

PATENT SPECIFICATION

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(54) AFTER-DYEING OR PRINTING-TREATMENT PROCESS FOR MIXED TEXTILE SUBSTRATES

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, 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 an after-dyeing or printing treatment process for dyed or printed synthetic fibre/natural cellulose mixed textile substrates, especially polyester/cellulose mixed textile substrates.

When dyeing or printing polyester/cellulose mixed textile substrates with a mixture of disperse and reactive dyestuffs, it is invariably the case that unbound disperse dye stains the cellulose fibres, and the removal of such dyestuff causes problems.

Accordingly, the present invention provides a process for treating synthetic fibre/natural cellulose mixed textile substrates which have been dyed or printed with at least one disperse and at least one reactive dye comprising, after fixation, reductively treating the dyed or printed substrate with an aqueous solution containing a reducing agent, the rH value of which being selected from a value of from 0 to 30 such as to decompose non-bound disperse dyestuff and render it colourless and/or decompose it such that it does not re build-up on the substrate whilst leaving the fixed reactive dyestuff substantially unaffected.

By synthetic fibre textile substrates as used herein is to be understood those which are dyeable with disperse dyes. Preferably, the substrate to be treated by the process of the invention is a polyester/cotton mixed substrate.

Treatment may be effected by immersing the substrate in an aqueous bath containing reducing agent or by printing the substrate with an aqueous solution containing reducing agent, preferably the former.

The rH value, which is a measure of the reducing power of an aqueous solution is defined by the variables redox potentials, pH value and temperature of the solution. A further variable of the reducing power is the treatment time. Thus, the necessary rH value to achieve the reductive decomposition of the non-fixed disperse dye whilst leaving the fixed reactive dye intact can be obtained by regulating the above-mentioned parameters. The reducing power of the treatment solution may also depend on the nature and concentration of the reducing agent.

The calculation of the rH value may be made in accordance with the following formula,

$$rH = \frac{U_{abs}}{0.0992 \cdot (273.16 + t^{\circ}C)} + 2pH$$

where

$t^{\circ}C$ is the temperature of the solution $U_{abs} = U_{gem} + U_{ref}$

where

U_{gem} is the measured potential, for example for a Platinum electrode with a reference electrode e.g. Ag/AgCl electrode in KCl (3M),

U_{ref} is the potential of the standard electrode (in relation to a hydrogen electrode).

The potential of several standard electrodes are known, for example for Ag/AgCl in KCl (3M) the potential is 260.918-(0.683 . t°C). Thus, for a system containing a platinum electrode in combination with a Ag/AgCl reference electrode in KCl(3M) the rH value is given by the following formula:

$$rH = \frac{U_{gem} + 260.918 - (0.683 \cdot t^{\circ}C)}{0.992 (273.16 + t^{\circ}C)} + 2pH$$

The optimal rH value will depend also on the dyestuffs used. Essentially, redox-systems with very low rH values of from 0 to 5, that is with relatively high reduction power, can be used only when reactive dyes having a special resistance to reduction are present. Reduction systems with high rH values, for example 15 to 30, which have low reduction power may be used when the disperse dye present is easily reducible or is saponifiable with alkali.

The rH value of the reduction system is preferably from 1 to 20. However, with systems having a medium reducing power i.e. having rH values of from 3 to 20 the choice of dyestuffs is optimal. The most preferred rH values are from 3 to 10.

As stated above, the reducing power of the system is not only dependent on the particular reducing agent(s) and the concentration thereof but also depends on the temperature, the pH and the treatment time.

Depending on the reducing agent employed, the higher the temperature of the treatment bath, the higher the reduction power, for example reduction systems based on sodium formaldehyde sulphonylate exhibit a marked increase in reduction power with rising temperature, the optimum reduction power of which systems only being reached at the boil. However, with other reducing agents, for example reduction systems based on sodiumdithionite, the optimal reduction strength is already reached at room temperature. The choice of reducing agent and of the temperature of the treatment will depend on the type of dyestuffs present, as in some cases at higher temperatures the reduced dyestuff may go onto the fibre again and cause undesired colouration of the white parts of a print or undesired dulling of light shades. Therefore, in some cases, the reductive treatment is advantageously carried out discontinuously in several baths, optionally having successively increasing temperatures, in order to enable the quickest possible removal of unbound dyestuff and of thickeners whilst preventing the reassembly of the destroyed dye particles and their re-build-up on the substrate. The temperature(s) of the treatment bath(s) may vary from 10 to 120°C, and is preferably from 30 to 100°C, more preferably from 30 to 80°C. When the substrate is printed with the reducing system it may be stored at room temperature or subjected to a short treatment (i.e. up to 10 minutes) with saturated steam.

