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VAT DYEING OF CELLULOSE ACETATE

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This invention relates to uniform or local colouration of textile materials more particularly textile materials consisting of or containing fibres of cellulose acetate or other cellulose ester or ether.

It has long been the practice to colour cellulose textile material, e. g. fabrics, with vat dyes by applying the unreduced vat dye in conjunction with a formaldehyde sulphonylate and an alkali such as sodium or potassium carbonate, and thereafter steaming the material and subjecting it to oxidation. This method, while very successful for cellulose textile materials yields but indifferent results when applied to a textile material of cellulose acetate fibres. Unless the conditions are such that very substantial saponification of the material takes place, the fixation of the dye is very poor and the resulting colourations are of low resistance to rubbing. By including a thiocyanate in the mixture of vat dye, formaldehyde sulphonylate and alkali, some improvement in fastness to rubbing can be obtained, but the disadvantage remains that the material undergoes a considerable degree of saponification.

We have now found that excellent colourations of very good resistance to rubbing can be obtained with little or no saponification of the material by impregnating the material with an unreduced vat dye, an aldehyde sulphonylate, a hydroxy-alkylamine, and a thiocyanate, and thereafter steaming the material and subjecting it to oxidation to reoxidise to the parent vat dye the leuco compound thereof produced and fixed on the material upon steaming. Preferably the dye, aldehyde-sulphonylate, hydroxy alkylamine, and thiocyanate are applied together in an aqueous medium which may be applied over the whole surface of the fabric or locally according to the effect required. Very good results can be obtained with indigoid vat dyes and with very many anthracene vat dyes. The colourations are not only of good resistance to rubbing as indicated above, but possess also the excellent fastness to light and washing normally associated with colourations produced on cellulose textiles by means of vat dyes.

The hydroxy alkylamine may be of the type $\text{NR}_1\text{R}_2\text{R}_3$ wherein R_1 is hydroxy-alkyl (e. g. hydroxy-ethyl or hydroxy-propyl), R_2 is hydrogen, hydroxy-alkyl, unsubstituted alkyl, cycloalkyl, or aralkyl, and R_3 is hydrogen, hydroxy-alkyl, unsubstituted alkyl, cycloalkyl, or aralkyl. Examples of suitable hydroxy-alkylamines are mono-, di- and tri-ethanolamine, mono-, di- and tri-propanolamine, hydroxyethyl-diethylamine, hydroxyethyl-ethylamine, cyclohexyl-diethanolamine, cyclohexyl-mono-ethanolamine, and benzyl-hydroxyethyl-amine. Monoethanolamine has

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been found of particular advantage in that when material uniformly or locally impregnated with the dye compositions is dried (as is usually desirable before the steaming operation) it does not become tacky as is the case when triethanolamine, for example, is used in place of the monoethanolamine.

The proportion of alkylolamine may be from 5-25% by weight of the dye composition employed. The optimum proportion depends on the particular hydroxy alkylamine employed and the particular vat dye. For example, in the case of indigoid vat dyes the proportion may be from 5-15% for example 10% of monoethanolamine or a slightly greater proportion of triethanolamine, say, 15%. In the case of many anthraquinone vat dyes rather higher proportions of hydroxy alkylamine are desirable, for example, from 15-25% by weight of the dye composition. Using 20% by weight of monoethanolamine very good results can be obtained with a wide range of vat dyes. Such high proportion in general leads to a slight saponification of the material which may be reduced or avoided by reducing the proportion of monoethanolamine to, say, 15% by weight of the dye composition.

From the point of view of cost of materials part of the hydroxy-alkylamine may advantageously be replaced by about one third of its weight of sodium carbonate or other alkali-metal carbonate. The content of hydroxy-alkylamine should not however be less than about 4% or 5%. Thus the material may be impregnated with a dye composition containing at least 4% of the hydroxy-alkylamine together with an alkali-metal carbonate, the sum of the percentage of the hydroxy-alkylamine and three times the percentage of alkali-metal carbonate being from 10 to 25. In the case of using an indigoid vat dye the sum may be for instance from 10 to 20 while in the case of using an anthraquinone vat dye the sum may advantageously be from 15 to 25.

As the thiocyanate, an alkali metal or ammonium thiocyanate is preferred, although the use of other water-soluble thiocyanates, for example, alkaline earth or zinc thiocyanates is not excluded from the scope of the invention. Sodium or potassium thiocyanate is preferred.

The aldehyde sulphonylate employed is preferably a formaldehyde sulphonylate, particularly sodium formaldehyde sulphonylate. These aldehyde sulphonylates only become active reducing agents at fairly high temperatures. In our new process the steaming treatment provides the requisite high temperature and it is at this stage that the vat dye is reduced and fixed on the material in the reduced or leuco form.

