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STEP-WISE PROCESS FOR COLORING AND FINISHING CELLULOSE MATERIALS WHEREIN A CATIONIC DYE-FIXING AGENT IS EMPLOYED WITH THE RESIN FINISHING AGENT

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9 Claims. (Cl. 8—18)

This invention relates to a new colouration process. More particularly, the invention relates to a process for the finishing of cellulose textile fabrics coloured with "reactive" dyestuffs whereby a very high level of fixation of dyestuff on the fibre is combined with excellent quality of dyeing.

It is well known to dye or print cellulose textile fabrics with reactive dyestuffs, and thereafter to submit the fabric to a conventional finishing treatment to obtain a crease-resistant or dimensionally stabilised coloured fabric. It has now been found that in such a process, a valuable effect may be obtained by adding a cationic dye-fixing agent to the liquor from which the resin-finishing agent is applied. This procedure prevents unfixed dyestuff from dissolving in the resin-finishing bath, and assists fixation so that the expensive and time-consuming washing process normally required when dyeing with "reactive" dyestuffs can be dispensed with between the dyeing and finishing steps, and is considerably shortened and frequently may be dispensed with entirely after the resin-curing step.

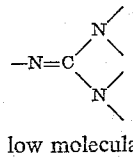
By a "cationic dye-fixing agent," we mean an organic compound free from anionic water-solubilising groups such as sulphonic acid groups, but containing one or more ammonium groups, and frequently, but not always, an aliphatic chain of 6 or more carbon atoms. As examples of such compounds there may be mentioned the following classes:

(a) Compounds having an ammonium group and at least one aliphatic or cycloaliphatic residue having at least 10 carbon atoms. Such substances are named in United Kingdom specifications Nos. 339,962, 366,918, 441,767, 443,588, 646,921 and 496,611. These substances may be applied in conjunction with a copper salt as described in United Kingdom specification No. 535,582.

(b) The condensation products of formaldehyde with dicyandiamide, or mixtures of urea and dicyandiamide in the presence of amine or ammonium salts. Such products are described in United Kingdom specifications Nos. 19783/38, 576,562 and 651,139. These products may also be applied in conjunction with a copper salt.

(c) The condensation products of aldehydes with hydroxyalkyl derivatives of amino and imino compounds, in the presence of salts of nitrogen containing inorganic or organic bases. Such products are described in United Kingdom specification No. 611,235.

(d) The water-soluble condensation products of nitrogen-containing complex copper compounds with compounds containing at least once the grouping:



and with aldehydes of low molecular weight. Such products are described and claimed in United Kingdom specification No. 736,792.

(e) The acid salts of the condensates of cyanamide, dicyandiamide N-substituted dicyandiamides, guanidine and

N-substituted guanidines, with polyalkyleneimines. Such products are described and claimed in United Kingdom specifications Nos. 522,539, 657,753, 755,478 and 755,519.

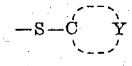
(f) Arylene and alkylene biguanides such as those described and claimed in United Kingdom specification No. 705,838 and their polymers.

(g) The quaternary salts of polyaminoethylacrylates and other polymerised ethylenically unsaturated compounds containing primary, secondary or tertiary amino groups.

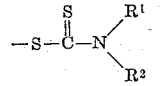
Thus according to the present invention there is provided the improvement in the process of colouring textile materials consisting wholly or partly of fibrous cellulose by application of a reactive dyestuff, thereafter applying a resin-finishing agent and thereafter baking the treated material to cure the resin, which improvement consists of adding to the aqueous liquor containing the resin-finishing agent, a cationic dye fixing agent as hereinbefore defined.

By a reactive dyestuff we mean a water-soluble dyestuff which contains a reactive halogen atom or other substituent capable of reacting with the resin or fibre so that the remainder of the dyestuff becomes attached to the resin or fibre through a covalent bond. As examples of such dyestuffs, there may be mentioned, for example, dyestuffs containing s-triazinyl or pyrimidyl radicals carrying labile atoms or groups directly attached to the ring, and dyestuffs containing a beta-halogenopropionyl, beta-halogenoethylsulphonyl, beta - halogenoethylsulphamyl, beta-sulphatoethylsulphonyl, beta - hydroxyethylsulphonyl, chloro-acetylamino, beta-(chloromethyl)-beta-sulphatoethylsulphamyl, acryloylamino, beta-(alkyl- and aryl-sulphonyloxy) alkyl sulphonyl, beta-acyloxyalkyl-sulphonyl, vinyl- sulphonyl, alkyl phosphite or sulphon fluoride radical.

