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# DYEING CELLULOSE DERIVATIVES AND AFTER-TREATING FOR IMPROVED WASHFASTNESS

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This invention relates to dyeing and relates more particularly to the dyeing of cellulose acetate to produce colored materials of improved washfastness.

As is well known, textile materials having a basis of cellulose acetate and other organic derivatives of cellulose are generally dyed by means of aqueous dyebaths containing dyestuffs of the type known as dispersed cellulose acetate dyestuffs. However, the fastness to washing of the resulting colored materials has not been as good as desired. For example, for certain purposes it is necessary to have colored materials which are substantially fast to washing at 120 or 130° F. The cellulose acetate textile materials dyed in the usual manner with dispersed cellulose acetate dyestuffs are not substantially wash fast at these temperatures.

It is, therefore, an object of this invention to provide a novel method for the dyeing of textile materials having a basis of cellulose acetate or other organic derivatives of cellulose, which will be free from the foregoing and other disadvantages.

Another object of this invention is to provide a new method of dyeing textile materials having a basis of cellulose acetate with dispersed cellulose acetate dyes to produce colored materials which are substantially fast to washing at 120 or 130° F.

Other objects of this invention will be apparent from the following detailed description and claims.

In accordance with this invention textile material having a basis of cellulose acetate or other organic derivatives of cellulose is dyed with a dispersed cellulose acetate dyestuff carrying a reactive group or groups and the dyed textile material is then treated with a soluble, heat-curable amidogen-formaldehyde condensate formed by the condensation of formaldehyde and a compound containing a reactive —NH— group, such as urea, cyclic ethylene urea, or melamine. Thereafter, the textile material is cured by heating to effect a reaction in the fibers between the dyestuff and the amidogen-formaldehyde condensate. For best results this reaction should be carried out in the presence of a catalyst.

The process of this invention is applicable to textile materials consisting essentially of cellulose acetate or other organic derivatives of cellulose such as cellulose esters, e.g. cellulose propionate, cellulose butyrate, cellulose acetate-propionate or cellulose acetate-butyrate, and cellulose ethers, e.g. ethyl or benzyl cellulose. The process of this invention may also be applied to textile materials comprising blends of fibers of cellulose acetate, or other organic derivatives of cellulose, with fibers of other materials, such as regenerated cellulose, e.g. viscose rayon or cuprammonium rayon; polyamides such as nylon, e.g. the polyamide of hexamethylene diamine and adipic acid or of 6-aminocaproic acid; polyurethanes; acrylonitrile polymers and copolymers; polyesters such as polyethylene terephthalate; cotton; and animal fibers such as wool and mohair. However, it has been found to be particularly suitable for the treatment of fabrics consisting essentially



of cellulose acetate, i.e. either the usual acetone-soluble cellulose acetate or the substantially acetone-insoluble cellulose acetates of very high acetyl value such as the triacetate, alone or in combination with regenerated cellulose. It has also been found that the process of the present invention is suitable for the treatment of textile materials consisting essentially of other fibers dyeable with dispersed cellulose acetate dyestuffs; thus, the application of the process of this invention to all-nylon fabrics has resulted in an improvement in the washfastness of the dyed fabrics.

The dispersed cellulose acetate dyestuffs employed in the practice of this invention contain groups reactive with the amidogen-formaldehyde condensate. Such groups may be, for example, alcoholic or phenolic hydroxyl groups, unsubstituted amino groups, i.e. —$NH_2$, or monosubstituted amino groups, i.e. —NHR where R is an aromatic or aliphatic radical having a carbon atom connected to the nitrogen atom.

