent. Preferably the reaction is carried out in the absence of solvent at a temperature of 140-160°C, and for most combinations of reagents, ammonia is evolved. The reagents are preferably reacted in a molar ratio of 0.1 to 1 mole of cyanamide, dicyandiamide, guanidine or bisguanidine per mole of reactive amino groups, and when dicyandiamide is reacted with a polyalkylene polyamine, the molar ratio of the reactants is more preferably from 2:1 to 1:2, particularly about 1:1.

The textile fibres which can be pretreated with Compound A include cellulose fibres by which is meant both natural cellulose such as cotton and regenerated or synthetic cellulose such as viscose or rayon, or a mixture thereof. Cellulose acetate fibres, nitrogen-containing fibres such as polyacrylonitrile and natural or synthetic polyamides such as wool, silk or nylon may also be used. Leather can also be treated.

The fibres may be in the form of loose fibres or yarns or fabrics, or in any suitable form. The fibres may be blended with other fibres which are susceptible of treatment by the process of the invention or with fibres which are not so susceptible. For example, cotton and regenerated cellulose fibres may be blended together or individually with polyester fibres, the latter being dyed with disperse dyes, (although when not blended, polyester fibres may be pretreated with Compound A and then dyed to some extent). Fibres blends and yarn blends may be used.

The fibres after pretreatment with Compound A may be dyed or printed with anionic dyestuffs, including direct dyes, acid dyes and reactive dyes. Other dyes that may be used include sulphur, vat, azoic, phthalocyanine, formazan, chrome, di- or triphenylmethane and indigo dyestuffs.

The pretreatment according to the invention is especially advantageous where the textile fibres are dyed or printed with reactive dyes and these dyes are applied under acidic or neutral conditions. Because the process enables a relatively high amount of Compound A to be fixed to the fibres, it is possible to dye fibres with good quality deep and/or dark colour shades such as deep reds, navy blues and blacks. Prior to this invention such fibres and fabrics could only be produced with limited colour depth from neutral or acid systems.

Most reactive dyes may be applied under acidic or neutral conditions, generally in the range of pH 3.5 to 7.0, more preferably pH 4.0 to 7.0. The pretreated fibres may also be dyed in alkaline conditions, and in particular it has been found that good lightfastness and brightness can be obtained when the fibres are dyed in a pH range of about pH 8.0 to 9.0. The usual alkaline conditions typically pH 12 to 13 can also be used. Preferred reactive dyes are those containing a 5- or 6-membered heterocyclic ring having aromatic character and containing 2 or 3 nitrogen atoms, which is substituted by 1-3 halogen atoms which can be split off as anions during fixation. The reactive group can also be a vinylsulphonyl-, vinylcarbonyl-, sulphato- or sulphate ester group. Such dyes are known under the designation C.I. Reactive Dyes. Suitable reactive dyes include C.I. Reactive Reds 2, 6, 8, 120, 123 and 171; C.I. Reactive Blues 94, 104, 114, 116, 163, 168, 172 and 193; C.I. Reactive Yellows 7, 84 and 111; C.I. Reactive Oranges 4, 14 and 69; C.I. Reactive Browns 10 and 23; C.I. Reactive Black 8 and C.I. Reactive Violet 33. Other suitable reactive dyes include C.I. Reactive Red 41, C.I. Reactive Yellow 152, C.I. Reactive Red 147, C.I. Reactive Orange 62; or mixtures thereof. Reactive dyes containing more than one type of reactive group in the same dye molecule can also be used.

Examples of suitable direct dyes are those having at least two sulphonic acid or sulphonamide groups in the dye molecule, more preferably 3-8 such groups, particularly 4-6. Particularly preferred are highly substantive direct dyes which show a high degree of exhaustion on cotton when dyed by the conventional exhaustion process. Preferably the direct dyes have a molecular weight above 1000, more preferably above 1200. Preferably the direct dyes are in the form of 1:1 or 1:2 metal complexes, particularly copper complexes.

Particularly suitable direct dyes are those meeting the criteria set out in US Patent 4,410,652, the dyes whose formulae are listed in that US patent, and those listed in US Patent 4,439,203 under their Colour Index numbers.