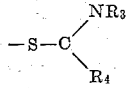
By a labile atom or group, we means an atom or group which is bound by a covalent bond to a carbon atom of the pyrimidine or triazine nucleus but which readily dissociates under the influence of heat or alkalis, especially in the presence of moisture, to form an ion or an uncharged molecule. As examples of such atoms or groups, there may be mentioned, for example, bromine, or, preferably, chlorine atoms, sulphonic acid groups, thiocyano groups, negatively substituted aryloxy and arylthio groups, such as sulphophenoxy, sulphophenylthio, nitrosulphophenoxy, disulphophenoxy and sulphonaphthoxy groups, quaternary ammonium groups, groups of the formula:



wherein Y represents the group of atoms necessary to form a 5- or 6-membered heterocyclic ring which may carry substituents or form part of a fused ring system; groups of the formula:



wherein R^1 and R^2 each represents the same or different alkyl, cycloalkyl, aryl or aralkyl groups, or R^1 and R^2 together form, together with the nitrogen atom, a 5- or 6-membered heterocyclic ring; and groups of the formula:



wherein R_3 and R_4 may be the same or different and each represents a hydrogen atom or an alkyl, aryl or aralkyl group.

The dyestuffs in these classes may be for example nitro dyestuffs or dyestuffs of the azo, anthraquinone or phthalocyanine series, and may be metal free or may

contain metal in complex formation. Specific examples of suitable dyestuffs are described in United Kingdom specification No. 209,723 in Examples 1 and 2, United Kingdom specification No. 298,494 in Example 1, in United Kingdom specifications Nos. 460,224, 733,471, 740,533, 775,308, 772,030, 774,925, 780,591, 781,930, 785,120, 785,222, 802,198, 805,562, 826,689 and 852,604, and 937,182 and 924,990.

There may also be used dyestuffs containing hydroxyl, amino, hydroxyalkylamino, guanyl hydrazide, semicarbazide or thiosemicarbazide groups linked to a triazine nucleus or hydroxyalkylamino groups linked to a pyrimidine nucleus or to the alkyl radical of an alkylsulphonyl, alkylsulphamyl, alkylcarbonyl or alkylcarbonamide group. Dyestuffs of these types have been described, for example in United Kingdom specification No. 209,723 in Example 1, in United States Patent No. 2,768,158 and United Kingdom specifications 904,227, 929,425 and 927,404, and the use of dyestuffs of these types has been described, for example in French Patents Nos. 1,206,833 and 1,208,532.

The dyestuff is applied to the textile material by immersion of the material in an aqueous solution of the dyestuff preferably by padding or by application of a printing paste containing the dyestuff. The printing paste may be applied by any of the usual methods, such as by roller, block, screen or stencil. The dyestuff solution may contain other additions commonly used in the art of dyeing with reactive dyestuffs, for example, urea, wetting agents, such as alkali metal alkylated naphthalene sulphonates and condensates of ethylene oxide with alkylated phenols, fatty alcohols or fatty amines, migration inhibitor such as sodium chloride, sodium sulphate or sodium alginate and, usually, an acid binding agent to aid reaction with the fabric. The acid-binding agent is only necessary to achieve reaction with the fabric, and where the dyestuff is capable of reaction with the resin, there is no need to use an acid-binding agent. It is preferred to use a mild alkali, such as sodium carbonate or bicarbonate, as the acid-binding agent to minimise neutralisation of any acid or acid salt which may be used as curing catalyst in the subsequent processing.

After application of the dyestuff solution, the fabric is preferably dried at atmospheric temperature, but may also be dried at elevated temperatures for example by treating with hot air at a temperature of between 50° C. and 100° C. and if desired, may then be baked or steamed, for example by treatment in an oven or on a stenter for about 3 to 5 minutes at a temperature of 120 to 150° C. or by treatment with steam in a steamer at a temperature of 100 to 105° C. for about 2 to 20 minutes. Before drying, fabric which has been dyed, particularly when containing viscose rayon, is advantageously allowed to stand in a moist condition for a period of time, which may be from 15 minutes to 24 hours, preferably from 30 minutes to 2 hours, the treatment leading to improved fixation and diffusion of the dyestuff into the fibres, and hence to improved quality and appearance of dyeing.

The printing pastes containing the dyestuff may also contain the additives usually used with "reactive" dyestuffs such as urea, sodium, m-nitro-benzene sulphonate, wetting agents of the types indicated above and thickening agents such as sodium alginate, ethyl cellulose, starch, locust bean gum, and, preferably, oil-in-water emulsions and water-in-oil emulsions.

After application of the printing paste, the fabric is preferably dried, for example by passage over heated rollers, and may, if desired, then be baked or steamed for, for example, from 2 to 20 minutes.

The dried textile fabric is then treated with the resin-finishing agent, for example by padding the material through an aqueous solution or suspension of the agent. The solution or suspension may contain other commonly-used additives for example curing catalysts for the resin-finishing agent, which may be acidic or alkaline as necessary, anionic and nonionic surface active agents, lubricating agents, softening agents, water repellents and stiffening or bodying agents, as well as the cationic dye-fixing agents.