The choice of the pH of the treatment solution will also depend on the reducing agent employed. Where reducing agents which are not soluble in alkali medium are used, the pH value will be under 7. However, in principle, with exception of the above case, the treatment may be carried out over the whole pH range so long as the fibre is not deleteriously affected. Suitably, the treatment is carried out in neutral to strongly alkali medium (7 to 14). When using strong alkali it should be considered that, whilst the removal of the hydrolysable disperse dye may be accelerated, the stability of the bond between some reactive dyes and the fibre and the properties of polyester itself may be deleteriously affected. Suitable agents for adjusting the pH include sodium hydroxide, sodium carbonate, trisodium phosphate, formic acid and acetic acid.

The treatment time in the reduction bath depends on the reduction system, the depth of dyeing and/or of print and the dyestuff used. Generally the treatment time is between 5 seconds and 1 hour. For the treatment in one bath the treatment time is preferably between 1 to 10 minutes, more preferably between 1 to 5 minutes. In the multi-bath treatment, the treatment time generally totals from about 5 minutes to 40 minutes, preferably 5 to 30 minutes, with about 20 minutes being most preferred.

The treatment may be continuous or discontinuous. When the treatment is carried out in a continuous process the reduction baths should be periodically controlled and adjusted where necessary. The control of the reduction potential of the baths may be made using redox indicators. For rH values from 2 to 4.5 Neutral Red which changes from red to colourless is suitable, for rH values from 4 to 7.5 Indathrene Yellow G-paper which changes from yellow to blue is suitable and for values from 13.5 to 15.5 Methylene Blue which changes from blue to colourless is

suitable. Details about the use of such indicators and the indicators suitable for other rH values can be found in Melland 30/1949, page 113.

The reducing agent for the treatment may, in principle, be any organic or inorganic compound which permits the obtention of the above-mentioned rH values and which are suitable for use in aqueous media; such reducing agents can be found in the Colour Index.

Suitable reducing agents include hydrogensulphide, sulphur dioxide, thioureadioxide, sulphites, sulphides (such as sodium sulphide, ammonium sulphide), polysulphides, strongly electropositive metals, metal salts in the lower valence states (such as Fe(II)-, Zn (II)-, Ti(III)- and CrII-salts), organic oxidizable compounds (such as aldehydes and sugars, especially glucose), reducing agents used in vat dyeings and/or printing processes (such as sodium bisulphite, formaldehydesulphoxylates especially the sodium, calcium and zinc compounds, dithionites especially sodium dithionite, aminomethanesulphinates and nitrilotri-1-ethanesulphinates especially the sodium salts).

Preferred reducing agents are sodium- or zinc-formaldehyde sulphoxylate, sodiumhydrogensulphide, glucose, fructose, lactose and dextrin.

The amount of reducing agent can vary depending on the other variables which influence the rH value. Suitably the treatment bath contains the reducing agent in amounts of from 0.1 to 10 g/l, preferably 0.5 to 5 g/l.

It is advantageous to rinse the dyed and fixed textile substrate with cold water to remove excess unfixed dyestuff, fixing agents and thickeners before subjecting the substrate to the reductive treatment. As stated above, the reductive treatment may be effected in several baths, in which case the substrate may also be subjected to intermediate rinsing and washing processes.

After the treatment with the reduction bath or baths, the substrate is preferably neutralized, e.g. with acetic acid, and then rinsed in cold water.

It is advantageous to employ 0.5 to 2 g/l of a conventional organic detergent in the reduction bath(s) (and in the wash baths when employed) in order to increase the washing out of and prevent the re take-up of the reduced reaction products.

The treatment may also be carried out in the presence of water softeners and/or complex forming agents.

The process of the present invention may, in principle, be used for treating substrates dyed with disperse dyes as given in the Colour Index. These are disperse dyestuffs of the nitro-, aminoketone-, ketoimine-, methine-, azomethine-, nitrodiphenylamine-, quinoline-, aminonaphthacumarine-, cumarine-, azo- and anthraquinone series. It is to be appreciated that it will not give equal results with all disperse dyes.