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The aqueous dye compositions need to be suitably thickened for local application and some degree of thickening is generally desirable when the dye compositions are applied over the whole surface of a fabric, for example, by mechanical impregnation methods, e. g. padding or all over printing. British gum is a very suitable thickener for our purposes though other thickeners may be employed, for example gum tragacanth.

Additions to the dye compositions other than those indicated above are not in general desirable or necessary. However, we do not exclude the presence for instance, of other swelling agents for cellulose acetate, for example, organic liquid swelling agents such as diethylene glycol or thiodiglycol. An addition which has been found useful more particularly in the case of indigoid dyes is urea; this may be incorporated in the dye composition for instance, in a proportion of 5-12%, e. g. 10%. Hygroscopic liquids such as glycerol are often beneficial.

When colouring fabrics consisting of or containing cellulose acetate fibres the dye composition may be applied over the whole surface of the fabric, for example by padding or all-over printing, or it may be applied locally, for example by roller or screen printing methods. Although it is in general convenient to apply the dye and other components of the composition in the form of a single aqueous preparation, it is not essential. For example, the dye may first be applied to the material, e. g. as an aqueous dispersion and the material then dried before application of the remaining components in a separate operation.

The material carrying the dye and other components of the compositions is preferably dried prior to the steaming operation. The latter may be effected in the manner customary in the art of printing vat dyes on textile materials. For the purposes of the present process a steaming of from 30-50 mins. at 104° C. has been found effective. This can be carried out for instance in a cottage steamer or in a continuous steamer. Substantially air-free steam is desirable.

The steamed material carries the vat dye in the leuco form and should be subjected to oxidation to convert the leuco compound to the parent vat dye. This may be effected conveniently by means of an aqueous solution of sodium perborate or percarbonate. Following the oxidation the material is preferably soaped, if desired after acidifying, and such soaping may be carried out with an aqueous soap solution at, say, 80° C. Higher temperatures are undesirable if delustring is to be avoided. The soaping may be replaced or supplemented by a steaming treatment. One purpose of the soaping and/or steaming is to cause the vat dye to exhibit its true shade as measured by the shade normally yielded on cellulose material.

The textile material coloured in accordance with the invention may be entirely of cellulose acetate fibres which may be present either as continuous filaments or as staple fibre. Textile materials containing cellulose acetate fibres in association with fibres of other materials, for example, animal fibres or natural or regenerated cellulose fibres may also be coloured by the new process. Mixed textile fabrics, for example, may be composed of cellulose acetate yarns in association with yarns of wool, silk, or other fibres. Again, the fabrics may consist of or contain yarns which contain both cellulose acetate staple fibres and fibres of other materials such as wool or cellulose.

By applying the dye compositions locally to

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fabrics dyed with a dischargeable dye it is possible to obtain discharge effects due to the action of the aldehyde sulphonylate under the influence of the steaming treatment.

The invention is illustrated by the following examples, the "parts" referred to being parts by weight.

Example I

A cellulose acetate fabric is padded with the following composition:

	Parts
Durindone Blue 4 BCS (tetrabromindigo) ---	15
Formosul -----	10
Sodium thiocyanate-----	15
Monoethanolamine -----	10
Water -----	25
British gum (30%)-----	15
Urea -----	10
	100

The padding is conducted so as to leave about 80% of the composition thereon, based on the weight of the material. The fabric is then dried, steamed for 40 minutes at 104° C., washed in cold water and oxidised in an aqueous solution containing 1 g. per litre of sodium percarbonate at 60° C. The material is then washed in water and finally soaped for half an hour at 80° C. in a 2 g. per litre aqueous soap solution. An excellent dyeing of very good fastness to rubbing is obtained.

Example II

A cellulose acetate fabric is printed with the following composition:

	Parts
Caledon Brilliant Purple 4 RPS (dichloroisodibenzanthrone) -----	2.5
Formosul -----	10
Sodium thiocyanate-----	15
Monoethanolamine -----	20
British gum (30%)-----	40
Water -----	12.5
	100

The material is then dried, steamed, oxidised and soaped in the manner indicated in Example I. A print of good colour value and good fastness to rubbing is obtained.

