

## UNITED STATES PATENT OFFICE

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VAT DYEING PROCESS FOR CELLULOSE  
ACETATE TEXTILE MATERIAL

George W. Seymour, George C. Ward, and Robert  
L. Hunter, Cumberland, Md., assignors to Cella-  
nese Corporation of America, a corporation of  
Delaware

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This invention relates to the dyeing of cellulose acetate or other organic acid ester of cellulose textile materials, and relates more particularly to an improved process for the dyeing of said textile materials with indigoid vat dyestuffs.

An object of this invention is the provision of an improved process for the application of indigoid vat dyestuffs in the dyeing of textile materials having a basis of cellulose acetate or other organic acid ester of cellulose.

Another object of this invention is to provide an improved process for dyeing cellulose acetate or other organic acid ester of cellulose material with indigoid vat dyestuffs whereby no deleterious saponification of said organic acid ester of cellulose material is effected.

A further object of this invention is to provide an improved process for dyeing cellulose acetate or other organic acid ester of cellulose textile materials with indigoid vat dyestuffs in deep, level shades which are fast to washing, to light and to acid-fading, and which are substantially free from crocking or other undesirable characteristics.

Other objects of this invention will appear from the following detailed description.

The application of indigoid vat dyestuffs to cellulose acetate or other organic acid ester of cellulose textile material by the usual methods is quite unsatisfactory. The use of strong bases such as sodium hydroxide and strong reducing agents such as sodium hydrosulfite for solubilizing the indigoid vat dyestuff effects at least a partial saponification of the cellulose acetate material to form regenerated cellulose. The resulting dyed textile material is found to be very prone to crocking which is quite undesirable.

We have found that cellulose acetate or other organic acid ester of cellulose textile materials may now be dyed rapidly and satisfactorily with indigoid vat dyestuffs in deep, level shades free from crocking, without employing strong bases to solubilize said vat dyes. In accordance with the process of our invention, these advantageous results are obtained by employing a novel pigment-padding dyeing procedure whereby the cellulose acetate textile material to be dyed is padded with an aqueous suspension of the indigoid vat dyestuff, dried, repadded with an aqueous alkaline solution of a sulfoxylate formaldehyde reducing agent for said indigoid vat dye containing a hydroxy-substituted aliphatic amine, steamed while wet to reduce the dyestuff to the leuco form, and then oxidized back to the final color in a suitable aqueous oxidizing bath. The

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dyed textile material obtained, after oxidation is completed, is then soaped, rinsed and finished in the usual manner. The dyed cellulose acetate textile materials obtained not only exhibit excellent resistance to washing to light and to acid fading but are substantially free from the crocking usually observed when said indigoid vat dyestuffs are applied to cellulose acetate or other organic acid ester of cellulose materials in the usual manner wherein strong bases are employed. Furthermore, no saponification of the cellulose acetate material takes place.

Any suitable indigoid vat dyestuff may be employed in accordance with our novel dyeing process. Examples of suitable dyestuffs are Ciba Brilliant Scarlet, Ciba Red R (C. I. 1229), Ciba Navy RB, Ciba Brown G (C. I. Pr. 121), Helindone Green B, Ciba Red 3B (C. I. 1212), Sulfanthrene Black PG, Sulfanthrene Orange R (C. I. 1217) and Ciba Yellow G.

The aqueous dyestuff suspension is applied, as stated, by padding operations employing a suitable padding mangle provided with one or more nips so that the desired penetration may be achieved. Usually, the indigoid vat dyestuff suspension is prepared by adding the finely-divided dyestuff to water in an amount necessary to yield the desired concentration and the liquid then agitated to produce a uniform suspension. In some instances, it may be desirable to employ dispersing agents such as Turkey Red oil or sulfated long chain aliphatic alcohols, e. g. lauryl alcohol, to aid in producing a more stable and uniform suspension of the finely divided dyestuff. The concentration of dyestuff in the dyebath may vary depending upon the depth of shade desired in the dyed cellulose acetate material. Usually, dyebaths containing from 0.2 to 20% by weight of dyestuff on the weight of the bath are satisfactory for use in the padding operation.

After the cellulose acetate textile material has been padded with the dyestuff suspension, it is preferably dried before being padded with the aqueous sulfoxylate formaldehyde and amine solution. Drying may be conveniently effected by passing the padded material into a tower through which heated air is circulated. Heated drums or cans may also be employed for drying the padded cellulose acetate material.

The dried cellulose acetate material with the indigoid vat dyestuff present thereon is then padded with an aqueous solution of a sulfoxylate formaldehyde reducing agent which solution is rendered alkaline by the addition of a hydroxy-

substituted aliphatic amine thereto. The hydroxy-substituted aliphatic amine serves as a mild alkaline agent to solubilize and aid the reduction of the indigoid vat dyestuff. Examples of suitable amines which may be employed in conjunction with the sulfoxylate formaldehyde are mono-ethanolamine, di-ethanolamine, tri-ethanolamine, tri-isopropanolamine, etc., but optimum results are obtained employing di-ethanolamine. The sulfoxylated formaldehyde which we have found to yield the most desirable results in effecting the desired reduction of the indigoid vat dyestuff to the leuco form is sodium sulfoxylate formaldehyde. The latter forms soluble reaction products on reduction of the indigoid vat dyestuffs. The aqueous solution employed in padding the textile material carrying the dyestuff may contain from 2 to 15% by weight on the solution of the hydroxy-substituted aliphatic amine.