Especially suitable are azo dyes, in particular monoazo dyes, with those azo dyes which have a (lower)alkoxycarbonyl(lower)alkyl-, (lower)-alkylcarbonyloxy(lower)alkyl- or cyano(lower)alkyl-amino group in the coupling component being especially suitable. Also very suitable are anthraquinone dyes which have a (lower)alkoxycarbonyl(lower)alkylamino or (lower)alkylcarbonyloxy(lower)alkylamino group.

By "lower" as used herein is meant alkyl and alkoxy radicals having 1 to 6 carbon atoms. The preferred lower alkyl and alkoxy radicals having 1 to 4, especially 1 to 2 carbon atoms.

Representative disperse dyes which may be treated in accordance with the process of the present invention are C.I. Disperse Yellow 42, C.I. Disperse Yellow 49, C.I. Disperse Yellow 126, C.I. Disperse Yellow 202, C.I. Disperse Red 72, C.I. Disperse Red 74, C.I. Disperse Red 107, C.I. Disperse Red 202, C.I. Disperse Red 306, C.I. Disperse Violet 77, C.I. Disperse Blue 75, C.I. Disperse Blue 79, C.I. Disperse Blue 176, C.I. Disperse Blue 177, C.I. Disperse Blue 257 and C.I. Disperse Blue 286.

A general condition for the process of the present invention is that the non-fixed disperse dye particles are quickly decomposed and that the decomposition products have a very small or practically negligible affinity for cellulose or polyester and thus do not build-up again on the substrate during the treatment. The rate of decomposition and the build-up of the decomposition products for a particular disperse dyestuff may be tested by the following method:

Increasing concentrations of disperse dye are charged in baths with mechanical stirrers. After boiling point is reached 2 g/l sodium formaldehydesulphoxylate, 2 ml/l caustic soda 36°Bé and a white polyester/cotton substrate are added thereto. (Liquor to goods ratio 40:1). The bath is held for 5 minutes at the boil. Subsequently the substrate is rinsed in running water and dried.

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Disperse dyes which are especially suitable for the process of the present invention show no staining or colouration of the white test polyester and cotton fabric at concentrations of at least 1.0×10^{-4} mol/litre.

The reactive dyes used to dye the polyester/cellulose substrates to be treated by the process according to the invention may, in principle, be any water soluble reactive dye which contains at least one fibre reactive group and include reactive dyes of the azo (monoazo, polyazo and metalazo)-, anthraquinone-, formazane-, triphenyldioxazine-, nitro- and phthalocyanine series having at least one fibre reactive group. Examples of suitable dyes are those having at least one reactive group selected from vinylsulphonyl, sulphatoethylsulphonyl, sulphatoethylsulphonamido, thiosulphatoethylsulphonamido, sulphatoethylsulphonacrylamido, methyltaurinoethylsulphonyl acrylamido, α -haloacrylamido, chloropropylamido, sulphatopropylamido, haloaceticacidamido, mono- and di halo-1,3,5-triazinyl, trichloropyrimidinyl, mono-chlorodifluoropyrimidinyl, methylsulphonylchloromethylpyrimidinyl, dichloroquinoxalinyl and dichloropyrazinyl radicals. Also suitable are dyes having reactive groups derived from halocarboxylic acids, especially chloroacetyl, β -chloropropionyl, α - β -dibromopropionyl and α - β -dichloropropionyl radicals.

Especially suitable reactive dyes are those which have a good fixation yield, very good solubility, low substantivity, good stability of fixed dye on the fabric, and which on treating in an aqueous medium having a low rH value at a high temperature for a long period of time give dyeings or prints which do not exhibit loss of dye strength or change of dye shade.

Specific screening methods for reactive dyes are as follows:

1. A chequered standard depth print made on cotton or cotton/polyester fabric with reactive dyes is treated after fixation for 5 to 10 minutes at 40°C with 2 g/l zincformaldehydesulphoxylate and 1 ml/l formic acid at pH 3 in a paddle bath or liquor circulating bath with a liquor to goods ratio of 40:1.

2. A chequered standard depth print made on cotton or cotton/polyester fabric with a reactive dye is treated after fixation for 5 to 10 minutes at 90 to 95°C with 2 g/l sodium formaldehyde sulphoxylate and 2 ml/l caustic soda 36°Be in a paddle bath or liquor circulating bath at liquor to goods ratio of 40:1.

3. A standard depth print made on cotton or polyester/cotton fabric with a reactive dye is treated, after fixation, for 5 to 10 minutes at 60°C with 2 ml/l sodiumhydrogen sulphide and 2 ml/l caustic soda 36°Be in a paddle bath or liquor circulating bath with a liquor to goods ratio of 40:1.