A further group of particularly suitable dyes has the properties both of direct dyes and of reactive dyes. They

are highly substantive as described above, and also contain in their molecule one or more halogens attached to aromatic heterocyclic rings, which can be split off as an anion under alkali fixation conditions. Preferred dyestuffs of this type contain one or two mono- or di-halo (particularly chloro-) substituted triazinyl groups. Examples of such dyestuffs are given in published European patent application 151,370A.

The dye may be applied to the pretreated fibres by any suitable method, for example by exhaustion or padding.

Prior to this invention, when dye was applied by a padding process and particularly when applied to cellulosic fibres, it was necessary to batch, sky, steam or otherwise treat the fibres after padding in order to fix the dye to the fibres. It has now been found that by using the process according to the present invention this subsequent fixation step is not necessary. Thus the invention has the substantial advantage that the fibres can be dyed continuously, that is to say they can be pad-dyed and then washed and dried without the need for an intermediate fixation step.

The process according to the invention also provides particular advantages when used to dye loose fibres, especially loose cellulosic fibres. In general, cellulosic fibres, if they are dyed at all, are dyed only to pale shades as deeper, fuller shades can only be obtained by immersing the fibres in a dye bath for a considerable length of time, often in excess of seven hours. By using the process according to the present invention the dye time for obtaining full and deep shades can be considerably reduced, for example to 30 minutes, more preferably 10 minutes or less. Furthermore the loose fibres can be pretreated and dyed by a continuous method, it being neither necessary to dry the fibres after pretreating with Compound A nor to provide a fixation period after dyeing. Instead the fibres can be pretreated, dyed and washed during the normal washing stages that form part of standard fibre processing. Preferably the pretreating, dyeing and washing steps take place in successive baths, the fibres advantageously being squeezed between each bath. Each step need take only 3 minutes or less, although longer times may be taken if desired. Although it is usual to pretreat and dye cotton fibres after they have been scoured and bleached, it is also possible to dye cotton fibres that have been opened and decontaminated from metal particles but are otherwise untreated.

Tone-in-tone and colour-and-white differential dyeing effects may be obtained by using cellulosic fibres which have been pretreated according to the process of the invention in combination with untreated cellulosic fibres. For example, 100% cotton fabrics may be knitted or woven in a pattern such as stripes defined by treated and untreated yarns, to give ecru fabric which may be dyed on demand in various colourways. High, medium and low contrast tone-in-tone effects may be achieved using reactive dyes applied under alkaline conditions or mildly acidic conditions. Colour and white effects may be achieved using selected reactive dyes. Dye selection can be used to produce differential dyeing.

A further advantage of using direct or reactive dyes is the covering of 'dead' cotton (immature fibres which tend to clump together and are dyed less easily), enabling the usual white specks on the dyed fabric to be eliminated. The same applies to "miniblends" comprising cotton with small quantities of synthetic fibres such as polyester.

The invention will now be illustrated by the following Examples. Unless otherwise stated all parts and percentages are by weight and in the case of the pretreatment bath or dye bath compositions are based upon the dry weight of the textile fibre substrate.

Example 1

A prebleached 100% cotton interlock fabric was immersed in a bath containing an aqueous solution of 8.25 per cent w/wf sulphate salt of reaction product of dicyandiamide and diethylenetriamine. (This salt is hereinafter referred to as "Compound A1"). A method for its preparation is given in EP 151,370A, page 19, Example 1). The liquor to goods ratio was 15:1. The fabric was immersed and agitated in the solution for 5 minutes at ambient temperature and then 4 grams per litre of sodium hydroxide added. The temperature of the bath was increased to 40°C at 2°C per minute and the fabric continued to be treated for a further 20 minutes, after which it was rinsed twice in cold water.

The amount of Compound A1 fixed to the cotton was assessed by Kjeldhal nitrogen determination and was found to be 2.08% w/wf.

Example 1A

Example 1 was repeated except that the sodium hydroxide was added after the bath temperature had been increased to 40°C. The same amount of Compound A1, 2.08% w/wf, was found to be fixed to the cotton.

Example 2

A number of experiments, similar to that of Example 1, were carried out with varying concentrations of Compound A1 and sodium hydroxide and also temperature, to determine the optimum conditions for fixing Compound A1 to the cotton.

The general procedure was as follows: a prebleached 100% cotton interlock fabric was immersed for 5 minutes at room temperature in an aqueous solution of x% Compound A1. An amount, y grams per litre, of sodium hydroxide was then added and the cotton immersed with agitation for a further 5 minutes after which the temperature of the solution was raised to z°C and held there for 30 minutes. The fabric was then rinsed in cold water.

