This invention relates to dyeing and relates more particularly to dyeing with disperse cellulose acetate dye-stuffs.

In dyeing with disperse cellulose acetate dye-stuffs, it is customary to bring the textile material to be dyed into contact with a heated bath comprising an aqueous perspiration of the dyestuff. This procedure is eminently satisfactory in the case of certain textile materials such as textile materials having a basis of the usual cellulose acetate of commerce (e.g. cellulose acetate having an acetyl value of 54-55%, calculated as combined acetic acid). In treating this material the dyeing generally takes place at a fairly rapid rate to produce a desired depth of shade, even when the disperse cellulose acetate dyestuff is of the "high temperature slow dyeing" type. However, when the same process is employed for the dyeing of a textile material having a basis of a cellulose ester of low hydroxyl content (e.g. cellulose acetate having an acetyl value of 59% or more, calculated as combined acetic acid) or a basis of a linear polyester of high melting point (e.g. polyethylene terephthalate or other carboxylic acid polyester melting above 200°C, preferably above 230°C), the dyeing proceeds much more slowly and it is difficult to obtain deep shades.

It is an object of this invention to provide a new and improved process for the more rapid and complete dyeing of difficulty dyeable textile materials, such as textile material having a basis of cellulose esters of low hydroxyl content or linear polyesters of high melting point, with disperse cellulose acetate dyestuffs.

Another object of this invention is the provision of a novel aqueous dyebath comprising a disperse cellulose acetate dyestuff and a particularly effective dyeing assistant.

Other objects of this invention will be apparent from the following detailed description and claims. In this description and claims all proportions are by weight unless otherwise indicated.

In accordance with one aspect of this invention a textile material having a basis of a cellulose ester of low hydroxyl content or a polyester of high melting point, or of both, is colored by means of an aqueous dyebath containing a disperse cellulose acetate dyestuff in the presence of butyl benzoate. It is found that the presence of the butyl benzoate greatly increases the rate of dyeing and the degree of exhaustion of the dyebath. Also, the butyl benzoate has a low degree of toxicity, can be incorporated in the dyebath without disturbing the stability thereof, and its use enables level dyeings of excellent crock resistance to be obtained.

The dyestuffs used in the practice of this invention may be any of the disperse cellulose acetate dyestuffs known to the art. It is preferred to employ those dyestuffs which are of the high temperature slow dyeing type since the use of these materials generally results in dyeings which have a very high degree of washfastness and usually are superior in resistance to gas fading, to light fading and to sublimation. Examples of dyestuffs of this type are 2-nitro-4-sulfonamido diphenylamine; 4'-ethyl 2- nitrophenyl azo 4'-hydroxy-3-propylsulfonamide; 4-nitro-2-methoxyphenyl azo 4'-bis (beta-hydroxy-ethyl) amino-2'-acetylanobenzene; 4-nitro-2-methylsulfonphenyl azo 4'-(N-beta-hydroxy-ethyl-N-diluroethy) amino-benzene; 4-nitro-2-chlorophenyl azo 4'-bis(beta-hydroxyethyl) amino-2'-methyl-benzene; 1-hydroxy-6-nitro-4-chromenylamine-4 - hydroxyethylamino-3 - hydroxy-6-dinitrophenyl azo 4'-bis(hydroxyethyl) amino-2'-acetylanobenzene; a mixture of 1,4-dihydroxy-ethylamino)-5,8-dihydroxy anthraquinone and 1-amino-4-anilino anthraquinone; 1,5-dihydroxy-8-nitro-4-(meta-alpha-hydroxyethyl) anilino anthraquinone; 1,8-dihydroxy-4-(para-beta-hydroxyethyl) anilino-5-nitro anthraquinone; 1-amino-4-anilino anthraquinone and 2,4-dinitro-6-chlorophenyl azo 4'-bis(hydroxyethyl) amino-2'-acetylanilino-5'-methoxy benzene. These dyestuffs, as sold, are in the form of mixtures of a dispersing agent, such as sodium lignosulfonate or the sodium salt of formaldehyde-naphthalene sulfonic acid condensation product, with the actual dye material, and usually contain about 30 to 45% of the actual dye material. Commercial dyestuffs of this type include those sold under the names "Setacel Blue G"; "Eastman Blue GLF"; "Interchemical Blue RLF-40" (Pr. 227); "Celliton Blue AF" (Pr. 227); "Red Y"; "Celliton Blue Green BA" (Pr. 229); "Eastone Red 2B-GLF"; "Amaezl Red 2B"; "Amaezl Yellow CW"; "Eastone Red GLF"; "Amaezl Rubin IX" (Pr. 239); "Scarlet III" (Pr. 244); "Interchemical Blue BGLF-40"; "Interchemical Blue-Green BALF-40" (Pr. 229); "Amaezl Violet Blue FSI", "Lenar Blue RLS", "Interchemical Blue GSP" and "Eastone Red N-GLF". All of these dyestuffs are characterized by the fact that when applied to the ordinary cellulose acetate textile materials, of 54 to 55% acetyl value, under certain standard conditions at 80°C, they will dye said textile materials in full shades, but when the same dyestuffs are applied to said textile materials, under said standard conditions at a lower temperature, e.g. 60°C, the textile materials will be dyed to a substantially smaller extent, e.g. in shades whose depths are only about 65% or less of the depths of the full shades. The standard conditions mentioned above involve a treatment of 1 part by weight of the fabric in 50 parts by weight of an aqueous dyebath comprising 0.5 gram per liter of soap, e.g. sodium oleate, and 1% (based on the weight of the fabric) of dyestuff.