The criteria for judging the prints are as stated above with the maximum allowable reduction in depth of dyeing of the print being to a value 4—5 on the grey scale (no visible change).

The process according to the present invention may be used for treating textile substrates which have been dyed or printed with at least one disperse dye and at least one reactive dye by any of the known dyeing and printing methods. Suitably, dyeing with the reactive and disperse dye(s) may be carried out simultaneously.

The process according to the present invention, by decomposing any non-fixed disperse dye and possibly non-bound reactive dye, reduces the amount of normal washing of dyeings and prints and thus saves water and energy. Furthermore, the quality of the dyeings and prints is improved as non-fixed dyestuff is removed and thus results in dyeings being obtained which are more brilliant and exhibit improved wet fastnesses. In some cases the light fastness is also improved. In the case of prints, undesired staining of the white parts or of the lighter shade parts with dyestuff present in the wash baths is avoided.

The following Examples further serve to illustrate the invention. In the Examples the parts and percentages are by weight and the temperatures are in degrees Centigrade.

EXAMPLE 1

A tone-in-tone print on polyester/cotton 67:33 is made as follows:

A printing paste containing:

5	36 parts of C.I. Disperse Orange 30 (liq. 50%)	
	7 parts of C.I. Disperse Red 167 (liq. 50%)	
	20 parts of C.I. Disperse Blue 79 (liq. 50%)	5
	23 parts of C.I. Reactive Orange 62	
	1.5 parts of C.I. Reactive Red 119	
	12.5 parts of C.I. Reactive Blue 104	
10	450 parts of "Manutex F" 8% (Trade Mark Commercial thickener)	10
	80 parts of urea	
	X parts of water	
	10 parts of sodium bicarbonate	
	10 parts of a mild reduction inhibitor (<i>m</i> -nitrobenzoic acid)	
15	1000 parts of printing paste	15

is produced by mixing and stirring.

The mixed fabric is printed with this printing paste on a screen printing machine, then dried as usual and subjected for 6 minutes to superheated steam fixation at 175°. It is subsequently further treated on a washing machine as follows:

20 It is firstly rinsed cold in an overflow followed by a boiling treatment, at a liquid/goods ratio of 40:1, with water containing 3 ml/l of caustic soda 36°Bé and 2 g/l of Na-formaldehyde sulphonylate, for 4 minutes. The treatment bath has a rH value between 3.0 and 4.5.

25 It is then neutralised with acetic acid. Finally, it is rinsed cold and then dried.

A brilliant print having a dark brown shade, with a pure white base is obtained. 25

The print possess good wet-fastness and rubbing-fastness.

30 Instead of the one treatment at the boil the textile may be treated in several baths having lower temperatures; with treatment at 40° the rH value is between 16.5 and 18, with treatment at 60° the rH value is between 12.5 and 13.5, and with treatment at 80° the rH value is between 6.0 and 8.5.

A liquor ratio of 20:1 instead of 40:1 also gives similar results.

35 Equally good results may be obtained using 5 g/l of sodium carbonate instead of 3 ml/l of caustic soda 36°Bé. Instead of using the superheated steam fixation method for 6 minutes at 175°, the printed textile material may also be fixed for 1 minute in dry heat at 210°, whereby again equally good results are obtained.

When the treatment baths additionally contain water softeners (depending on the degree of hardness) similar results are obtained.

EXAMPLE 2

40 Continuous tone-in-tone dyeing on polyester/cotton 67:33 with disperse and reactive dyestuffs. Using a dyestuff mixture containing:

33 parts of C.I. Disperse Red 167
56 parts of C.I. Reactive Red 147
11 parts of C.I. Reactive Orange 62

45 a single-bath, one-stage continuous dyeing process is set up with the following padding liquor composition:

	40 g/l of disperse/reactive dyestuff mixture	
	60 g/l of urea	
	8 g/l of sodium bicarbonate	
50	10 g/l of common salt	
	20 g/l migration inhibitor, e.g. "Sandapol AM" liquid.	50

The liquor is cold padded with a dry weight increase of 70%, the textile is then dried. Subsequently, the textile material is subjected to thermosol treatment for 60 seconds at 210° and is subjected to aftertreatment as described in Example 1.

A dyeing having a brilliant red shade which is dyed tone-in-tone is obtained.

