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COLOURING CELLULOSE TRIACETATE TEXTILE MATERIALS

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This invention relates to the colouration of textile material of cellulose acetate of high acetyl value by the formation of azo dyes thereon. The invention is particularly concerned with the colouration of textile material of cellulose acetate having an acetyl value above 59%. Cellulose acetate of acetyl value above 59% is hereinafter referred to as cellulose triacetate.

It is well known that a wide range of shades of good fastness properties, particularly to washing, can be obtained on cellulose textiles by forming azo dyes thereon from diazotisable amino compounds and certain coupling components, notably arylamides of 2:3-hydroxynaphthoic acids and some other ortho-hydroxy caboxylic acids, e.g. 2-hydroxy-carbazole-3-carboxylic acid and 3-hydroxy-diphenylene oxide-2-carboxylic acid. Further coupling components which can be used for this purpose include arylamides and certain other amides of aceto-acetic acid and other beta-ketocarboxylic acids; these latter compounds are capable of yielding yellow shades with appropriate diazo compounds. All of the foregoing types of coupling components are commonly referred to as naphthols by reason of the fact that they are employed for colouring textile materials in much the same way as beta-naphthol was very extensively employed. It will be noted, however, that they are not all derivatives of beta-naphthol though this is true of the arylamides of 2:3-hydroxynaphthoic acid. They are, however, like beta-naphthol and the aforesaid arylamides, characterised by being able to couple with diazo compounds at a carbon atom adjacent to a carbon atom carrying a hydroxy group and for this reason all are often referred to as enolic coupling components. The arylamides of beta-ketocarboxylic acids contain the group $—CH_2CO—$ which can be written as $—CH=C(OH)—$; hence there is a justification for describing these compounds also as enolic coupling components.

The foregoing coupling components are characterised by yielding with simple diazo compounds, e.g. diazotised aniline or diazotised para-nitroaniline or parachloraniline, azo dyes which are insoluble in water. Further, these water-insoluble azo dyes are such as exhibit substantially no affinity for textile material of acetone-soluble cellulose acetate when applied to the latter in the form of simple aqueous dispersions.

It is further known that, providing a suitable technique is followed, it is possible to use many of the same azo dye components for colouring cellulose acetate textile material. For the latter purpose, the material is allowed to take-up the coupling component from an aqueous dispersion of the latter, particularly a neutral or slightly acid or slightly alkaline dispersions. Further, it is desirable that both the diazotisable base and the coupling component should be incorporated in the cellulose acetate and the material then treated so as to diazotise the base and effect coupling of the resulting diazo compound with a coupling component. To this end both the diazotisable base and the coupling component may be applied to the cellulose acetate material as an aqueous dispersion, conventiently the same aqueous dispersion. Formation of the azo dye on the material can then be carried out by treating the material with an aqueous bath made up with sodium nitrite and an acid,

following which the material is preferably given an alkaline treatment, for example, treatment in a soap bath containing alkali.

In attempting to apply such methods to the colouring of cellulose triacetate textile materials we have found that the foregoing coupling components are taken up much less readily and/or to a less extent than is the case with ordinary acetone-soluble cellulose acetate materials and that in consequence the coupling component employed is, as a rule, very incompletely utilised and only pale shades obtained.

We have now found that the up-take of enolic coupling components by cellulose triacetate from aqueous baths can be greatly facilitated by means of substantially water-insoluble organic substances, particularly such as are solvents for the coupling component and compatible with or even solvents for the cellulose triacetate. We have found that diethyl phthalate is a particularly useful and valuable substance for this purpose. Thus, if cellulose triacetate textile material is treated for 1 hour at 98–100° C. in a neutral 40:1 bath having dispersed therein 2% of Naphthol AS/BG (based on the weight of the cellulose triacetate) and 4 g.p.l. of diethyl phthalate, the amount of the naphthol taken up is roughly double that taken up in the absence of the diethyl phthalate, other conditions being the same. Similar, though rather less marked improvement in take-up of Naphthol AS/BG is observed if the cellulose triacetate is first treated with an aqueous dispersion of the diethyl phthalate and then with an aqueous dispersion of the Naphthol AS/BG. As the diethyl phthalate or other substantially water-insoluble organic compounds are compatible with and may even be solvents for the cellulose triacetate they are taken up by the latter from the aqueous bath; in other words they have substantive affinity for the cellulose triacetate.