As examples of resin-finishing agents which may be used, there may be mentioned acetal cellulose reactants (as defined in the Textile Research Journal for 1959 at page 74) and, more particularly, mixtures comprising the methylol derivatives or lower alkyl ethers of methylol derivatives of monomeric or polymeric compounds containing a plurality of amino or mono substituted amino groups, said compounds being known from the art or used in practice for the formation of resins by condensation with formaldehyde. Suitable compounds include, for example monomeric nitrogen compounds such as urea, thiourea, substituted ureas and thioureas, dicyandiamide, dicyandiamidine, biguanides, amides, carbamates, allophanates and heterocyclic compounds such as aminotriazines, urons, ureins, ureides, imidazolidones, triazones and hydantoins or mixtures of such compounds, and polymeric nitrogen compounds such as the polymeric amides made by the reaction of dibasic acids with diamines. The lower alkyl ethers of the methylol derivatives of these compounds include for example the methyl, ethyl, propyl and butyl ethers. Other resin-finishing agents which may be used are condensation products of ketones with aldehydes, in particular, CH_2O.

As examples of acid catalysts which may be used there may be mentioned salts formed from weakbases and mineral acids such as zinc chloride, ammonium sulphate and ammonium chloride, mineral acid salts of organic amines, weak acids, for example organic acids such as oxalic acids and substantially neutral substances which develop acidity on heating or steaming, such as magnesium chloride and ammonium thiocyanate; mixtures of such catalysts may be used.

As examples of alkaline catalyst which may be used there may be mentioned sodium bicarbonate and sodium carbonate.

The aqueous solution used for application of the resin-forming composition may contain between 3% and 40% and preferably between 5% and 30% of the resin-forming compositions and between 0.1% and 5% and preferably between 0.5% and 3.0% of acid or alkali catalyst.

As examples of lubricating and softening agents which may be used, there may be mentioned, for example dispersions of natural or synthetic waxes, methylol stearamide and the quaternary ammonium salts of United Kingdom specification No. 808,265 (which in low concentration act as lubricants rather than as cationic dye-fixing agents). The amount of dye-fixing agent used can vary within wide limits, in some cases as little as 0.005 gram per litre of padding liquor being effective whilst in other cases as much as 1.5 grams per litre is required. These amounts are those at which a reasonable effect is shown and the use of higher quantities up to 25 to 30 grams per litre will give improved results.

The baking stage may be carried out at a wide range of temperatures, provided the temperature is sufficiently high to cure the resin. The times of baking will depend upon the temperature used, a short period of heating, for example, about 10 seconds, being sufficient at temperatures of the order of 200° C. whilst a period of about 1 to 5, usually 3, minutes is required at a temperature of about 155° C. The baking temperatures are preferably maintained at between 120° C. and 200° C. adjusting the time to minimise thermal degradation of the cellulose.

If desired, the textile material can be given a short washing treatment, for example, a treatment in a weakly alkaline aqueous solution of soap or detergent at the boil for about 1 minute. This washing treatment serves the purpose of removing small amounts of unpolymerised resin-forming agent and the residual acidity caused by the acid catalyst or the decomposition products thereof.

The invention is illustrated but not limited by the following examples in which parts and percentages are by weight:

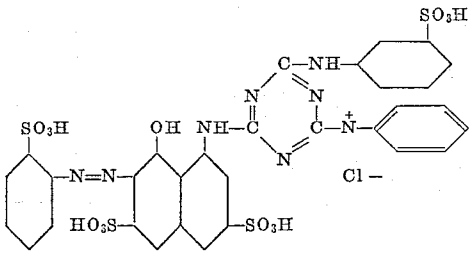
Example 1

100 parts of viscose rayon fabric are padded with a solution containing 10 parts of the copper complex of 2-(5' - sulpho-2'-hydroxyphenylazo)-6-(2'',4''-dichloro-6''-s-triazinyl - amino)-1-naphthol-3,5-disulphonic acid, 10 parts of sodium bicarbonate and 5 parts of sodium triisopropyl naphthalene sulphonate in 975 parts of water, squeezed, maintained in a moist condition at atmospheric temperature for 1 hour and dried at 70° C. in a hot air drier.