Similar results may be obtained by replacing the Caledon Brilliant Purple 4 RPS by any of the following dyes:

- 55 Caledon Yellow GS Flavanthrone
- Caledon Yellow 5 G Schultz, 7th edition, Supplementary vol. I, page 46, No. 1274a
- Caledon Yellow 2 R
- Caledon Yellow GKP
- 60 Caledon Red FFS Schultz, 7th edition, No. 1221
- Caledon Red BN Colour Index No. 1162
- Caledon Brilliant Red 3 B
- Caledon Red Violet 2 RN Schultz, 7th edition, No. 1260
- 65 Caledon Jade Green 4 GS
- Caledon Jade Green XS 12:12'-dimethoxydibenzanthrone
- Caledon Green 2 G
- 70 Caledon Olive Green B product of ring closure of 13 - (alpha - anthraquinonylamino) - benzanthrone
- Caledon Brown R 4:5'-dibenzoylamino-1:2:2':1'-dianthraquinone carbazole
- Caledon Ming Blue X an ether of 12:12'-dihydroxy-di-benzanthrone

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Caledon Dark Blue GS ethylene ether of 12:12'-dihydroxy-dibenzanthrone
Caledon Dark Blue BM dibenzanthrone

Example III

A cellulose acetate fabric is padded with the following composition:

	Parts
Caledon Jade Green XS	10
Formosul	10
Monoethanolamine	20
Sodium thiocyanate	15
British gum (30%)	20
Water	25
	100

The padding is conducted so as to leave about 80% of the composition thereon, based on the weight of the material. The material is thereafter dried, steamed, oxidised and soaped in the manner described in Example I.

Similar results may be obtained by replacing the Caledon Jade Green XS by any of the following Caledon dyes:

Caledon Yellow GKP
Brilliant Purple 4 RPS
Green 2 G
Olive Green B
Brown R
Dark Blue GS

Example IV

A padding liquor is made up of:

	Parts
Durindone Blue 4 BCS paste (I. C. I.)	10
Formosul	8
Sodium carbonate	4
Monoethanolamine	5
Sodium thiocyanate	10
Glycerine	3
Gum tragacanth (6% aqueous solution)	15
Water	45
	100

Cellulose acetate woven fabric is padded with this liquor so as to leave about 80% of the liquor thereon, based on the dry weight of the fabric. The fabric is then dried, steamed twice for 15 minutes at 104-105° C., and oxidised and finished as described in Example I. A royal blue shade is obtained.

Example V

A padding liquor is made up of:

	Parts
Caledon Brilliant Purple 4 RPS paste (I. C. I.)	10
Formosul	8
Sodium carbonate	6
Monoethanolamine	5
Sodium thiocyanate	15
Glycerine	3
Gum tragacanth (6%)	15
Water	38
	100

Cellulose acetate is padded with this liquor, dried, steamed, and oxidised as described in Example IV to give a full purple shade of good fastness to rubbing.

The invention has been described more particularly with reference to the colouring of textile materials consisting of or containing cellulose ace-

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tate fibers; the new process may also be applied to textile materials consisting of or containing fibres of other cellulose esters of carboxylic acids or of cellulose ethers. Examples of such esters and ethers are cellulose acetate-propionate, cellulose acetate-butyrate, cellulose propionate, and ethyl benzyl cellulose.

According to a modification of the invention the hydroxy aliphatic amine may be replaced by another water-soluble primary, secondary, or tertiary amine base. Said bases should be of relatively low volatility, for example, of boiling point above 140° C. so that they are substantially retained by the material at least up to the point at which steaming is effected. As an example benzylamine may be mentioned.

Having described our invention, what we desire to secure by Letters Patent is:

1. Process for the colouration of textile material comprising fibres of cellulose acetate, which comprises impregnating the material with an aqueous preparation containing an unreduced vat dye, a thiocyanate, sodium formaldehyde sulfoxylate, monoethanolamine and an alkali metal carbonate, the preparation containing at least 4% of the monoethanolamine and the sum of the percentage of monoethanolamine and three times the percentage of alkali metal carbonate being from 10 to 25, and thereafter drying and steaming the material and subjecting it to oxidation to reoxidise to the parent vat dye the leuco compound thereof produced and fixed on the material by the steaming.

2. Process for the production of pattern effects on textile fabrics comprising fibres of cellulose acetate, which comprises printing the material with a thickened aqueous preparation containing an unreduced vat dye, a thiocyanate, sodium formaldehyde sulfoxylate, monoethanolamine and an alkali metal carbonate, the preparation containing at least 4% of the monoethanolamine and the sum of the percentage of monoethanolamine and three times the percentage of alkali metal carbonate being from 10 to 25, and thereafter drying and steaming the material and subjecting it to oxidation to reoxidise to the parent vat dye the leuco compound thereof produced and fixed on the material by the steaming.

3. A process for the colouration of textile material comprising fibres of cellulose acetate, which comprises impregnating the material with an aqueous preparation containing an unreduced vat dye, sodium formaldehyde sulfoxylate, from 5 to 20% of monoethanolamine and from 10 to 15% of sodium thiocyanate, the latter being the sole cellulose acetate swelling agent in the preparation, and thereafter drying and steaming the material and subjecting it to oxidation to reoxidise to the parent vat dye the leuco compound thereof produced and fixed on the material by the steaming.

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