The present invention particularly contemplates the incorporation in cellulose triacetate textile material of an azo coupling component of the kind indicated above by a process in which the fibre is permitted to take-up the coupling component from an equeous bath in the presence of diethyl phthalate or other water-insoluble substance of the kind indicated above, the latter being present in the bath or already in the fibre. The invention also includes the conversion of a coupling component so incorporated into the material, into an azo dye by coupling with a diazo compound and particularly with a diazo compound formed by diazotising a diazotisable base present in the fibre with the coupling component. The base may be incorporated from the same bath as, and either simultaneously with or separately from the coupling component, or from a separate bath. The amount of the water-insoluble organic substance in the bath may be for example from 10 to 40% based on the weight of the cellulose triacetate.

As already indicated diethyl phthalate is particularly suitable for the purposes of the invention but many other substances, particularly liquids, may be employed. For example any of the substantially water-insoluble assistants prescribed in United States application S. No. 472,758 filed Dec. 2, 1954, now U.S. Patent No. 2,982,597, for assisting the incorporation of disperse dyes in cellulose triacetate textile material. There may be used for instance other esters of phthalic acid, e.g. dimethyl phthalate or dipropyl phthalate, esters of benzene monocarboxylic acids, e.g. methyl benzoate, or methyl salicylate, trialkyl phosphates e.g. tripropyl or tributyl phosphates or tri-beta-chlorethyl phosphate and chlorobenzene. All these have substantive affinity for cellulose triacetate and are taken up by the latter from aqueous dispersions of them.

Aqueous baths containing the organic substance, or both the organic substance and the coupling component,

preferably also contain a dispersing agent. The latter may be of anionic character, e.g. Turkey red oil or a dispersing agent of the higher fatty alcohol sulphate or alkyl-aryl-sulphonate type. Again, it may be a non-ionic dispersing agent, e.g. of the kind obtainable by condensing a higher fatty alcohol or a higher fatty acid or castor oil with ethylene oxide in proportion sufficient to render the reaction product water-soluble. The dispersing agent serves to maintain the organic substance and/or the coupling component in a state of dispersion.

The following coupling components may be incorporated by the new process:

(*a*) Arylamides of 2:3-hydroxynaphthoic acid, e.g. the anilide, ortho-toluidide, meta-nitro-anilide, ortho-methoxy-anilide, p-methoxyanilide (Naphthol AS/RL), 2′:5′-dimethoxy-anilide (Naphthol AS/BG), 4′-methoxy-2′-methyl-anilide (Naphthol AS/LT), 5′-chloro-2′-methyl-anilide, or 4′-chloro-2′-methyl-anilide;

(*b*) Arylamides of 2-hydroxy-anthracene-3-carboxylic acid, e.g. the ortho toluidide;

(*c*) Arylamides of 2-hydroxy-carbazole-3-carboxylic acid, e.g. the p-chlor-anilide (Naphthol AS/LB);

(*d*) Arylamides of 3-hydroxy-diphenylene-oxide-2-carboxylic acid, e.g. the 2′:5′-dimethoxy-anilide (Naphthol AS/DB);

(*e*) Di-acylacetyl derivatives of aromatic diamines, e.g. di-(acetoacetyl)-ortho-tolidine (Naphthol AS/G);

(*f*) Acylacetyl-derivatives of amino-hetero-cyclic compounds, e.g. 2-acetoacetylamino-6-ethoxy-benzthiazole.