55 EXAMPLE 3

Instead of the disperse dyestuff mixture used in Example 1, 31.5 parts of C.I.

Disperse Blue 79 are used, and instead of the reactive dyestuff mixture used in Example 1, 36 parts of C.I. Reactive Blue 104 and 3 parts of C.I. Reactive Blue 105 are used. A dark blue print is obtained, which has an advantageous resist of the white unprinted parts. The print has good wet fastness. Instead of the aftertreatment described in Example 1, a continuous wash process may be used, e.g. rinsing cold in a first wash bath, in a second wash bath treating it for 60 seconds at 40° with 2 g/l of "Lyogen DFT" (Trade Mark; dispersing agent), in a third wash bath treating it for 3 minutes with 3 g/l of a Na-formaldehyde sulfoxylate and 3 ml/l of caustic soda 36°Bé at 80° (rH value between 8 and 10), in a fourth wash bath neutralizing with acetic acid and in a fifth wash bath rinsing cold.

Similar results are obtained by additionally using a non-ionic detergent in wash compartment 3.

EXAMPLE 4

Instead of the dyestuff mixture used in Example 2, for continuous dyeing

7.2 parts of C.I. Disperse Yellow 49

35.7 parts of C.I. Disperse Yellow 42

57.1 parts of C.I. Reactive Yellow 25

are used. 50 g/l of disperse-reactive dyestuff mixture are added to the padding liquor described in Example 2. The thermosol dyeing obtained is aftertreated in the following manner:

In a first wash bath it is rinsed cold, in a second wash bath it is treated at 40° for 1 minute with a bath of 2 g/l "Lyogen DFT" (dispersing agent), in a third wash bath it is subjected to cold treatment for 3 minutes with 3 ml/l caustic soda 36°Bé, 0.1 ml/l of sodium dithionite and 1 g/l of a non-ionic detergent (the cold treatment bath has a rH value between 9.5 and 11), in a fourth wash bath it is neutralized with acetic acid and in a fifth wash bath it is rinsed cold.

Optimum fastness is obtained with a preliminary boiling treatment for 1 minute in the fifth wash bath with a non-ionic detergent.

EXAMPLE 5

A print on polyester cotton is made in accordance with the procedure described in Example 1, with the exception that instead of the disperse dyestuff mixture of Example 1, 15 parts of C.I. Disperse Blue 75 are used and instead of the reactive dyestuffs of Example 1, 12 parts of C.I. Reactive Violet 23 are used.

Aftertreatment takes place as follows: in a first wash bath rinsing cold, in a second and third wash bath treatment with 2 g/l of zinc formaldehyde-sulphoxylate and 1 ml/l of formic acid (80%) at a pH of 3 and at 40° (the rH value in the second and third wash baths is between 2.5 and 4.0), in a fourth wash bath rinsing clear (in an overflow), in a fifth wash bath soaping at the boil (with a common detergent), and in a sixth wash bath rinsing clear in an overflow.

A blue print is obtained, which has an advantageous reserve on the white unprinted surfaces.

EXAMPLE 6

As well as the possibility of effecting the reductive treatment during the washing processes, the process may be effected as follows:

The solution containing reduction agents is applied to the textile substrate after fixation. Then the dyeings are treated either whilst wet, partly or completely dry, by storing the goods at room or higher temperature or by treating them with steam or with other sources of energy. Subsequently, the washing-out process is effected so as to remove the unfixed, decomposed dyestuff particles, chemicals and dyeing additives.

The application of the solution containing a reduction agent may be effected by a 1000 point roller, a fully-engraved flat or rotary screen, a spraying apparatus or a slop-padder. The amount of the reduction system to be applied and the subsequent treatment method are selected such that only the unfixed dyestuff particles are destroyed.

A polyester/cotton 67/33 mixed fabric is printed and fixed as described in Example 1. A thickened solution containing

20 g/l of carob bean flour derivative, and
2 g/l of glucose in water

is subsequently applied by a 1000 point roller. The dry weight increase is 70%. The

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substrate is then dried and treated for 5 minutes in saturated steam at 102°. Finally, the fabric is rinsed in cold water, soaped at 60° to boiling point with a solution containing 0.5 g/l of a non-ionic washing agent, rinsed again and finally dried. A vivid dark-brown print is obtained having good fastnesses whereby the unprinted parts remain practically pure white. Equally good results are obtained by using instead of the 2 parts glucose.