While the high temperature slow dyeing type of disperse dyestuff is preferred it will be understood that the process of this invention may also be used with the low temperature or medium temperature types of disperse cellulose acetate dyestuffs. Examples of such dyestuffs are 2-nitro-4-sulfonamido diphenylamine, p-nitrophenyl azo diethyl aniline and 1-amino-4-hydroxy anthraquinone.

The proportion of butyl benzoate which is employed in the dyebath of this invention may be varied depending, for example, on the particular dyestuff employed and the depth of shade desired. One suitable range is 5 to 30% based on the weight of the textile material being dyed.

The butyl benzoate is preferably added to the dyebath in the form of an aqueous emulsion containing, for example, about 5 to 10% of the butyl benzoate and also containing an emulsifying agent. Best results are obtained by the use of such emulsifying agents as "Nekal NS" (comprising a 30-35% aqueous solution of the sulfate ester obtained by adding sodium bisulfite to the unsaturated tricarboxylic acid produced by dehydration of citric acid) "Alipal CO-436" (a sulfate ester of an alkyl phenoxypolyoxyethylenol), "Pluronic L-64" (a
reaction product of polypropylene glycol with ethylene oxide having an ethylene oxide content of 40% and a molecular weight of about 3000), "Emulphor ELA-719" (a polyoxyethylated castor oil containing 70–75% ethylene oxide groups), and "Span 20" (sorbitan monolaurate). A typical portion of emulsifying agent is about 1/2 to 2/3, preferably 1/2 to 1/2, of the weight of the butyl benzate. It is convenient to form the emulsion by first mixing the emulsifier and the butyl benzate and then adding warm water while stirring.

Of the butyl benzates, n-butyl benzate is the preferred material, but other butyl benzoates, such as isobutyl benzate, may be employed, alone or mixed with the n-butyl ester.

The butyl benzate may, if desired, be mixed with other materials which act as assistants to increase the rate of fixing the cloth. One such assistant is tripropyolphosphate, which is particularly useful in such processes as the dyeing of the cellulose ester of low hydroxyl content in a jig, wherein the liquor ratio (i.e. the ratio of the weight of the dye to the weight of the textile material) is low, e.g. 1:1 to 5:1, and the concentrations of dyestuff and butyl benzoate in the dye bath are relatively high. Thus, the replacement of part (e.g. 10 to 50%) of the butyl benzate in the dyeing of the cellulose ester of low hydroxyl content in a jig dyeing helps to solubilize the butyl benzate and results in dyed cellulose ester textile materials which have even less tendency to crock. Another useful assistant which may be used to replace part (e.g. 10 to 50%) of the butyl benzate in the dyeing of the cellulose ester of low hydroxyl content is a surface-active substance known as "Solvone #1." The dyeing conditions such as the dye bath temperature, the pH of the dye bath, the amount of dyestuff said bath, e.g. at temperatures of 100 to 140°C. With respect to the other dyeing conditions, a dye bath pH in the range of 6 to 8.5 has been found to give excellent results, while the proportion of dyestuff may be of the same order as that generally employed in dyeing containing disperse cellulose acetate dyestuffs, e.g. about 0.1 to 6% (based on the weight of the textile material). For best results the dye bath should not be too dilute; for which dyeing, a liquor ratio not above 10:1 and preferably about 30:1 to 12:1 is preferred. In jigg dyeing, best results are obtained when the amount of butyl benzate is not over 15%, preferably 10% or less, based on the weight of the textile material.