The following variables were studied:

Concentration of Compound A1 $x = 2.75, 5.50, 8.25, 16.5\text{w/wf}$
 Concentration of NaOH $y = 0.1, 0.2, 0.5, 1, 2, 2.5, 3, 4, 5, 7, 10\text{g/l}$
 Temperature $z = 20, 30, 40, 50, 60^\circ\text{C}$

The amount of Compound A1 fixed onto the cotton fibres was then assessed by dye testing in an aqueous solution of 1g/l of the dye C.I. Reactive Blue 114, the solution having a pH value of 5.7 and a liquor to goods ratio of 50:1. The fabric was immersed in the boiling dye solution for 15 minutes and then rinsed with water. The greater the intensity of the resulting colour, the greater the amount of Compound A1 fixed to the cotton.

It was found that, for all concentrations of Compound A1, the dyeability increased with temperature up to 40 to 50°C and then decreased.

Similarly, for each Compound A1 concentration, the dyeability increased with increasing levels of sodium hydroxide up to a specific level depending upon the concentration of Compound A1, and then decreased. These results are shown in Table 1 below.

Table 1

Compound A1 concentration (%)	2.75	5.50	8.25	16.5
Optimum concentration of NaOH (g/l)	1-2	2-3	3-5	5-7

The actual amount of Compound A1 fixed to the cotton was assessed by Kjeldahl nitrogen determination and the results are given in Table 2.

Table 2

Concentration of Compound A1 in solution (% w/wf)	2.75	5.50	8.25	16.5
Concentration of NaOH (g/l)	2.0	2.5	4.0	5.0
Amount of Compound A1 fixed to cotton (% w/wf)	1.06	1.72	2.08	2.95

Example 3

Samples of prebleached 100% cotton interlock fabric were pad treated by the general technique of padding (using ambient temperature) with a solution containing x g/l Compound A1 and y g/l sodium hydroxide for a time of z minutes, followed by skying or batching.

The following variables were studied:

Concentration of Compound A1 $x = 16.5, 27.5, 55.0, 82.5, 165\text{g/l}$

Concentration of NaOH $y = 2.5, 5.0, 10, 20\text{g/l}$

Sky/batch time $z = 2.0$ minutes, 1.0, 24 hours

In one treatment the batching was replaced with a steam treatment for 2 minutes at 102°C.

It was found that the amount of Compound A1 fixed to the cotton increased with increasing alkali concentration. However above a concentration of 20g/l alkaline stability problems started to occur.

Both steaming and extended batching times aided fixation. This is shown in Table 3 where padding was carried out using a Compound A1 concentration of 55.0g/l and a sodium hydroxide concentration of 20g/l.

Table 3

5	Amount of Compound A1 fixed (% w/wf)	
10	Batching Time: 2 minutes	1.40
	1 hour	2.37
	24 hours	2.71
15	Steaming Time: 2 minutes	2.17

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Example 4

A 100 per cent cotton interlock fabric was pretreated with Compound A1 as described in Example 1.

25 The treated fabric was then dyed with reactive dyes under acidic conditions (pH 6-7) by immersing the fabric at a 15:1 liquor to goods ratio in an aqueous dyebath at room temperature comprising:

80 per cent acetic acid - 0.22 ml/l

C.I. Reactive Blue 193 - 4.7 per cent

C.I. Reactive Red 147 - 2.0 per cent

C.I. Reactive Orange 107 - 0.12 per cent

30 50 g/l Glaubers Salt were then added over 15 minutes and the temperature of the dyebath raised to 95°C at 2°C per minute. Dyeing was continued for 30 minutes and the fabric rinsed with water at 40°C for 5 minutes. The dyed fabric was then washed in an aqueous bath containing 2 g/l anionic detergent at 100°C for 15 minutes, rinsed with cold water and dried.

A dyed fabric having a full black shade with good wet fastness properties was obtained.

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Example 5

A 100 per cent cotton interlock fabric was pretreated with Compound A1 as described in Example 1 except that 2.75 per cent w/wf Compound A1 and 2 g/l sodium hydroxide were used in the aqueous solution.