The fabric is then padded through 1000 parts of a solution containing 400 parts of a 60% aqueous solution of a urea-formaldehyde precondensate (obtained by stirring a mixture of 1 mole of urea and 1.6 moles of formaldehyde at pH 8.5 and 20° C. for 4½ hours), 15 parts of ammonium dihydrogen phosphate, 20 parts of the condensate of dicyandiamide, formaldehyde and ammonium chloride obtained as described in Recipe 1 of United Kingdom specification No. 651,139, 1.15 parts of aqueous ammonia of specific gravity 0.88 and 15 parts of a 25% aqueous dispersion of the product of Example 14 of United Kingdom specification No. 808,265. The fabric is then squeezed, dried on a pin stenter at 100° C. and baked at 150° C. for 3 minutes. The fabric is dyed a bluish-red shade having good fastness to severe washing treatments and is resistant to creasing.

The following table summarises further examples of the new process, following the procedure of Example 1 above, but substituting the dyestuff named in the first column for that used in the first padding solution and using the resin-finishing agent, acid catalyst and cationic dye-fixing agents named in the second, third and fourth columns for the urea-formaldehyde precondensate, the ammonium dihydrogen phosphate and the dicyandiamide/formaldehyde/ammonium chloride condensation product, respectively.

In each case a fabric is obtained having excellent fastness to creasing and coloured in the shade described in the fifth column; the dyeing has good fastness to severe washing:

Dyestuff	Resin-finishing agent	Acid catalyst	Cationic dye-fixing agent	Shade
2. Disodium 1-amino-4-(3'-β-sulphatoethylsulphonylanilino)anthraquinone-2-sulphonate, 5 parts.	As in Example 1	As in Example 1	As in Example 1	Bright reddish-blue.
3. The dyestuff having the formula:  10 parts	do	do	do	Bright-red.
4. 1-(2'',5''-dichloro-4'-sulphophenyl)-3-methyl-4-(5'-dichloro-s-triazinylamino-2'-sulphophenylazo)-5-pyrazolone, 25 parts.	70% aqueous solution of 1,3-dimethylol-2-imidazolidone, 80 parts.	Diethanolamine hydrochloride 10 parts.	1,4-phenylene biguanide hydrochloride, 10 parts.	Greenish-yellow.
5. 6-(N-dichloro-s-triazinyl-N-methyl)amino-1-hydroxy-2,2'-azonaphthalene-1',3,5'-trisulphonic acid, 10 parts.	As in Example 4	Magnesium chloride, 12 parts.	1,6-hexamethylene biguanide polymer, 20 parts.	Orange.
6. 1-(dichloro-s-triazinyl)amino-7-phenylazo-8-naphthol-3,6-disulphonic acid, 5 parts.	50% aqueous solution of hexamethoxymethylmelamine, 70 parts.	Magnesium chloride, 15 parts.	Cetyl pyridinium bromide, 20 parts.	Bluish-red.
7. 1-amino-4-[4'-(dichloro-s-triazinyl)amino anilino]anthraquinone-2,3',5-trisulphonic acid, 10 parts.	50% aqueous solution of 4,5-dihydroxy-1,3-methylol-2-imidazolidone, 70 parts.	Ammonium dihydrogen phosphate, 10 parts.	The polymer of the dimethyl sulphate quaternary ammonium salt of diethylaminoethyl methacrylate, 10 parts.	Greenish-blue.
8. The copper complex of 6-(dichloro-s-triazinyl)amino-2-[4'-(2'',5''-disulphophenylazo)-5'-methyl-2'-hydroxyphenylazo]-1-naphthol-3,5-disulphonic acid, 20 parts.	45% aqueous solution of trimethylol urea, 60 parts.	Magnesium chloride, 6 parts; tartaric acid, 1.4 parts.	Saturated aqueous solution of chlorohexidine hydrochloride, 30 parts.	Dark blue.
9. 1-amino-4-[4''-(dichloro-s-triazinyl)amino-2',2''-disulphostilben-4'-ylamino]anthraquinone-2,5-disulphonic acid, 10 parts.	60% aqueous solution of a 1:1.6' urea/formaldehyde condensate, 300 parts.	Diethanolamine hydrochloride, 10 parts.	1,6-hexamethylene biguanide polymer, 25 parts.	Green.
10. The 1:2-chromium complex of 6-(dichloro-s-triazinyl)amino-2-(2'-carboxyphenylazo)-1-naphthol-3-sulphonic acid, 10 parts.	50% aqueous solution of hexamethoxymethyl melamine 70 parts.	Ammonium dihydrogen phosphate, 15 parts.	1,4-phenylene biguanide polymer, 20 parts.	Reddish-brown.
11. The copper complex of 8-(2'-amino-4'-chloro-s-triazinyl)amino-1,1'-dihydroxy-2,2'-azo-naphthaoene-3,4'-6,8'-tetrasulphonic acid, 10 parts.	45% aqueous solution of trimethylol urea, 80 parts.	Zinc nitrate, 10 parts.	As in Example 1	Royal blue.
12. The copper complex of 8-(2'-m-sulphoanilino-4'-chloro-s-triazinyl)amino-2-(3''-chloro-5''-sulpho-2''-hydroxyphenylazo)-1-naphthol-3,6-disulphonic acid, 15 parts.	50% aqueous solution of 4,5-dihydroxy-1,3-dimethylol-2-imidazolidone, 80 parts.	Magnesium chloride, 12 parts.	Cetyl pyridinium bromide.	Purple.
13. 1-(2'-chloro-6'-methyl-4'-sulphophenyl)-3-methyl-4-(2'-methoxy-5'-β-sulphatoethyl-sulphonylphenylazo)-5-pyrazolone, 10 parts.	70% aqueous solution of 1,3-dimethylol-2-imidazolidone, 80 parts.	Zinc nitrate, 10 parts; tartaric acid, 1 part.	The condensate of ethylene bis-dicyandiamide with diethanolamine hydrochloride, 60 parts.	Greenish-yellow.
14. The copper complex of 1-(4'-sulphophenyl)-3-methyl-4-(2'-hydroxy-5'-β-sulphatoethylsulphonylphenylazo)-5-pyrazolone, 15 parts.	50% aqueous solution of hexamethoxymethylmelamine, 70 parts.	Diethanolemine hydrochloride, 7 parts; ammonium nitrate, 3 parts.	Saturated aqueous solution of chlorohexidine hydrochloride, 30 parts.	Reddish-yellow.