The new process is of particular value, especially if full shades are required, when the coupling component is the 4′-methoxyanilide, the 2′:5′-dimethoxyanilide, or the 2′-methyl-4′-methoxyanilide of 2:3-hydroxynaphthoic acid, or di-(acetoacetyl)-ortho-tolidine, or the 2′:5′-dimethoxyanilide of 3-hydroxy-diphenylene oxide-2-carboxylic acid. The take-up of these coupling components by cellulose triacetate from aqueous dispersions is very greatly increased by the diethyl phthalate or similar substance. In the absence of the latter the take-up is insufficient to permit full shades to be obtained.

The diazotisable bases which may be employed include 4-chloro-2-amino-1-methyl-benzene, 2:5 - dichloroaniline, 2-chloraniline, 4-nitro-aniline, 5-nitro-2-amino-1-methyl-benzene, 4-chloro-2-amino-1-methoxy-benzene, 5-nitro-2 - amino-1-methoxy-benzene, 2 - amino-1-methoxy - benzene-4-sulphonic acid diethylamide, 2-amino-1-methoxy-benzene-4-ethylsulphone, 2:5-diethoxy-4-benzoyl - amino-aniline, amino-azo-toluene, 4-aminobenzene-azo-4′-amino-2′-acetylamino-5′-methoxy-benzene (4:4′ - diamino-2′-acetylamino-5′-methoxy-azobenzene), amino - azo-cresol-methylether (2′:5-dimethoxy-2:5′-dimethyl-4-amino-azobenzene) and 2:2′:5:5′ - tetramethoxy-4-amino-azo-benzene. By using a combination of 3-hydroxy-diphenylene-oxide-2-carboxylic acid 2′:5′-dimethoxyanilide with amino-azo-cresol-methyl-ether a valuable nigger brown shade having a light fastness of 6 can be obtained, while a black-brown shade can be obtained from the same coupling component and 2:2′:5:5′-tetramethoxy-4-amino-azobenzene.

The aqueous baths from which the coupling components are applied may be neutral, slightly acid, or slightly alkaline; for example they may have a pH value of 6 to 8. The aqueous bath may be prepared by dissolving the coupling component in about the minimum necessary amount of aqueous caustic soda and adding the resulting solution to the necessary amount of water containing a suitable dispersing agent. The pH value of the bath may then be adjusted to the desired value, e.g. pH 7 to 7.5, by addition of acid, for instance formic or acetic acid. The diethyl phthalate or other assistant employed is preferably first converted into a concentrated emulsion by mixing with a dispersing agent and with a little water and the emulsion likewise added to the bath. If the bath is alkaline, say pH 9 to 12, at the time of adding the assistant and the latter is diethylphthalate or other hydrolysable ester the alkalinity of the bath will usually be rapidly reduced by the ester, the latter being hydrolysed in the process. As already indicated, it is convenient to include the diazotisable amino compound in the same bath. The baths are preferably employed at relatively high temperatures, for example 95 to 98 or 100° C.

Following the incorporation of the coupling component and diazotisable amine in the cellulose triacetate material, the latter is, as indicated above, subjected to treatment to diazotise the amine and effect coupling of the resulting diazo compound with the coupling component. This diazotisation may be effected by means of a nitrous acid bath and particularly by means of an aqueous bath prepared with sodium nitrite and an acid, e.g. a mineral acid such as hydrochloric acid or an organic acid such as acetic or formic acid. Diazotisation may be effected at ordinary temperatures or at rather higher temperature, e.g. temperatures up to 40–50° C. Following the diazotisation treatment the material is preferably given a mild alkaline treatment for example treatment in a bath containing soap or other detergent together with an alkali e.g. sodium carbonate. This soaping treatment may be effected or completed at 70 to 85° C. or higher e.g. at 95°–100° C.