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2 g/l of sodium-formaldehyde sulphonylate and 3 ml/l of NaOH 30 Bé, or
2 g/l of zinc formaldehyde sulphonylate and
0.5 ml/l of formic acid (80%).

EXAMPLE 7

10 A print on polyester/cotton 67:33 was made with a printing paste as described in Example 1 except that in place of the disperse dye mixture mentioned in Example 1, 15 parts of C.I. Disperse Yellow 126 are used and instead of the reactive dyestuff mixture mentioned in Example 1, 30 parts of C.I. Reactive Yellow 25 are used.

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After the print is rinsed cold in an overflow an aftertreatment at a liquor to goods ratio of 40:1 is effected for 5 minutes at 60° with a solution containing 2 g/l sodium hydrogensulphide (Na HS), 2 ml/l caustic soda 36°Be, the measured rH value being between 12.5 and 13.5, followed by neutralisation and rinsing cold. The sodium hydrogensulphide may be present in a mixture of sulphides in water. Brilliant prints with white base are obtained.

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Similar results are obtained if 5 g/l sodium carbonate are used instead of 2 ml/l caustic soda. The measured rH value of such solution is also between 12.5 and 13.5. Alternately 5 g/l of trisodiumphosphate may be used in place of the sodium carbonate, in which case the rH value is between 12 and 13.

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A treatment temperature of 95° instead of 60° with varying alkali systems and practically the same rH value also gives similar results.

EXAMPLE 8

30 A print is made as described in Example 1 with the exception that instead of the disperse dye mixture of Example 1, 24 parts of C.I. Disperse Yellow 126 (liquid 50%) and 40 parts of C.I. Disperse Red 72 (liquid 50%) are used and instead of the reactive dyestuff mixture of Example 1, 24 parts of C.I. Reactive Yellow 25, 1.8 parts C.I. Reactive Orange 64 and 6.2 parts Reactive Red 147 are used.

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The aftertreatment is carried out as follows:

35 The fabric is rinsed cold and treated at a liquor to goods ratio of 40:1 for 5 minutes in three baths each containing 3 g/l glucose, 5 g/l sodium carbonate, 0.5 g/l non-ionic surfactant and 1 g/l of a commercial water softener.

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40 The treatment is commenced at 60° whereby the rH value is from 20 to 22. In the second bath where the temperature is 80° the rH value is between 14 and 16. In the third bath the treatment is at 95°, the measured rH value is between 9 and 12.5. Subsequently, the fabric is neutralized and rinsed in cold running water. A brilliant print having a white background is obtained.

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Similar results are obtained when 2 ml/l caustic soda 36°Bé are used in place of the 5 g/l sodium carbonate, practically the same rH values being obtained.

45 In place of the 3 g/l glucose, 3 g/l of fructose can be used in all the baths, whereby in the bath at 60° the rH value is between 20 and 22, in the bath at 80° it is between 14 and 17 and in the bath at 95° it is between 9 and 11.5.

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Alternatively, 3 g/l ascorbic acid may be used instead of the fructose, whereby in the bath at 60° the rH value is between 16 and 18, in the bath at 80° it is between 12 and 14 and in the bath at 95° it is between 9 and 13.

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Instead of ascorbic acid, 3 g/l lactose may be used whereby the rH values of the baths at 60°, 80° and 95° are between 20 and 22, 15 and 18 and 9 and 13, respectively.

55 Instead of lactose, 3 g/l of dextrin may be used whereby the rH values of the baths at 60°, 80° and 95° are between 20 and 22, 18 and 20 and 10 and 15, respectively.

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EXAMPLE 9

60 A print is made as described in Example 1 with the exception that 6 parts C.I. Disperse Yellow 126 and 14 parts C.I. Disperse Blue 176 are used instead of the disperse dyestuff mixture of Example 1, and 8 parts of C.I. Reactive Yellow 25 and 8 parts C.I. Reactive Blue 105 are used.

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The fabric is then rinsed in water and is then treated in aqueous solution containing 1 g/l sodium formaldehydesulphoxylate, 1 g/l glucose and 2 ml/l caustic soda 36°Bé. The treatment is carried out at 60°, 80°, and at the boil whereby the rH values are between 13 and 16, 7 and 9 and 5 and 6.5, respectively. A print with good white base is obtained.

The same results can be obtained by treatment in baths at 40° and 60° which only contain conventional washing and dispersing agent or a non-ionic detergent, followed by treatment in the baths at 80° and at the boil in the presence of the above described reducing mixture.