Best results, that is the greatest degree of improvement in washfastness caused by the after-treatment with the amidogen-formaldehyde condensate, have been obtained when the dyestuff contains a plurality of alcoholic or phenolic hydroxyl groups, or both an amino group and a hydroxyl group. For example, the treatment with the amidogen-formaldehyde condensate produces a marked improvement in the washfastness of the following highly reactive blue dyestuffs: 1,4-di(hydroxyethylamino) anthraquinone, 1,8-dihydroxy-4-p-(β-hydroxyethyl)phenylamino-5-nitro anthraquinone, 1,4-di(hydroxyethylamino)-5,8-dihydroxy anthraquinone, 1,5-dihydroxy-4-p-(α-hydroxyethyl)phenylamino-8-nitro anthraquinone. The treatment also markedly improves the washfastness of the following highly reactive red azo dyestuffs: unsubstituted 4-nitrophenyl azo 4′-bis(β-hydroxyethyl)aminobenzene and the same dyestuff carrying a 2′-chloro substituent, or a 2′-methyl substituent, or both a 2-chloro and a 2′-methyl substituent, or a 2′-acetylamino substituent, or both a 2-methoxy and a 2′-acetylamino substituent. There is also a marked improvement in the washfastness of materials dyed with the highly reactive pink dyestuffs, 1-amino-4-hydroxy anthraquinone and 1-amino-2-methoxy-4-hydroxy anthraquinone, and the highly reactive orange dyestuff 4-nitro-2,6-dichlorophenyl azo 4′-bis(β-hydroxyethyl)amino-2-′-chlorobenzene.

Other suitable highly reactive dyestuffs for use in the practice of this invention are the yellow 2-nitro-4-sulfonamidodiphenylamines carrying alcoholic hydroxyl substituents. Examples of materials of this type are the following novel yellow dyestuffs: 2-nitrodiphenylamine-4-sulfon-β-hydroxypropylamide and the same compound carrying a 4′-ethoxy substituent, 2-nitrodiphenylamine-4-sulfon-hydroxy-t-butylamide and the same compound carrying a 4′-ethoxy substituent, 2-nitrodiphenylamine-4-sulfon(N-ethyl-N-β-hydroxyethyl)amide, 2-nitrodiphenylamine-4-sulfon-α,α-dimethyl-β-hydroxypropylamide, 2-nitrodiphenylamine-4-sulfon-α-hydroxymethylpropylamide, 2-nitrodiphenylamine-4-sulfon-bis(β-hydroxypropyl)amide and the same compound carry a 4′-ethoxy substituent. Other examples of such materials are the orange-yellow dyestuffs, 4′-ethoxy-2-nitrodiphenylamide-4-sulfon-α-methyl-β-hydroxypropylamide and the 4′-ethoxy-2-nitrodiphenylamine-4-sulfon-α-hydroxymethylpropylamide, which are the subjects of the copending application of Adams and Salvin, Serial No. 430,408, filed on even date herewith, now abandoned. Especially good results with respect to washfastness are obtained when there is employed the 2-nitrodiphenylamine-4-sulfon (N-β-hydroxyethyl)anilide described in the copending application of Adams and Salvin, Serial No. 430,410, filed on even date herewith.

The dyestuffs mentioned in the preceding paragraphs are of the highly reactive type. However, if desired, less reactive dyestuffs may be employed in the practice of this invention. The degree of improvement in washfastness obtained when the less reactive dyestuffs are used is smaller, but still significant. In this case, in order to obtain the desired degree of washfastness there should be employed those of the less reactive dyestuffs which are themselves intrinsically difficult to wash out of the cellulose acetate textile material. Thus, even though the treatment with the amidogen-formaldehyde condensate effects a smaller degree of improvement in washfastness, the combination of this improvement and the intrinsic washfastness of the dyed material results in a product having the desired properties. Examples of suitable dyestuffs of this type are the yellow dyestuff, 2-nitro-diphenylamine-4-sulfonanilide and the red dyestuff, 4-nitro-2-methylsulfonephenyl azo 4'-(N-β-hydroxyethyl-N-difluoroethyl)aminobenzene.