The reduction of the indigoid vat dyestuff present on the cellulose acetate textile material to the leuco form is then effected by steaming the wet fabric in an ager for from 2 to 20 minutes at a temperature of 95 to 105° C. Most advantageously, the steaming is continued for about six minutes to obtain maximum depth of shade on oxidation.

To oxidize the reduced or leuco vat dyestuff, the cellulose acetate textile material is withdrawn from the ager and then entered into an aqueous oxidizing bath containing from 0.1 to 2% by weight of sodium dichromate and 0.1 to 2% by weight of glacial acetic acid and maintained therein for 2 to 30 minutes with the oxidizing bath at a temperature of 20 to 60° C. The oxidation may also be effected employing oxidizing agents such as sodium perborate, hydrogen peroxide, and the like. This oxidation treatment causes the leuco vat dyestuff to be converted back to the final shade and the dyed cellulose acetate textile material is then soaped, rinsed, dried and finished. Little or no wash-down in shade is observed.

The dyed cellulose acetate textile materials obtained are not only fast to light, to acid-fading and substantially free from crocking but the dyed textile materials in addition exhibit an unusual degree of resistance to washing even when subjected to the drastic washing tests which are usually employed only for testing the fastness of vat dyed cotton materials.

In order further to illustrate our invention but without being limited thereto, the following example is given:

#### Example

A cellulose acetate fabric of satin weave is padded with a 10% by weight suspension of Ciba Red R (C. I. 1229) employing a suitable padding mangle to thoroughly impregnate the fabric and the padded fabric is then dried in a drying chamber maintained at a temperature of 100° C. The dried fabric is then padded with an aqueous reducing bath containing 10% by weight of sodium sulfoxylate formaldehyde and 10% by weight of di-ethanolamine. While still wet, the fabric is steamed in an ager at 99° C. for six minutes to reduce the vat dye completely. The reduced leuco indigoid vat dye on the fabric is then oxidized by immersing the latter for 5 minutes in a 0.3% by weight aqueous solution of sodium dichromate containing 0.2% by weight of glacial acetic acid maintained at 30° C. The dyed fabric is then removed, soaped

for 30 minutes at 70° in 0.3% soap solution, rinsed and dried. The cellulose acetate fabric is dyed a fair red shade having a resistance to acid fading of 2 A. A. T. C. C. units, good fastness to light on exposure in the "Fadometer" for 75 hours, a good resistance to crocking as measured by 20 cycles of the A. A. T. C. C. crockmeter, and very good fastness to washing by the test outlined in Federal Specification CCC-T-191a, Item IV, a test normally applied only to vat dyed cottons.

While our invention has been more particularly described in connection with the dyeing of cellulose acetate textile materials, this novel dyeing process is equally valuable in the dyeing of other organic ester of cellulose textile materials which may be adversely affected by the strong alkaline nature of the dye baths normally employed in said indigoid vat dyeing operations. Examples of other organic ester of cellulose materials are cellulose propionate, cellulose butyrate, and mixed esters of cellulose such as cellulose aceto-propionate and cellulose aceto-butyrate. Our novel dyeing process may also be employed in the dyeing of cellulose ether materials such as ethyl cellulose and benzyl cellulose. While cellulose ethers are not subject to undesirable saponification during vat dyeing operations the fastness of the colors obtained on said cellulose ester materials may be substantially improved by employing our novel process in the coloration of said materials.

Our process is applicable not only to the dyeing of fabrics but other textile materials such as yarns, filaments or staple fiber in the form of a top or roving may also be dyed in unusually fast colors employing vat dyes.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

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

1. Process for the coloration of cellulose acetate textile materials, which comprises mechanically impregnating a cellulose acetate textile material with an aqueous suspension of an indigoid vat dyestuff, drying the dyestuff impregnated textile material, impregnating the latter with an aqueous solution containing 2 to 15% by weight of sodium sulfoxylate formaldehyde and 5 to 10% by weight of di-ethanolamine, steaming the wet textile material until the indigoid vat dyestuff is reduced to the leuco form, and then oxidizing the leuco indigoid vat dyestuff to the final colored form in an aqueous solution of sodium dichromate acidified with acetic acid.
2. Process for the coloration of cellulose acetate textile materials, which comprises mechanically impregnating a cellulose acetate textile material with an aqueous suspension of an indigoid vat dyestuff, drying the dyestuff impregnated textile material, impregnating the latter with an aqueous solution containing 2 to 15% by weight of sodium sulfoxylate formaldehyde and 5 to 10% by weight of di-ethanolamine, steaming the wet textile material until the indigoid vat dyestuff is reduced to the leuco form, and then oxidizing the leuco indigoid vat dyestuff to the final colored form in a 0.1 to 2% by weight aqueous solution of sodium dichromate acidified with 0.1 to 2% by weight of acetic acid.
3. Process for the coloration of cellulose ace-

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tate textile materials, which comprises mechanically impregnating a cellulose acetate textile material with an aqueous suspension of an indigoid vat dyestuff, drying the dyestuff impregnated textile material, impregnating the latter with an aqueous solution containing 2 to 15% by weight of sodium sulfoxylate formaldehyde and 5 to 10% by weight of di-ethanolamine, steaming the wet textile material for 2 to 20 minutes at 95 to 105° C. until the indigoid vat dyestuff is reduced to the leuco form, and then oxidizing the leuco indigoid vat dyestuff to the final colored form in an 0.1 to 2% by weight aqueous solution of sodium dichromate acidified with 0.1 to 2% by weight of acetic acid.

GEORGE W. SEYMOUR.  
GEORGE C. WARD.  
ROBERT L. HUNTER.

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