40 The treated fabric was then dyed with reactive dyes under acidic conditions (pH 6-7). The fabric was immersed in an aqueous dyebath at room temperature containing 0.22 ml/l 80 per cent acetic acid. The liquor to goods ratio was 15:1. 1 g/l of a levelling and anti-precipitant agent, Lyocol ES (tradename), was added followed, after 15 minutes, by the addition over 10 minutes of reactive dyes: 1.5 per cent of the dye C.I. Reactive Red 41 and 2.5 percent C.I. Reactive Orange 254. 40g g/l of Glaubers Salt was then added over 15 minutes and the temperature of the bath was raised to 95°C at 2°C per minute. Dyeing was continued for 30 minutes after which the fabric was rinsed with water at 40°C for 5 minutes. The dyed fabric was then washed with an aqueous anionic detergent solution at 100°C for 15 minutes, rinsed with cold water and dried.

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A dyed fabric having a deep red with good wet fastness properties was obtained.

Example 6

50 Cotton fibres were decontaminated, scoured and bleached using conventional methods. The fibres were then washed successively with water in three wash baths, each wash lasting 3 minutes with squeezing of the fibres between each bath. The liquor to good ratio was 150:1. The fibres were dried with hot air after centrifuging.

During the washing stages the fibres were pretreated with Compound A1 and dyed as follows:

55 To the first wash bath was added 22g/l Compound A and 6g/l sodium hydroxide. The temperature of the bath was raised to 40°C and the cotton fibres immersed in the bath with agitation for 3 minutes. 3.30% w/wf of Compound A was fixed to the fibres.

60 After passing through a mangle the fibres entered the second wash bath where they were dyed with reactive dyes under acid conditions for 3 minutes at 95°C. The bath contained 0.5g/l acetic acid, 1g/l of an antiprecipitating agent, Lycol ES, and the reactive dyes: 1g/l C.I. Reactive Blue 114 and 0.16 g/l C.I. Reactive Red 41.

After passing through another mangle, the dyed fibres were washed with water in the third wash bath for 3 minutes at 95°C.

Cotton fibres having a full royal blue shade with good wet and light fastness properties were obtained.

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Examples 7 to 10

Example 6 was repeated except the dyes were changed to produce different coloured cotton fibres.

Example 7: 2.5g/l C.I. Reactive Red 41

1g/l C.I. Reactive Yellow 152

30g/l Sodium chloride (electrolyte)

Bright red fibres were obtained.

Example 8: 0.15g/l C.I. Reactive Yellow 142

0.0015g/l C.I. Reactive Red 41

Bright yellow fibres were obtained.

Example 9: 1.5g/l C.I. Reactive Blue 193

0.5g/l C.I. Reactive Violet 33

0.1g/l C.I. Reactive Orange 62

Medium navy fibres were obtained.

Example 10: 2.0g/l C.I. Reactive Blue 193

1.2g/l C.I. Reactive Violet 33

1.1g/l C.I. Reactive Orange 62

50g/l Sodium chloride (electrolyte)

Black fibres were obtained.

In each Example dyed cotton fibres having full colour shades with good wet and light fastness properties were obtained.

Example 11

Cotton fibres were opened, decontaminated and formed into a continuous web. They were then scoured and peroxide bleached on a continuous pad stream preparation range, and dried on cans.

The continuous web of bleached fibre was then passed through a pad through at 40°C containing 27.5g/l Lyocol ES. The dwell time of the fibre in the liquor was 15 seconds. After passing through the treatment bath the fibre was passed between rollers to give 105% liquor pick up. This was followed by two cold water treatments for 15 seconds and can drying.

The fibre was found to be uniformly treated with 1.8% w/wf of Compound A1 fixed to the fibres.

Example 12

A 100% cotton interlock fabric pretreated with Compound A1 as described in Example 1A except that 2.75% w/wf Compound A1 and 0.6g/l sodium hydroxide were used in the aqueous solution. The liquor to goods ratio was 20:1.

The treated fabric was then dyed with sulphur dyes. The fabric was immersed in an aqueous dyebath of 40°C containing 15g/l sodium sulphide. The liquor to goods ratio was 20:1. After 5 minutes 6% of the dye C.I. Solubilised Sulphur Blue 4 (50%) was added. The temperature of the dyebath was raised to 85°C at 2°C per minute. Once the bath had reached 85°C, 25g/l common salt was added and dyeing continued for 45 minutes.

