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# DIETHYLENE GLYCOL DIACETATE AS AN ASSISTANT IN THE DYEING OF CELLULOSE TRIACETATE

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This invention relates to the colouring of textile materials of cellulose acetates, of high acetyl value, e.g. acetyl value above 59% calculated as acetic acid. For convenience, cellulose acetates having acetyl values of above 59% are hereinafter referred to as cellulose triacetates. The invention is more particularly concerned with the local colouring of textile fabrics of cellulose acetates of this kind.

The local colouring of textile fabrics of ordinary cellulose acetate, that is acetone-soluble secondary cellulose acetate, has long been effected by printing with suitable dyes, e.g. the well known disperse dyes, followed by steaming for the purpose of causing the dye to enter and so be fixed in the cellulose acetate; the steaming may be carried out in conventional textile fabric continuous steamers in which steaming is effected at substantially atmospheric pressure. Often an assistant is included with the dye in the printing composition in order to assist the entry of the dye into the cellulose acetate; diethylene glycol and thiodiglycol have been largely used as assistants for this purpose. We have found that in the case of textile fabrics of cellulose triacetates it is very difficult to obtain a satisfactory fixation of colouring matter by the printing methods employed for secondary cellulose acetate such as are referred to above. While a great movement can be secured by steaming with saturated steam under pressure (for example pressures up to 30 lbs. per sq. in.) this procedure is not very convenient since the only pressure steamers commercially available (for example the cottage steamer) are essentially devices for batch operation.

We have now found that triacetin (glycerol triacetate) and other esters of polyhydric alcohols (including dihydric alcohols) with carboxylic acids, particularly acetic acid or other lower fatty acid, are very valuable agents for assisting the fixation of dyes on cellulose triacetate textile materials by steaming. For example, satisfactory prints can be obtained from a wide range of disperse dyes by printing them onto cellulose triacetate fabrics as thickened aqueous pastes containing 15–25% of triacetin and then steaming the materials at about atmospheric pressure.

While triacetin has been found especially useful for assisting the fixation of dyes on cellulose triacetate textiles by steaming, other carboxylic esters of polyhydric alcohols may be employed, particularly esters such as the lower fatty acid ($C_1$ to $C_4$) esters of ethylene glycol, propylene glycol (1:2 or 1:3), glycerol, diethylene glycol, triethylene glycol or other polyethylene glycol; examples are glycerol diacetate, diethylene glycol diacetate, glycerol triformate, diethylene glycol monoacetate, ethylene glycol mono- or diacetate. Mixtures of such esters may also be employed, for example a mixture composed of a



major proportion of triacetin with minor proportions of glycerol diacetate and/or glycerol monoacetate. The ester is preferably one having a boiling point above 200° C.

The dyes which may be fixed on cellulose triacetates by the use of the foregoing esters include a wide range of disperse dyes of the kind which are capable of colouring secondary cellulose acetate textile material when applied thereto in the form of aqueous dispersions. Such dyes may be of the azo, anthraquinone, or nitro-diphenylamine types. The following specific dyes may be instanced:

## AZO DYES

The azo dyes from the following pairs of components, the first being the diazo component in each case.

(*a*) Para-amino-acetanilide and parahydroxy-diphenyl;
(*b*) Para-nitroaniline and N-di-beta-hydroxyethyl meta-chloraniline;
(*c*) 4-nitro-2-chloraniline and N-di-beta-hydroxyethyl meta-toluidine;
(*d*) Amino-azo-benzene and phenol.

The commercial azo dye Eastone Fast Red GLF may likewise be used.

## ANTHRAQUINONE DYES

(*a*) 1:4-diamino-2-methoxy-anthraquinone;
(*b*) 1:4-di(beta-hydroxyethylamino)-5:8-dihydroxy-anthraquinone;
(*c*) 1-amino-4-phenylamino anthraquinone-2-carboxylic acid-beta-hydroxyethylamide;
(*d*) 1-amino-4-phenylamino anthraquinone;
(*e*) The dye mixture obtainable by condensing leuco quinizarin with a mixture in equimolecular proportions of methylamine and beta-hydroxy-ethylamine;
(*f*) 1-hydroxy-ethylamino-anthraquinone;
(*g*) Eastman Fast Blue GLF.