The materials coloured by the new process are, in general of very good resistance to hot soaping treatments, but under these conditions a certain amount of staining of any white cellulose acetate material in contact with the coloured material during the hot soaping treatment may be evidenced. This is possibly due to the coloured material containing small amounts of the original base or of decomposition products of its diazo compound. We have found that any such tendency to stain white cellulose acetate may be substantially reduced or entirely eliminated by subjecting the coloured material to a mild reducing treatment, particularly treatment with a hot acidified aqueous solution of a formaldehyde sulphoxylate. Such a treatment may comprise for instance, subjecting the material for 1 hour at 75° C. to an aqueous bath prepared with 1 g.p.l. of Adinol T (sodium oleyl taurine), 1 cc. per l. of acetic acid and 0.5 g.p.l. of sodium formaldehyde sulphoxylate.

The invention is illustrated by the following examples:

Example 1

A treatment bath is made up from the following:

40 l. water
40 g. Lissapol C (sodium oleyl sulphate)
25 g. Fast Red B Base (5-nitro-2-amino-1-methoxy-benzene)
50 g. Naphthol AS/LB
33.3 g. caustic soda flakes
200 g. diethyl phthalate.

The bath is prepared as follows:

The base is pasted with 10 g. of the Lissapol C and brought to the boil with a little water, the resulting dispersion being then added to the main body of water. The naphthol is pasted with a little water, a solution of the caustic soda in a little water added and the mixture warmed until the naphthol is dissolved; the solution is then added to the main body of water. The diethyl phthalate is emulsified with the remaining Lissapol C and a little water in a mechanical emulsifier and the resulting emulsion likewise added to the main body of water.

1 kg. of a fabric of cellulose triacetate yarn is entered into the foregoing treatment bath, the latter being at 50° C. The temperature is raised to 95–98° C. in the course of 30 mins, and the processing of the material continued for a further 2 hours at this temperature. The material is then washed off and introduced into 40 litres of water to which have been added 320 mls. of glacial acetic acid and 160 g. of sodium nitrite. Treatment is

commenced at 20° C. and the temperature raised to 45° C. during 15 mins, and maintained at this for a further 15 mins. After rinsing the material in a 1 gr. per l. aqueous solution of sodium carbonate, it is treated for 1 hour at 75–80° C. in a 1 g.p.l. aqueous solution of soap or other detergent. The material is finally rinsed and dried and is found to be coloured in a full mahogany shade.

Example 2

A fabric of cellulose triacetate yarn is dyed in the manner described in Example 1, except that, before addition of the emulsified diethyl phthalate, the bath is brought to pH 7.0–7.5 by addition of dilute acetic acid.

Example 3

A treatment bath is made up from the following:

40 l. water
40 g. Lissapol C
30 g. 4 - aminobenzeneazo-4'-amino-2'-acetylamino-5-methoxybenzene
50 g. Naphthol AS/LT
16.6 g. caustic soda flakes
200 g. diethyl phthalate.

The preparation of the bath is effected in the manner described in Example 1. 1 kg. of a fabric of cellulose triacetate yarn is then processed in this bath in the manner described in Example 1 and then diazotised and further treated as described in that example. A full black shade is obtained.

Example 4

A fabric of cellulose triacetate yarn is dyed in the manner described in Example 3 except that, before addition of the emulsified diethyl phthalate, the bath is brought to pH 7.0–7.5 by addition of dilute acetic acid.

Example 5

A treatment bath is prepared from the following:

30 g. Lissapol C (sodium oleyl sulphate)
14 g. amino-azo-cresol-methyl-ether
30 g. Naphthol AS/DB
20 g. caustic soda flakes
150 g. diethyl phthalate
30 l. water.

The preparation of the bath is effected as in Example 1.

1 kg. of a fabric of cellulose triacetate is entered into the above bath at 50° C., the temperature raised to 95–98° C. in 30 minutes and processing carried out for a further 2 hours at this temperature.

The fabric is then washed off and diazotised in the following bath:

30 l. water
240 ml. glacial acetic acid
120 g. sodium nitrite.

The fabric is entered at 20° C., and the temperature raised to 45° C. in 30 minutes, being maintained at this for a further 30 minutes.

After rinsing in dilute sodium carbonate, the material is soaped off in 2 g.p.l. aqueous soap solution for 1 hour at 75–80° C. The fabric is dyed a nigger brown shade.