Dyestuff	Resin-finishing agent	Acid catalyst	Cationic dye-fixing agent	Shade
15. 2-(2'-methoxy-5'-β-sulphatoethylsulphonylphenylazo)-1-naphthol-5-sulphonic acid, 10 parts.	As in Example 1	Zinc nitrate, 10 parts.	As in Example 1	Red.
16. The copper complex of 8-acetylamino-2-(2'-hydroxy-5'-β-sulphatoethylsulphonylphenylazo)-1-naphthol-3,6-disulphonic acid 5 parts.	45% aqueous solution of trimethylol urea, 40 parts; 50% aqueous solution of hexamethoxy methylmelamine, 40 parts.	Ammonium dihydrogen phosphate, 15 parts.	1,6-hexamethylene biguanide polymer, 25 parts.	Violet.

Example 17

In this example, the procedure followed is that of Example 1, with the exception that the sodium bicarbonate is omitted from the first padding solution.

The coloured fabric so obtained has a lower fastness to severe washing treatments, but has a commercially satisfactory standard of fastness to the mild washing treatments normally recommended for viscose rayon fabrics.

The following table lists dyestuffs which can be used in the above procedure in place of these named in Example 1. The second padding liquor can be formulated in accordance with any of those described in Examples 1 to 16 inclusive.

Example	Dyestuff	Shade
18	The product obtained by condensing copper phthalocyanine tetra- (3')- sulphonchloride with 1.5 moles of β-chloroethylamine in the presence of ammonia.	Turquoise.
19	The product obtained by condensing copper phthalocyanine tri- (3')- sulphonchloride monosulphonic acid with 1.5 moles of β-chloroethylamine.	Do.
20	The product obtained by condensing copper phthalocyanine tri- (3')- sulphonchloride monosulphonic acid with one mole of p-phenylene diamine sulphonic acid in the presence of ammonia and reacting with 1 mole of 2,4,6-trichloropyrimidine.	Do.
21	The 1:2-chromium complex of 6-(2'-methoxy-4'-chloro-s-triazinylamino)-2-(2''-carboxyphenylazo)-1-naphthol-3-sulphonic acid.	Reddish-brown.
22	A mixture of 1 part of the 1:2-cobalt and 3 parts of the 1:2-chromium complex of 6-(2'-amino-4'-chloro-s-triazinylamino)-6'-nitro-1,2'-dihydroxy-2,1'-azonaphthalene-3,4'-disulphonic acid.	Dark grey.
23	The copper complex of 6-(2'-m-sulphoanilino-4'-chloro-s-triazinylamino)-2-[4''-(2,5-disulphophenylazo)-5''-methyl-2''-hydroxyphenylazo]-1-3,5-disulphonic acid.	Dark blue.
24	The product obtained by condensing copper phthalocyanine tri- (3') -sulphonchloride monosulphonic acid with 1 mole of 2-amino-4-chloro-6-(4'-amino-3'-sulphoanilino)-s-triazine.	Turquoise.
25	1-(2',5'-dichloro-4'-sulphophenyl)-3-methyl-4-[5''-(2,5,6-trichloropyrimidin-4-ylamino)-2'-sulphophenylazo]-5-pyrazolone.	Greenish-yellow.
26	8-[2',4'-di (hydroxymethylamino)-s-triazin-6'-ylamino]-2-(2''-sulphophenylazo) -1-naphthol-3,5-disulphonic acid.	Bright red.
27	8-[2',4'-di (pentahydroxy-n-hexylamino)-s-triazin-6'-ylamino]-2-(2'-sulphophenylazo)-1-naphthol-3,6-disulphonic acid.	Do.