The textile material may be dyed in any desired form, e.g. in the form of yarn, staple fiber, or fabric, which may be woven, non-woven, warp-knitted or circular-knitted. It may have a basis of a cellulose ester containing at most 0.29% alcohols of hydroxyl groups per anhydroglucose unit in the cellulose molecules thereof, such as highly esterified cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate-formate, cellulose acetate-propionate or cellulose acetate-butyrate. The preferred cellulose ester material is cellulose acetate of about 61% to 62.5% acetyl value, calculated as combined acetic acid. As previously stated, the textile material may have a basis of flax, hemp, or a linear polyester whose melting point is above 200°C, preferably above 220°C, for example, a glycol terephthalate, such as polyethylene terephthalate, or a polyester of an aromatic hydroxy acid such as the homopolyester of 4-(p-hydroxyethoxy)-3-methyl benzene acid, alone or blended with fillaments of the aforesaid cellulose ester.

After the dyeing of textile material it may be subjected to a heat-treatment operation, which, in the case of the cellulose ester of low hydroxyl content, has the effect of improving the washfastness and resistance to oxidative-fading of the dye on the material and also improves the safe ironing temperature, resistance to shrinkage on pressing with moist steam and resistance to glazing of the textile material, as is now well known in the art. One suitable heat treatment involves passing the cellulose ester fabric through an infra-red heater or over heated plates or rollers, so that the surface of the fabric attains a temperature of, for example, 230°C.

The following examples are given to illustrate this invention further:

**Example I**

A fabric woven of yarns of cellulose acetate of 61.5% acetyl value is immersed and agitated in an aqueous dye bath maintained at 95°C and containing 2%, based on the weight of the fabric, of a blue disperse dyestuff comprising 1,8-dihydroxy-4-(para-beta-hydroxyethyl) anilido-3-nitro anthranilquinone, 10%, based on the weight of the fabric, of n-butyl benzate, 1.2%, based on the weight of the fabric, of the emulsifier "Nekal NS," and 2.5%, based on the weight of the fabric of, "Jepon T-77" (comprising 77% of sodium N-methyl N-oleyl taurate and, the balance, sodium sulfate), the liquor ratio being 50:1. For comparative purposes, other pieces of the same fabric are dyed under identical conditions with dye baths which are otherwise the same except that in one case (hereinafter termed the "control dyebath") the butyl benzate and "Nekal NS" are omitted, while in another case the butyl benzate is replaced by an equal weight of another assistant, namely, methyl salicylate. The proportion of the dye absorbed from the dyebath is measured in each case. After one half hour of dyeing, the fabrics dyed in the presence of butyl benzate and methyl salicylate have absorbed 81% and 16%, respectively, more dye than the fabric dyed in the control dyebath. After one hour of dyeing, the corresponding percentages are 105% and 89%, respectively.

**Example II**

Example I is repeated except that the fabric used is woven of yarns of polyethylene terephthalate ("Dacron"). After one half hour the fabrics dyed in the presence of butyl benzate and methyl salicylate have absorbed 330% and 286%, respectively more dye than the fabric dyed in the control dyebath. After one hour the corresponding percentages are 187% and 170%, respectively.

**Example III**

Example I is repeated except that the blue dyestuff is replaced by a red disperse dyestuff comprising 4-nitro-2-methylsulfonphenyazo 4'-(N-beta-hydroxy-ethyl-N-di-fluoroethyl) aminobenzene and the comparative experiment involving methyl salicylate is omitted. After one half hour of dyeing the fabric dyed in the presence of butyl benzate has absorbed 30% more dye than the fabric dyed in the control dyebath. After one hour the corresponding percentage is 23.6%.

**Example IV**

Example III is repeated except that the fabric used is woven of yarns of polyethylene terephthalate ("Dacron"). After one half hour of dyeing the fabric dyed in the presence of butyl benzate has absorbed 640% more dye than the fabric dyed in the control dyebath. After one hour the corresponding percentage is 607%.