EXAMPLE 10

A print on polyester/cotton 67:33 is made in conventional manner with a printing paste containing:

28 Parts C.I. Disperse Yellow 126	} all in liquid form (50%)
42 Parts C.I. Disperse Red 72	
70 Parts C.I. Disperse Blue 286	
53 Parts C.I. Reactive Black 34	
7 Parts C.I. Reactive Orange 62	
500 Parts Manutex F, 8% (Trade Mark; commercially available thickener)	
50 Parts urea	
10 Parts sodium bicarbonate	
10 Parts reduction stabilizer, e.g. "Revatol S", and water to make the paste up to 1000 parts.	

The printed and fixed material is rinsed cold and is treated for 5 minutes in a bath at 40°, then in a bath at 60°, then in a bath at 80° and finally in a bath at 95°, at a liquor to goods ratio of 40:1 with each of the baths containing 2 g/l sodium formaldehydesulphoxylate, 2 ml/l caustic soda 36°Bé, 1 g/l water softener and 0.5 g/l of a washing or dispersing agent. The bath at 40° has a rH value between 18 and 20, the bath at 60°, a value between 12 and 16, the bath at 80°, a value between 6 and 9 and the bath at 95°, a value between 4.5 and 6. Subsequently, the fabric is neutralized and rinsed in running water. A deep black print with white background is obtained. The print has good wet fastness.

The residue of reducing agent in each bath is measured. In order to assess the percentage of used reducing agent a titration is made, or alternatively a potentiometric titration may be made whereby the turning point between the reducing power and oxidation power may be read off.

Taking the amount of reducing agent at the beginning of treatment in each bath as being 100% and conducting a titration after the treatment in each bath, it is found that the amount of the residual reducing agent present after treatment at 40° is 99%, after treatment at 60° is 98%, after treatment at 80° is 94% and after treatment at 95° is 90%.

Equally good results are obtained when, instead of a liquor to goods ratio of 40:1, it is raised from 20:1 to 100:1.

WHAT WE CLAIM IS:—

1. A process for treating synthetic fibre/natural cellulose mixed textile substrates which have been dyed or printed with at least one disperse and at least one reactive dye comprising, after fixation, reductively treating the dyed or printed substrate with an aqueous solution containing a reducing agent, the rH value of which bath being selected from a value of from 0 to 30 such as to decompose non-bound disperse dyestuff and render it colourless and/or decompose it such that it will not re build-up on the substrate whilst leaving the fixed reactive dyestuff substantially unaffected.

2. A process according to Claim 1, in which the substrate is polyester/cotton.

3. A process according to Claim 1 or Claim 2, in which the rH value is from 1 to 20.

4. A process according to any one of the preceding claims, in which the rH value is from 3 to 20.

5. A process according to any one of the preceding claims, in which the substrate is printed with an aqueous solution containing a reducing agent.

6. A process according to Claim 5, in which the substrate is subsequently stored at room temperature or treated with saturated steam followed by rinsing and washing.

The fabric is then rinsed in water and is then treated in aqueous solution containing 1 g/l sodium formaldehydesulphoxylate, 1 g/l glucose and 2 ml/l caustic soda 36°Bé. The treatment is carried out at 60°, 80°, and at the boil whereby the rH values are between 13 and 16, 7 and 9 and 5 and 6.5, respectively. A print with good white base is obtained.

The same results can be obtained by treatment in baths at 40° and 60° which only contain conventional washing and dispersing agent or a non-ionic detergent, followed by treatment in the baths at 80° and at the boil in the presence of the above described reducing mixture.

EXAMPLE 10

A print on polyester/cotton 67:33 is made in conventional manner with a printing paste containing:

28 Parts C.I. Disperse Yellow 126	} all in liquid form (50%)
42 Parts C.I. Disperse Red 72	
70 Parts C.I. Disperse Blue 286	
53 Parts C.I. Reactive Black 34	
7 Parts C.I. Reactive Orange 62	
500 Parts Manutex F, 8% (Trade Mark; commercially available thickener)	
50 Parts urea	
10 Parts sodium bicarbonate	
10 Parts reduction stabilizer, e.g. "Revatol S", and water to make the paste up to 1000 parts.	