A similar result is obtained if the pH value of the bath is adjusted to 7.0 to 7.5 by addition of dilute acetic acid before addition of the emulsified diethyl phthalate.

Example 6

A treatment bath is made up from the following:

40 l. water
40 g. Lissapol C
20 g. Fast Red RC Base (4-chlor-2-amino-anisole)
20 g. Naphthol AS/BG
6.6 g. caustic soda flakes
200 g. diethyl phthalate

The bath is prepared in the manner described in Example 1 except that the pH value is adjusted to 7.0–7.5 by addition of dilute acetic acid before adding the emulsified diethyl phthalate.

1 kg. of a fabric of cellulose triacetate yarn is then processed in this bath in the manner described in Example 1, and then diazotised and further treated as described in that example. A full bright scarlet is obtained.

Example 7

A treatment bath is prepared from the following:

40 l. water
40 g. Lissapol C
20 g. Fast Bordeaux GP Base (1-amino-2-nitro-4-methoxy-benzene)
20 g. Naphthol AS/BG
6.6 g. caustic soda flakes
200 g. diethyl phthalate

The bath is prepared in the manner described in Example 1 except that the pH value is adjusted to 7.0–7.5 by addition of dilute acetic acid before adding the emulsified diethyl phthalate.

1 kg. of a fabric of cellulose triacetate yarn is then processed in this bath in the manner described in Example 1, and then diazotised and further treated as described in that example. A deep crimson is obtained.

Example 8

A treatment bath is prepared from the following:

40 l. water
40 g. Lissapol C
10 g. Fast Red GG Base (para nitro aniline)
10 g. Naphthol AS/G
3.3 g. Caustic soda flakes
200 g. diethyl phthalate.

The bath is prepared in the manner described in Example 1 except that the pH value is adjusted to 7.0–7.5 by addition of dilute acetic acid before adding the emulsified diethyl phthalate.

1 kg. of a fabric of cellulose triacetate yarn is then processed in this bath in the manner described in Example 1, and then diazotised and further treated as described in that example. A full golden yellow is obtained.

In any of the above examples the diethyl phthalate may be replaced by tri-n-propylphosphate with similar results.

Textile fibres of high acetyl cellulose acetate to be coloured in accordance with the invention may be those made by a melt spinning process, especially a process described in United States applications S. Nos. 243,994 filed August 28, 1951, now abandoned, 292,772 filed June 10, 1952, now U.S. Patent No. 2,888,711, 304,441 filed August 14, 1952, now abandoned, 338,834 filed Feb. 25, 1953, now U.S. Patent No. 2,982,597, or 423,743 filed April 16, 1954, now abandoned. In one such process a powdered cellulose ester is urged (e.g. by a rapidly reciprocating tamper) against the side of a heated plate having spinning orifices therein, the powdered ester is fused by the heat applied to the plate, the fused ester is drawn away from the orifices in the form of filaments, and fresh powdered ester is continuously fed to the plate. The spinning orifices may be circular, or they may be in the form of slits or of two or more closely spaced or intersecting holes, as described in United States application S. No. 338,834. In another process cellulose triacetate in the form of a coherent rod or a block or tablet of uniform cross-section is pressed axially against a heated plate having spinning orifices therein. Wet and dry spinning methods may also be used to form the cellulose acetate fibres. Thus solutions of high acetyl cellulose acetate in mixtures of methylene or ethylene chloride with methyl or ethyl alcohol or acetic acid, or in acetic acid alone, may be extruded as filaments and set either by means of a coagulating liquid or by an evaporative method. For ex-

ample solutions of cellulose triacetate in mixtures of methylene or ethylene chloride with acetic acid may be extruded into a coagulating liquid comprising an aqueous alcohol, especially aqueous ethyl alcohol of concentration about 90–95%, as described in United States Patent No. 2,657,973, or solutions in acetic acid may be extruded into aqueous acetic acid which may with advantage contain a fairly high proportion of ammonium or an alkali metal acetate, an alkaline earth metal acetate or magnesium acetate, or of some other salt.