Example 28

100 parts of a mercerised cotton fabric are padded with a solution containing 5 parts of 1-amino-4[4'-(2''-chloro-4'' - m-sulphoanilino-6''-s-triazinylamino)anilino]anthraquinone-2,3'-disulphonic acid, 10 parts of sodium bicarbonate and 5 parts of sodium triisopropyl naphthalene sulphonte in 980 parts of water, squeezed, dried at 70° C. in a hot air drier, and baked for 3 minutes at 150° C.

The fabric is then padded through an aqueous solution containing 80 parts of a 40% aqueous solution of 1,3-dimethylol - 5-β-hydroxyethyl-hexahydrotriazin-2-one, 10 parts of zinc nitrate hexahydrate, 20 parts of the condensate of dicyandiamide, formaldehyde and ammonium chloride obtained as described in Recipe 1 of United Kingdom specification No. 651139, 1.15 parts of aqueous ammonia of specific gravity 0.88, 5 parts of a 50% aqueous dispersion of methylol stearamide, 1 part of the product obtained by condensing cetyl alcohol with 17 moles of ethylene oxide and 1 part of acetic acid in each 1000 parts. The fabric is then squeezed, dried on a stenter at 100° C. and baked at 150° C. for 5 minutes.

The fabric is then washed at 100° C. for 1 minute with a solution contining 3 parts of sodium carbonate and 1 part of the reaction product of octyl phenol with 8 moles of ethylene oxide per 1000 parts water, rinsed and dried. The fabric is dyed a greenish-blue shade which is fast to severe washing treatments and resistant to creasing.

If in the above example the dyestuff is replaced by 10 parts of the product obtained by condensing 1 mole of tetrachloropyrimidine with 3-methyl-1-(2',5'-dichloro-4'-sulphophenyl) - 4 - (5''-amino-2''-sulphophenylazo)-5-pyrazolone, the fabric is dyed a fast greenish-yellow shade and is resistant to creasing.

Example 29

A printing paste containing:

	Parts
Dyestuff of Example 1 of specification No. 846,949	2
Water	32
Oil-in-water emulsion thickening	55
Sodium alginate thickening (4% sodium alginate)	9
Sodium m-nitrobenzenesulphonate	1
Sodium bicarbonate	1
	100

is printed on mercerised cotton fabric and the fabric is dried at 70° C. and then treated for 5 minutes with steam at atmospheric pressure.

The printed fabric is then padded in the resin pad liquor described in Example 28, dried and heat baked for 3 minutes at 150° C. The fabric is then washed as described in Example 28 and finally dried.

A bluish-red print is obtained on the cotton which possesses good fastness to light and washing and which is resistant to creasing.

The emulsion thickening used in the above example may be obtained by adding 80 parts of white spirit to a rapidly stirred mixture of 5 parts of a 26.5% aqueous solution of the condensate of octyl phenol with 8 moles of ethylene oxide, 7½ parts of a 20% aqueous solution of the condensate of cetyl alcohol with 17 moles of ehtylene oxide, and 7½ parts of water.

Example 30

In place of the dyestuff used in Example 29 there are used 2 parts of the dyestuff of Example 2 of specification No. 838,335 and the resultant printing paste is printed on viscose rayon. The fabric is dried at 70° C. and then heat treated for 3 minutes at 140° C.

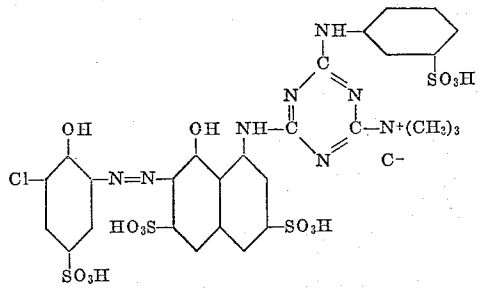
The printed fabric is then padded in the resin pad liquor described in Example 1 and heat treated for 3 minutes at 150° C. The fabric is then washed as described in Example 28, rinsed in water and finally dried.

A bright reddish-blue print is obtained on the viscose fabric possessing good fastness to light and washing and which is similar in strength to an unsoaped print produced by the same method.