The nitro diphenylamine dyes which may be employed include 2:4-dinitro-4′-amino-diphenylamine.

Again, metallised dyes may be fixed by the new process, for example metallised dyes of the type referred to in United States application Serial No. 550,209, filed November 30, 1955, including such as are free from sulphonic and carboxylic groups.

We have further found that the foregoing esters of polyhydric alcohols may be used to assist the fixation by steaming on cellulose triacetate textiles of organic substances which can be converted into a dye when on the cellulose triacetate. Thus the esters may be employed to assist the fixation of substances which like aniline, para-amino diphenylamine, and 2:4-diamino-diphenylamine, can be oxidised to colouring matter on the material by means of an oxidising agent which becomes effective during the steaming. By using a mixture of aniline and para-amino diphenylamine (diphenyl black base) in this way, for example as a thickened composition comprising triacetin, ethyl alcohol and the oxidising agent, a very satisfactory black can be printed on cellulose triacetate fabrics. Again, the esters may be used to assist fixation on the cellulose triacetate textiles of a substance capable of being converted to an azo dye on the material whether by diazotisation and coupling with a coupling component or by coupling with a diazo compound.

The esters are most conveniently utilised by printing, padding or otherwise impregnating the cellulose triacetate material with an aqueous preparation containing the ester and dye or substance convertible into a dye, the material being thereafter steamed.

The ester may comprise from 15 to 45% by weight of the composition. Satisfactory results can in general be obtained by using an aqueous composition containing triacetin to the extent of from 15 to 25% or 35% or diethylene glycol diacetate to the extent of 25 to 45%. Printing may be effected by conventional roller or screen printing methods and for this purpose the preparation applied may be thickened, for example with gum tragacanth or a water-soluble methyl cellulose.

From the point of view of stabilising aqueous preparations against separation of the ester when the latter is not miscible with water in the proportion present in the composition, a water miscible organic solvent for the ester may be included in the preparation, for example methyl, ethyl, or a propyl alcohol or mixture thereof. The proportion of alcohol employed should be sufficient to prevent separation of the ester; it may be, for instance, about the same as that indicated above for the polyhydric alcohol ester. Larger proportions of water-miscible organic solvent may however be used; for example the above alcohols may be used in proportions up to 75% based on the alcohol and water together. When a combination of ester and alcohol is employed, e.g. triacetin and ethyl alcohol, it is particularly advantageous to use methyl cellulose as the thickening agent since the latter is more compatible with such mixtures than are conventional thickeners such as gum tragacanth, gum arabic, and gums based on starch.

If desired a water-soluble thiocyanate, for instance, of an alkali metal, alkaline earth metal, or ammonium but particularly zinc thiocyanate, may be included in the composition. In this case it is often possible to reduce the proportion of ester considerably below that otherwise desirable and thereby to obtain a preparation which is both stable and effective, even when using esters of low solubility in water, e.g. triacetin, without using alcohol or other solvent for the ester. The omission of the alcohol facilitates the use of a wider range of thickening agents than is otherwise possible. Thus a very satisfactory printing preparation consists of dye, a gum of the gum senegal, gum arabic, or modified starch type, zinc thiocyanate to the extent of 5 to 15%, e.g. about 10%, and triacetin to the extent of 3 to 10%, e.g. about 5%, the remainder of the composition being water. However, thiocyanates are often useful even when an alcohol or other water-miscible organic solvent for the ester is employed; e.g. ammonium thiocyanate can be used with triacetin and ethyl alcohol, the thickening agent in this case being methyl cellulose. Again they are often useful when the ester is so miscible with water, as in the case of diethylene glycol diacetate, that the composition is homogeneous without the use of alcohol or other water miscible organic solvent for the ester.