The dyed fabric was rinsed in cold water and then oxidised by treating in a solution of 3g/l sodium perborate and 1g/l sodium bicarbonate for 30 minutes at 60°C.

The dyed fabric was then washed with an aqueous anionic detergent solution at 100°C for 15 minutes, rinsed with cold water and dried.

The resultant fabric was dyed to a deep navy shade that was deeper than that obtainable from comparable dyeing on cotton fabric without pretreatment.

Example 13

A 100% woven bleached cotton fabric was pad pretreated in Compound A1. The fabric was padded to 80% pick up in 27.5g/l Compound A1, 1cc/l of a wetting agent Sandozin NI (tradename), 10g/l sodium hydroxide followed by immediate rinsing in cold water and dried. The fabric was found to contain 1.6% w/wf fixed Compound A1.

The treated fabric was pad treated at 80% pick up in 2g/l of the dye C.I. Solubilised Vat Blue 6, 2cc/l of a wetting agent Lyogen WL liquid (tradename), 6g/l sodium nitrite. The padded fabric was batched under polythene for 4 hours.

The fabric was then padded wet in 20cc/l sulphuric acid, 1g/l of an anionic dispersant Lyocol O (tradename) followed by an immediate rinse in cold water.

The fabric was neutralised at 50°C in 1g/l soda ash and then washed off at the boil in alkaline detergent.

The resultant fabric was dyed to a blue shade much deeper than a comparable fabric dyed without

pretreatment.

Example 14

A 100% cotton interlock fabric was pretreated with Compound A1 as described in Example 1A except that 4.4% w/wf Compound A1 and 0.9g/l sodium hydroxide were used in the aqueous solution. The liquor to goods was 20:1.

The treated fabric was then dyed with chrome dyes. The fabric was immersed in an aqueous bath at room temperature containing 1.5% potassium dichromate, 1% formic acid to give a pH of 4.0. The temperature was raised to 98°C and the treatment continued for 30 minutes. The fabric was then rinsed cold for 5 minutes.

The fabric was then placed in an aqueous dyebath at 50°C containing 5% sodium sulphate, 0.2% acetic acid (to give pH 5.0) 0.1% of a heavy metal sequestrant Irgalon PA (tradename) and 0.5% of a levelling agent Albegal SET (tradename). The fabric was treated for 5 minutes and 1.5% of the dye C.I. Reactive Red 17 was added. The dyebath was raised to 98°C and dyeing continued for 60 minutes and the fabric finally rinsed at 70°C.

The resultant fabric was dyed to a full red shade whereas a comparable dyeing on an untreated substrate remained undyed.

Example 15

A 100% cotton interlock fabric was treated in Compound A1 as described in Example 1A except the concentration of Compound A1 used was 5.5% and the concentration of sodium hydroxide was 2g/l. The liquor to goods ratio was 10:1.

The treated fabric was immersed in an aqueous dyebath containing 4% w/wf of the dye C.I. Acid Black 172 at room temperature. The dyebath was raised to 95°C over 30 minutes and 20g/l sodium sulphate was added. The dyeing was continued for a further 30 minutes followed by rinsing at 70°C and in cold water.

The resultant fabric was dyed to a full black colour and demonstrated very good wet fastness.

Example 16

A 50% cotton, 50% polyester rib fabric was pretreated with Compound A1 as described in Example 1A except that 4.4% w/wf Compound A1 and 2.7 g/l sodium hydroxide were used in the aqueous solution.

The treated fabric was then dyed with reactive dyes and disperse dyes under acidic conditions (pH 5.5 - 6.0). The fabric was immersed in an aqueous dyebath at room temperature containing 1.0g/l buffer pH 5.7. The liquor to goods ratio was 10:1. 1g/l of a levelling and anti-precipitant agent, Lyocal ES, was added followed, after 15 minutes, by the addition over 10 minutes of reactive dyes: 2.0% C.I. Reactive Black 5, 1.3% Reactive Orange 107 and 1.1% C.I. Reactive Blue 203. The temperature of the dyebath was raised to 70°C at 2°C per minute. 20g/l Glaubers Salt was added over 10 minutes followed by the addition of 1.35% Dispersol Black D3G (tradename) and 0.255% C.I. Disperse Blue 79:1. The temperature of the bath was then raised to 95°C at 2°C per minute then to 135°C at 1°C per minute. Dyeing was continued for 60 minutes after which the fabric was rinsed with water at 40°C for 5 minutes.