Example 31

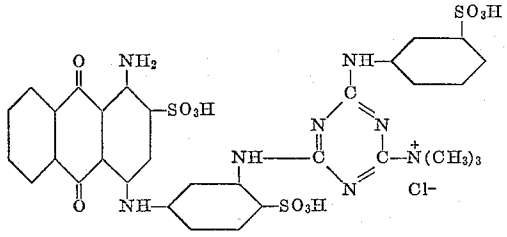
100 parts of a mercerised cotton poplin fabric are

padded with a solution containing 5 parts of the copper complex of the compound of the formula:



10 parts of sodium bicarbonate and 5 parts of sodium triisopropyl naphthalene sulphonate in 980 parts of water, squeezed, dried at 70° C. in a hot air drier and baked for 3 minutes at 150° C. The fabric is then padded through an aqueous solution containing 80 parts of a 40% aqueous solution of 1,3-dimethylol-5-beta-hydroxyethyl-hexahydro-triazin-2-one, 10 parts of zinc nitrate hexahydrate, 10 parts of hexamethylene biguanide polymer, 5 parts of a 50% aqueous dispersion of methylol stearamide, 1 part of the product obtained by condensing cetyl alcohol with 17 moles of ethylene oxide and 1 part of acetic acid in each 1000 parts. The fabric is then squeezed, dried on a stenter at 100° C. and baked at 150° C. for 5 minutes. The fabric is then washed at 80° C. for 1 minute with a solution containing 3 parts of sodium carbonate and 1 part of the reaction product of octyl phenol with 8 moles of ethylene oxide per 1000 parts of water, rinsed and dried. The fabric is dyed a purple shade which is fast to severe washing treatments and the fabric is resistant to creasing.

If the dyestuff used in the above example is replaced by 10 parts of the dyestuff of the formula:



the material is dyed a fast blue shade and is resistant to creasing.

Example 32

If in the process described in Example 1, the viscose rayon is replaced by a plain weave mercerised linen, and the fabric after baking is mercerised with a caustic soda solution of specific gravity between 1.25 and 1.3, rinsed neutralised and dried, a bluish-red linen fabric is obtained which is resistant to creasing.

Example 33

100 parts of bleached mercerised plain weave cotton fabric are padded, at 100% expression, with a solution containing, per 1000 parts, 10 parts of the copper complex of 6-(dichloro-s-triazinylamino)-2-[4'-(2'',5''-disulphophenylazo) - 5' - methyl - 2' - hydroxyphenylazo]-1-naphthol-3,5-disulphonic acid, 10 parts of sodium bicarbonate, 5 parts of sodium triisopropyl naphthalene sulphonate and is then dried in warm air at 70° C. The fabric is then padded, at 100% expression, through a solution containing, per 1000 parts, 200 parts of a 60% urea-formaldehyde precondensate, 30 parts of sodium bicarbonate, 62 parts of the condensation product of ethylene bisdicyandiamide and diethylene triamine hydrochloride, 5 parts of a 50% aqueous dispersion of methylol stearamide and 1 part of the condensation product of cetyl alcohol with 17 moles of ethylene oxide. It is then dried in warm air at 70° C. and baked for 3 minutes at 160° C. The fabric is then washed off as described in Example 28.

The fabric is then dried to a dark blue shade, which is fast to washing, and is resistant to creasing.

Example 34

100 parts of bleached mercerised botton poplin are padded with a solution containing 28 parts of the 1:2-chromium complex and 12 parts of the 1:2-cobalt complex of 1-(4'-chloro-6'-amino-s-triazine-2'-ylamino)-2 - (5''- nitro -2''- hydroxyphenylazo) - 8 - naphthol - 3,6-disulphonic acid, 5 parts of sodium triisopropyl naphthalene sulphonate and 10 parts of sodium bicarbonate in 1000 parts of water, squeezed to 100% expression, maintained in a moist condition for 45 minutes at atmospheric temperature and dried. The fabric is then padded through a solution containing 80 parts of a 40% aqueous solution of 1,3-dimethylol-5-β-hydroxyethylhexahydrotriazin-2-one, 6.5 parts of magnesium chloride hexahydrate, 2 parts of tartaric acid, 5 parts of a 50% aqueous dispersion of methylolstearamide, 1 part of the product obtained by condensing cetyl alcohol with 17 moles of ethylene oxide and 20 parts of the condensate of dicyandiamide, formaldehyde and ammonium chloride obtained as described in Recipe 1 of United Kingdom specification No. 651,139.

Example 35

A viscose rayon fabric is padded at 100% expression with a solution containing, per 1000 parts, 10 parts of 4-[5''-(dichloro-s-triazinylamino)-3''-sulphophenylazo] - 1-(4'-sulphophenyl)-3-carboxypyrazolone, 10 parts of sodium bicarbonate and 5 parts of sodium triisopropyl naphthalene sulphonate, and dried at 70° C.

The dried fabric is then subjected to the treatment described in the second paragraph of Example 1. It is dyed a reddish yellow shade having good fastness to mild washing treatments and is resistant to creasing.

Example 36

A viscose rayon fabric is padded at 100% expression with a solution containing, per 1000 parts, 10 parts of 1-amino-4-[4'-dichloro-s - triazinylaminoanilino]anthraquinone-2,3',5-trisulphonic acid and 5 parts of sodium butyl naphthalene sulphonate, and is then dried at 70° C.