Gas-fading inhibitors may be included in the compositions, these being more particularly desirable when the dye is one which is sensitive to gas-fading, for example an anthraquinone blue which is a derivative of 1:4-diamino-anthraquinone. A very suitable gas-fading inhibitor for the purpose is diphenylacetamidine which may be employed in a proportion of 2.5–5% based on the weight of the composition; 3–3.5% is usually a satisfactory proportion.

As already indicated, by employing esters of polyhydric alcohols in the manner indicated above, it is possible to obtain satisfactory fixation of dyes on cellulose triacetate materials by steaming at substantially atmospheric pressure. Such steaming may be effected for instance in continuous steamers of the well known types commonly employed in print works. Pressure steaming may however be employed if desired; for example, steaming may be effected in a cottage steamer with saturated steam at 5–20 or more lbs. per sq. in.

The invention is illustrated by the following examples in which the "parts" referred to are parts by weight.

*Example 1*

A fabric woven from cellulose triacetate continuous filament yarn is printed with the following composition:

| | Parts |
|---|---|
| Azo dye from diazotised para-amino acetanilide and paraphenyl phenol (10% aqueous paste) | 15 |
| Triacetin | 20 |
| Methylated spirits | 20 |
| Printing oil | 2 |
| Aqueous methyl cellulose thickening to make | 100 parts. |

The methyl cellulose thickening consists of a 12% solution of methyl cellulose, the latter having a viscosity of 10 centipoises when measured in 2% aqueous solution at 20° C.

After printing, the material is dried and steamed for 1 hr. at 220° F. in a continuous steamer, washed off in cold water and dried. A yellow print of good colour value is obtained.

In this example the triacetin may be replaced by an equal or rather greater amount of diethylene glycol diacetate, e.g. 25 to 30 parts, with similar results.

*Example 2*

Fabric of the kind referred to in Example 1 is roller printed with the following composition:

| | Parts |
|---|---|
| Azo dye from diazotised para-amino-acetanilide and para-phenyl-phenol (10% aqueous paste) | 20 |
| Zinc thiocyanate | 10 |
| Triacetin | 5 |
| Nafka Crystal Gum (40% aqueous solution) | 35 |
| Water to make | 100 parts. |

Nafka Crystal Gum is a product sold by W. A. Scholten's Chemische Fabriken, Netherlands.

The material is then dried and steamed for 1 hr. at 220° F. in a continuous steamer. It is then thoroughly washed off in cold water. A yellow print of good colour value is obtained.

The yellow dye referred to in the above examples may be replaced by other of the disperse dyes listed above.

*Example 3*

A cellulose triacetate fabric of the kind referred to in Example 1 is printed with the following composition:

| | Parts |
|---|---|
| Metallised azo dye (e.g. Orasol Navy Blue RB) | 2 |
| Triacetin | 30 |
| Ammonium thiocyanate | 4 |
| Methyl cellulose | 7 |
| Mixture of methylated spirit and water (3:1 by volume) to make | 100 parts. |

The methyl cellulose is of the same kind as that specified in Example 1.

After printing, the fabric is dried, steamed twice for 15 minutes at 218 to 220° F., washed off well and again dried. A navy blue print is obtained.

In this example the 30 parts of triacetin may be replaced by 30–40 parts of diethylene glycol diacetate with similar results.

*Example 4*

The following compositions A, B and C are made up.

A

| | Parts |
|---|---|
| Diphenyl black base | 7.5 |
| Aniline hydrochloride | 1.8 |
| Acetic acid | 4.0 |
| Lactic acid | 3.0 |
| Triacetin | 20.0 |
| Ammonium thiocyanate | 4.0 |
| Methyl cellulose | 8.0 |
| Mixture of methylated spirit and water (3:1 by volume) to make | 100 parts. |

In making (A) the ammonium thiocyanate, methyl cellulose, methylated spirit, and water and first mixed together to obtain a homogeneous thickening to which the other ingredients are added.