The dyed fabric was then washed with an aqueous anionic detergent solution at 100°C for 15 minutes, rinsed with cold water and dried.

A dyed fabric of a deep black colour with good wet fastness properties was obtained.

Example 17

A 100% acrylic ('Courtelle' - tradename) fabric was pad treated with Compound A1. The fabric was padded with 40g/l Compound A1, 20g/l sodium hydroxide to 80% pick up, batched under polythene for 4 hours, rinsed in cold water and dried.

The treatment fabric was then dyed with reactive dyes. The fabric was immersed in an aqueous dyebath at room temperature containing 0.22cc/l 80% acetic acid. The liquor to goods ratio was 15:1. After 5 minutes 3% of the dye C.I. Reactive Blue 114 was added. The dyebath temperature was then raised to 95°C and the dyeing continued for 30 minutes. The dyed fabric was then rinsed in hot and cold water followed by drying.

The result was a fabric dyed blue whereas a comparable untreated acrylic fabric remained undyed.

Example 18

A prebleached 100% cotton interlock was immersed in a bath containing an aqueous solution of 8.25 per cent Compound A1. The liquor to goods ratio was 10:1. The fabric was immersed and agitated in the solution for 5 minutes at ambient temperature. The temperature of the bath was increased to 40°C at 2°C per minute and then 4 grams per litre of potassium hydroxide added. The fabric continued to be treated for a further 20 minutes, after which it was rinsed twice in cold water.

The amount of Compound A1 fixed to the cotton was assessed by Kjeldhal nitrogen determination and was found to be 2.14% w/wf.

Claims

1. A process for the dyeing or printing of textile fibres which comprises pretreating the fibres before the dyeing or printing step, with a solution of a compound comprising the reaction product of a mono- or polyfunctional amine having one or more primary and/or secondary and/or tertiary amino groups with cyanamide, dicyandiamide, guanidine or bisguanidine, or with a solution of a labile salt of said compound, characterised in that the temperature of the solution is less than 50°C and the pH of the solution is greater than 11. 10
2. A process according to Claim 1 in which the pH value is obtained by the inclusion in the solution of sodium or potassium hydroxide in an amount between 0.05x and 0.30x where x is the amount in weight of the said compound or labile salt thereof present in the solution, provided that the concentration of sodium or potassium hydroxide in the solution does not exceed 20 g/l. 15
3. A process according to Claim 1 or Claim 2 in which the fibres are pretreated by an exhaustion process and the temperature of the solution is between 35 and 45°C.
4. A process according to Claim 1 or Claim 2 in which the fibres are pretreated by a padding process and the temperature of the solution is ambient temperature. 20
5. A process according to any one of the preceding claims in which the amount of the said compound or labile salt thereof present in the solution is at least 1.5 weight per cent based on the weight of the material which is to be treated.
6. A process according to any one of the preceding claims in which the said compound is the reaction product of diethylenetriamine with dicyandiamide. 25
7. A process according to any one of the preceding claims in which the fibres after being pretreated are dyed with a reactive dye under acid or neutral conditions.
8. A process for dyeing loose cellulosic fibres which comprises the successive steps of:
 - (a) pretreating the fibres by passing them through a bath containing a solution of a compound comprising the reaction product of a mono- or polyfunctional amine having one or more primary and/or secondary and/or tertiary amino groups with cyanamide, dicyandiamide, guanidine or bisguanidine, or with a solution of a labile salt of said compound, the pH of the solution being greater than 11; 30
 - (b) passing the fibres through a bath containing dye liquor to dye the fibres;
 - (c) washing the fibres; 35
 - (d) drying the fibres.
9. A process according to Claim 8, in which steps (a) to (c) are carried out in a total time of less than 30 minutes.
10. Dyed textile fibres having fixed thereon more than 2.0 per cent w/wf, of a pretreatment compound comprising the reaction product of a mono- or polyfunctional amine having one or more primary and/or secondary and/or tertiary amino groups with cyanamide, dicyandiamide, guanidine or bisguanidine. 40
11. Dyed cotton fibres having fixed thereon at least 1.0 per cent w/wf of a pretreatment compound comprising the reaction product of a mono- or polyfunctional amine having one or more primary and/or secondary and/or tertiary amino groups with cyanamide, dicyandiamide, guanidine or bisguanidine. 45