The fabric is then subjected to the treatment described in the second paragraph of Example 1. It is dyed a greenish blue shade fast to mild washing treatments and is resistant to creasing.

Example 37

100 parts of a mercerised cotton poplin fabric are padded at 100% expression with a solution containing 10 parts of 1-amino-4-(3'-dichloro-s-triazinylaminoanilino) anthraquinone-2,4'-disulphonic acid, 10 parts of sodium bicarbonate and 5 parts of sodium triisopropylnaphthalene sulphonate. It is then dried at 70° C. and baked for 3 minutes at 150° C.

The fabric is then subjected to the treatment described in the second paragraph of Example 28. It is dyed a reddish-blue shade which is fast to severe washing treatments and resistant to creasing.

What we claim is:

1. In the process of colouring cellulose materials comprising treatment with a reactive dye-stuff, thereafter applying a resin-finishing agent and thereafter baking the treated material to cure the resin, the improvement which consists in adding to the aqueous liquor containing the resin-finishing agent, an organic cationic dye-fixing agent free from anionic solubilizing groups and having at least one ammonium group.

2. Process according to claim 1 consisting essentially in the following sequence of steps:

(a) the textile material is immersed in an aqueous solution of the dyestuff containing an acid-binding agent,

(b) the fabric is thereafter maintained in a moist condition at atmospheric temperature for a period of time of from 15 minutes to 24 hours and is then dried,

(c) without any intermediate washing step, the material is treated with the liquor containing the resin-finishing agent and said cationic dye fixing agent, and

(d) the material is thereafter baked to cure the resin.

3. Process according to claim 1 consisting essentially in the following steps:

(a) the textile material is immersed in an aqueous solution of the dyestuff which is free from acid-binding agent,

(b) the fabric is thereafter maintained in a moist condition at atmospheric temperature for a period of time of from 15 minutes to 24 hours and is then dried,

(c) without any intermediate washing step, the material is treated with the liquor containing the resin-finishing agent and said cationic dye fixing agent, and

(d) the material is thereafter baked to cure the resin.

4. Process according to claim 1 consisting essentially in the following sequence of steps:

(a) the textile material is immersed in an aqueous solution of the dyestuff containing an acid-binding agent,

(b) the material is dried,

(c) without any intermediate washing step, the material is treated with the liquor containing the resin-finishing agent and cationic dye fixing agent, and

(d) the material is thereafter baked to cure the resin.

5. Process according to claim 1 consisting essentially in the following steps:

(a) the textile material is immersed in an aqueous solution of the dyestuff which is free from acid-binding agent,

(b) the material is dried,

(c) without any intermediate washing step, the material is treated with the liquor containing the resin-finishing agent and cationic dye fixing agent, and

(d) the material is thereafter baked to cure the resin.

6. Process according to claim 1 consisting essentially in the following sequence of steps:

(a) the textile material is immersed in an aqueous solution of the dyestuff containing an acid-binding agent,

(b) the material is dried and subjected to a baking step,

(c) without any intermediate washing step, the material is treated with the liquor containing the resin-finishing agent and cationic dye fixing agent, and

(d) the material is thereafter baked to cure the resin.

7. Process according to claim 1 consisting essentially in the following sequence of steps:

(a) the textile material is immersed in an aqueous solution of the dyestuff containing an acid-binding agent,

(b) the fabric is thereafter maintained in a moist condition at atmospheric temperature for a period of time of from 15 minutes to 24 hours and is then dried,

(c) the textile material is then subjected to a baking step,

(d) without any intermediate washing step, the material is treated with the liquor containing the resin-finishing agent and cationic dye fixing agent, and

(e) the material is thereafter baked to cure the resin.

8. Process according to claim 1 characterised in that the textile material after treatment is then subjected to a washing step to remove unpolymerised resin-forming agent and residual acid, and is dried.

9. Process according to claim 1 characterised in that a linen textile material treated, and thereafter it is subjected to a mercerisation step and washed to remove alkali and is dried.

References Cited by the Examiner

UNITED STATES PATENTS

2,768,158	10/56	Strobel et al.	8—1.2
3,116,103	12/63	Gamlen et al.	8—13

FOREIGN PATENTS

209,723	3/25	Great Britain.
496,611	12/38	Great Britain.
535,592	4/41	Great Britain.
611,235	10/48	Great Britain.
651,139	3/51	Great Britain.
705,838	3/54	Great Britain.
755,519	3/54	Great Britain.
736,792	9/55	Great Britain.
775,308	5/57	Great Britain.
785,222	10/57	Great Britain.
826,689	1/60	Great Britain.
846,505	8/60	Great Britain.

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