**Example V**

Example III is repeated except that the red dyestuff is replaced by the yellow disperse dyestuff "Interchemical Acetates Yellow HDLF-40." After one half hour of dyeing the fabric dyed in the presence of butyl benzate has absorbed 67.2% more dye than the fabric dyed in the control dyebath. After one hour the corresponding percentage is 23%. 
Example VI

Example III is repeated except that the fabric used is woven of yarns of polyethylene terephthalate ("Dacron"). After one hour of dyeing the fabric dyed in the presence of butyl benzoate has absorbed 406% more dye than the fabric dyed in the control dyebath. After one hour the corresponding percentage is 413%.

Example VII

Example I is repeated except that the fabric is made up of a blend of 20% of fibers of the cellulose acetate of 61.5% acetyl value and 50% of fibers of polyethylene terephthalate.

It is to be understood that the foregoing detailed description is merely given 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 dyeing of a textile material having a basis of a cellulose ester having at most 0.29 hydroxyl group per anhydroglucose unit, which comprises bringing said textile material into contact with an aqueous bath containing a disperse cellulose acetate dyestuff in the presence of butyl benzoate as an assistant for increasing the rate of dyeing.

2. Process for the dyeing of a textile material having a basis of a linear polyester of melting point above 200°C, which comprises bringing said textile material into contact with an aqueous bath containing a disperse cellulose acetate dyestuff in the presence of butyl benzoate as an assistant for increasing the rate of dyeing.

3. Process for the dyeing of a textile material having a basis of filaments of a cellulose ester having at most 0.29 hydroxyl group per anhydroglucose unit, and filaments of a linear polyester of melting point above 200°C, which comprises bringing said textile material into contact with an aqueous bath containing a disperse cellulose acetate dyestuff in the presence of butyl benzoate as an assistant for increasing the rate of dyeing.

4. Process for the dyeing of a textile material having a basis of cellulose acetate having an acetyl value of at least about 61% calculated as combined acetic acid and filaments of polyethylene terephthalate which comprises bringing said textile material into contact with an aqueous bath containing a disperse cellulose acetate dyestuff in the presence of butyl benzoate as an assistant for increasing the rate of dyeing.

5. Process for the dyeing of a textile material having a basis of polyethylene terephthalate which comprises bringing said textile material into contact with an aqueous bath containing a disperse cellulose acetate dyestuff in the presence of butyl benzoate as an assistant for increasing the rate of dyeing.

6. Process for the dyeing of a textile material having a basis of cellulose acetate having an acetyl value of at least about 61% calculated as combined acetic acid and filaments of polyethylene terephthalate which comprises bringing said textile material into contact with an aqueous bath containing a disperse cellulose acetate dyestuff in the presence of butyl benzoate as an assistant for increasing the rate of dyeing.

7. Process as set forth in claim 4 in which said disperse cellulose acetate dyestuff is of the high temperature slow dyeing type and the dyebath is heated to a temperature of at least 65°C and contains about 5 to 30%, based on the weight of the textile material, of butyl benzoate.

8. Process as set forth in claim 5 in which said disperse cellulose acetate dyestuff is of the high temperature slow dyeing type and the dyebath is heated to a temperature of at least 65°C and contains about 5 to 30%, based on the weight of the textile material, of butyl benzoate.

9. Process for the dyeing of a textile material having a basis of cellulose acetate having an acetyl value of at least about 61% calculated as combined acetic acid, which comprises bringing said textile material into contact with an aqueous bath containing a disperse cellulose acetate dyestuff in the presence of butyl benzoate as an assistant for increasing the rate of dyeing and tripropyl phosphate.

10. Process for the dyeing of a textile material having a basis of cellulose acetate having an acetyl value of at least about 61% calculated as combined acetic acid, which comprises bringing said textile material into contact with an aqueous bath containing a disperse cellulose acetate dyestuff in the presence of butyl benzoate as an assistant for increasing the rate of dyeing and tripropyl phosphate.

11. A dyebath comprising an aqueous medium containing a disperse cellulose acetate dyestuff and butyl benzoate as an assistant for increasing the rate of dyeing.

12. A dyebath comprising an aqueous medium containing a disperse cellulose acetate dyestuff and butyl benzoate as an assistant for increasing the rate of dyeing and tripropyl phosphate.

13. A dyebath comprising an aqueous medium containing a disperse cellulose acetate dyestuff and butyl benzoate as an assistant for increasing the rate of dyeing and a terpene.

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