The printed and fixed material is rinsed cold and is treated for 5 minutes in a bath at 40°, then in a bath at 60°, then in a bath at 80° and finally in a bath at 95°, at a liquor to goods ratio of 40:1 with each of the baths containing 2 g/l sodium formaldehydesulphoxylate, 2 ml/l caustic soda 36°Bé, 1 g/l water softener and 0.5 g/l of a washing or dispersing agent. The bath at 40° has a rH value between 18 and 20, the bath at 60°, a value between 12 and 16, the bath at 80°, a value between 6 and 9 and the bath at 95°, a value between 4.5 and 6. Subsequently, the fabric is neutralized and rinsed in running water. A deep black print with white background is obtained. The print has good wet fastness.

The residue of reducing agent in each bath is measured. In order to assess the percentage of used reducing agent a titration is made, or alternatively a potentiometric titration may be made whereby the turning point between the reducing power and oxidation power may be read off.

Taking the amount of reducing agent at the beginning of treatment in each bath as being 100% and conducting a titration after the treatment in each bath, it is found that the amount of the residual reducing agent present after treatment at 40° is 99%, after treatment at 60° is 98%, after treatment at 80° is 94% and after treatment at 95° is 90%.

Equally good results are obtained when, instead of a liquor to goods ratio of 40:1, it is raised from 20:1 to 100:1.

WHAT WE CLAIM IS:—

1. A process for treating synthetic fibre/natural cellulose mixed textile substrates which have been dyed or printed with at least one disperse and at least one reactive dye comprising, after fixation, reductively treating the dyed or printed substrate with an aqueous solution containing a reducing agent, the rH value of which bath being selected from a value of from 0 to 30 such as to decompose non-bound disperse dyestuff and render it colourless and/or decompose it such that it will not re build-up on the substrate whilst leaving the fixed reactive dyestuff substantially unaffected.

2. A process according to Claim 1, in which the substrate is polyester/cotton.

3. A process according to Claim 1 or Claim 2, in which the rH value is from 1 to 20.

4. A process according to any one of the preceding claims, in which the rH value is from 3 to 20.

5. A process according to any one of the preceding claims, in which the substrate is printed with an aqueous solution containing a reducing agent.

6. A process according to Claim 5, in which the substrate is subsequently stored at room temperature or treated with saturated steam followed by rinsing and washing.

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7. A process according to any one of Claims 1 to 4, in which the substrate is immersed in an aqueous bath containing a reducing agent.

8. A process according to any one of Claims 1 to 4, in which the substrate is immersed in a plurality of baths each containing reducing agent.

5 9. A process according to Claim 8, in which each successive bath containing reducing agent is of a higher temperature than the preceding one. 5

10. A process according to any one of Claims 7 to 9, in which the substrate is rinsed with cold water prior to the treatment in the bath or baths containing reducing agent.

10 11. A process according to any one of Claims 7 to 9, in which the treatment is carried out in alkali medium. 10

12. A process according to Claim 11, in which the substrate is subsequently neutralized and then rinsed in cold water.

15 13. A process according to any one of the preceding claims in which the reducing agent is selected from sodiumformaldehydesulphoxylate, sodiumhydrogensulphide, glucose, fructose, lactose and dextrin. 15

20 14. A process according to any one of the preceding claims in which the substrate has been dyed or printed with one or more disperse dyes selected from monoazo disperse dyes containing a (lower)alkylcarbonyloxy(lower)alkyl-, (lower)alkoxycarbonyl(lower)alkyl- or cyano(lower)alkylamino groups in the coupling component and anthraquinone disperse dyes containing a (lower)alkoxycarbonyl(lower)alkylamino or (lower)alkylcarbonyloxy(lower)alkylamino group. 20

25 15. A process according to any one of the preceding claims in which the substrate has been dyed or printed with one or more disperse dyes selected from C.I. Disperse Yellow 42, C.I. Disperse Yellow 49, C.I. Disperse Yellow 126, C.I. Disperse Yellow 202, C.I. Disperse Red 72, C.I. Disperse Red 74, C.I. Disperse Red 107, C.I. Disperse Red 202, C.I. Disperse Red 306, C.I. Disperse Violet 77, C.I. Disperse Blue 75, C.I. Disperse Blue 79, C.I. Disperse Blue 176, C.I. Disperse Blue 177, C.I. Disperse Blue 257 and C.I. Disperse Blue 286. 25

30 16. A process for reductively treating, after fixation, synthetic fibre/natural cellulose mixed textile substrates which have been dyed or printed with at least one disperse and at least one reactive dye substantially as hereinbefore described with reference to any one of Examples 1 to 10. 30

35 17. Dyed or printed textiles whenever obtained by a process according to any one of Claims 1 to 16. 35

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