Yet another method by which textile fibres of cellulose acetate of high acetyl value may be obtained is the further acetylation of a textile material of cellulose acetate of lower acetyl value. For instance, yarns or fabrics of acetone-soluble cellulose acetate may be further acetylated with acetic anhydride in the the presence of a diluent such as benzene, and of a basic or acid esterification catalyst such as pyridine, sulphuric acid, perchloric acid or hydrochloric acid, with or without a metal chloride such as zinc chloride or ferric chloride as described in United States Patents Nos. 2,159,011 and 2,159,012.

If desired the fibres of high acetyl cellulose acetate may be those having a high safe ironing such as are described, together with processes for their manufacture, in United States application S. No. 400,798 filed Dec. 28, 1953 now U.S. Patent No. 2,862,785. Alternatively the materials may, after colouring, be given a treatment such as is described in that application.

The cellulose triacetate yarn of the fabric coloured according to the examples is a product made by dry-spinning a solution of cellulose acetate of about 61% acetyl value in a mixture of methylene chloride and methyl alcohol (ratio about 93:7 by volume).

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

1. Method of incorporating an enolic azo coupling component in a cellulose triacetate textile material, which comprises allowing the material to take up the coupling component from an aqueous bath having dispersed therein both the coupling component and an assistant consisting essentially of a substantially water-insoluble oxygen containing organic ester which is a solvent for the coupling component and which has a substantive affinity for the cellulose triacetate.

2. A method according to claim 1, wherein the substantially water-insoluble organic substance is diethyl phthalate present to the extent of from 10–40% based on the weight of the textile materials.

3. Method of incorporating an enolic azo coupling component in a cellulose triacetate textile material, which comprises allowing the material to take up the coupling component from an aqueous bath at a temperature of 95° to 100° C. and having dispersed therein both the coupling component and from 10–40% of diethyl phthalate based on the weight of the textile material.

4. A method of colouring textile material of cellulose triacetate, which comprises allowing the material to take up an enolic azo coupling component and a diazotisable base from an aqueous bath having dispersed therein the coupling component, the base, and an assistant consisting essentially of from 10–40% based on the weight of the textile material of a substantially water-insoluble organic substance which is a solvent for the coupling component and which has a substantive affinity for the cellulose triacetate, and thereafter treating the material to effect diazotisation of the base and coupling of the resulting diazo compound with the coupling component on the material.

5. Method according to claim 4, wherein the enolic coupling component is the 2′:5′-dimethoxyanilide of 3-hydroxy-diphenylene-oxide-2-carboxylic acid.

6. Method according to claim 4, wherein the enolic coupling component is di-(acetoacetyl)-ortho-tolidine.

7. Method according to claim 4, wherein the aqueous bath has a pH value of from 6–8.

8. Method according to claim 4, wherein the enolic coupling component is an arylamide of 2:3-hydroxynaphthoic acid.

9. Method according to claim 8, wherein the arylamide is the 4′-methoxyanilide.

10. Method according to claim 8, wherein the arylamide is the 2′:5′-dimethoxyanilide.

11. Method according to claim 8, wherein the arylamide is the 2′-methyl-4′-methoxyanilide.

12. A method of colouring cellulose triacetate textile material, which comprises allowing the material to take up an enolic azo coupling component and a diazotisable base from an aqueous bath having dispersed therein the coupling component, the base and from 10–40%, based on the weight of the textile material, of diethyl phthalate, and thereafter treating the material to effect diazotisation of the base and coupling of the resulting diazo compound with the coupling component on the material.

13. Method of incorporating an enolic azo coupling component in a cellulose triacetate textile material, which comprises allowing the material to take up the coupling component from an aqueous bath having dispersed therein both the coupling component and from 10–40%, based on the weight of the textile material, of an assistant consisting essentially of a substantially water-insoluble organic substance which is a solvent for the coupling component and which has a substantive affinity for the cellulose triacetate.

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