B

| | Parts |
|---|---|
| Sodium chlorate | 3.75 |
| Water | 6.25 |
| | 10.0 |

C

| | Parts |
|---|---|
| Cerium chloride | 0.375 |
| Water | 2.125 |
| Aluminium chloride solution 52° Twaddell | 2.5 |
| | 5.0 |

Compositions A, B and C are mixed together immediately before roller-printing on to a cellulose triacetate fabric of the kind used according to Example 1. The material is then dried, steamed twice for 15 minutes at 218° to 220° F., washed off well, soaped lightly and dried. A good black is obtained.

For screen printing purposes the quantities of diphenyl black base and aniline hydrochloride should be reduced by about one third.

In this example the 30 parts of triacetin may be replaced by 30–40 parts of diethyleneglycol diacetate with similar results.

*Example 5*

A cellulose triacetate fabric of the kind referred to in Example 1 is printed with the following composition:

| | Parts |
|---|---|
| Azo dye from diazotised para-amino-acetanilide and paraphenyl phenol (10% aqueous paste) | 15 |
| Diethylene glycol diacetate | 30 |
| Methyl cellulose | 8 |
| Printing oil | 2 |
| Water to make 100 parts. | |

The methyl cellulose is of the same kind as that specified in Example 1.

After printing, the material is dried and steamed for 45 minutes at 220° F. in a continuous steamer. It is then thoroughly washed off in cold water and dried. A yellow print of good colour value is obtained. The yellow dye in this example may be replaced by other of the disperse dyes listed above.

*Example 6*

Fabric of the kind referred to in Example 1 is printed with the following composition:

| | Parts |
|---|---|
| Metallised azo dye (e.g. Orasol Navy Blue RB) | 2 |
| Diethylene glycol diacetate | 25 to 30 |
| Ammonium thiocyanate | 4 |
| Methyl cellulose | 8 |
| Water to make 100 parts. | |

The methyl cellulose is of the same kind as that specified in Example 1.

After printing, the fabric is dried, steamed for 45 minutes with dry steam at 220° F., washed off well and again dried. A navy blue print is obtained.

The textile fibres of high acetyl cellulose acetate may be those made by a melt-spinning process, especially a process described in United States applications Ser. Nos. 243,994, filed August 28, 1951, and now abandoned; 292,772, filed June 10, 1952, and now Patent No. 2,888,711; 304,441, filed August 14, 1952, and now abandoned; 338,834, filed February 25, 1953, and now Patent No. 2,831,748; or 423,743, filed April 16, 1954, and 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 Ser. 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 example, 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 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 point such as are described, together with processes for their manufacture in United States application Ser. No. 400,798, filed December 28, 1953, now 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 printed 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. Process for coloring cellulose triacetate which comprises applying thereto aqueous diethylene glycol diacetate and a coloring agent for said cellulose triacetate.

2. Process according to claim 1 wherein the diethylene glycol diacetate is applied as an aqueous composition comprising about 15 to 45% by weight of diethylene glycol diacetate.

3. Process according to claim 1 wherein the coloring agent is applied admixed with the aqueous diethylene glycol diacetate.

4. Process according to claim 1 including the further step of steaming the cellulose triacetate.

5. Process according to claim 1 wherein the composition contains an inorganic thiocyanate and a thickening agent.

6. Process according to claim 1 wherein the coloring agent comprises a substance convertible to a dyestuff on the cellulose triacetate.

7. Process for the coloration of textile fibers of cellulose triacetate which comprises applying a coloring agent thereto in a mixture of liquids consisting essentially of water and diethylene glycol diacetate.

8. Process for the production of coloured pattern effects on textile fabric of cellulose triacetate, which comprises printing the fabric with a thickened aqueous composition comprising a dye and diethylene glycol diacetate, the latter being present to the extent of 15 to 45% based on the weight of the composition, and thereafter steaming the material.

9. Process according to claim 8, wherein the dye is a cellulose acetate disperse dye.



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