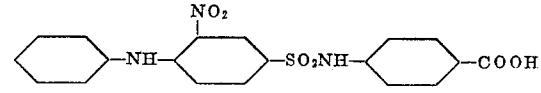
With certain dyestuffs a further improvement in the washfastness is obtained by combining the amidogen-formaldehyde condensate treatment with a treatment with a metallic chelating agent, such as a copper-containing condensation product. The use of the metallic chelating agent improves the washfastness of cellulose acetate dyed with those dispersed cellulose acetate dyestuffs which contain chelatable groups. Thus, the use of the chelating compound improves the washfastness of cellulose acetate dyed with dispersed cellulose acetate dyestuffs having a plurality of $-NH_2$ groups, or a plurality of phenolic hydroxyl groups, or a phenolic hydroxyl group and an $-NH_2$ group, such as are present in the blue and pink dyestuffs listed above, wherein such groups are in the proper spatial relation for chelation to occur. For example, chelation in the anthraquinone dyestuffs is promoted when the phenolic hydroxyl group or the amino group is peri to the carbonyl group of the anthraquinone, and, in the azo dyestuffs, when the hydroxy group is ortho to the azo group. With such chelatable dyestuffs there is an improvement in washfastness even when the chelating agent is applied as the sole reactive treating agent, without the amidogen-formaldehyde condensate. However, in the latter case the extent of this improvement is generally less than when the amidogen-formaldehyde condensate is the sole treating agent, and is much less than when the two treatments are combined. Also, although the chelating agent, when used alone, causes the pink dyestuffs listed above and the blue dyestuffs 1,4,5,8-tetraaminoanthraquinone and 1,4 - di - β - hydroxyethylamino-5,8-dihydroxyanthraquinone to change markedly in shade, this change in shade is greatly diminished when the chelating agent is used together with the amidogen-formaldehyde condensate.

As stated, the process of this invention is highly useful in the dyeing of textile materials comprising blends of cellulose acetate, or other organic derivatives of cellulose, and cellulose fibers, particularly regenerated cellulose fibers. The dispersed cellulose acetate dyestuffs have substantially no dyeing effect on regenerated cellulose. Accordingly, if it is desired to dye both components of the aforesaid blend it is necessary to employ an added dyestuff which has affinity for the regenerated cellulose, e. g. a direct dyestuff. Advantageously, the added dyestuff is of the type which is fixed on the regenerated cellulose fiber by an aftertreatment with a cationic fixing agent therefor. As is well known in the dyeing of cellulose such cationic fixing agents are commonly used in combination with metallic chelating agents. Examples of suitable fixable direct dyestuffs are those sold under the names "Cuprofix Yellow GL" (Pr. 526) "Cuprofix Brown GL," "Cuprofix Rubine BLN," "Cuprofix Rubine FBL," "Cuprofix Violet 2BL" (Pr. 429), "Cuprofix Navy Blue SL," "Cuprofix Blue FGL," "Cuprofix Blue LUL," "Cuprofix Blue RUL," "Cuprofix Black C concentrate"



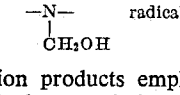
(Pr. 525), "Cuprofix Black OB concentrate" (Pr. 147), "Pontamine Fast Yellow 4GL" (Pr. 53), "Pontamine Fast Yellow RL," "Pontamine Fast Orange 2RL," "Pontamine Fast Orange RGL," "Pontamine Fast Brown BL" (Pr. 47), "Pontamine Fast Red 6 BL" (Pr. 428), "Pontamine Fast Red 3BL," "Pontamine Fast Violet 4RL" (Pr. 277), "Pontamine Fast Blue 3RL," "Pontamine Fast Blue BLL," "Pontamine Fast Blue CPL," "Pontamine Fast Blue GGL" (Pr. 432), "Pontamine Black PGR" (Pr. 372), "Pontamine Diazo Black OR" (Pr. 147). These dyestuffs are desirably incorporated into the aqueous dyebath together with the dispersed cellulose acetate dyestuff.

Most of the yellow dispersed cellulose acetate dyestuffs do not have a high affinity for nylon. Accordingly, when the process of this invention is applied to blends containing nylon and cellulose acetate, other yellow dyestuffs which are substantive to nylon should be employed. Examples of such nylon-substantive yellow dyestuffs are the premetallized colors sold under the names "Irgalan," e.g. "Irgalan Yellow 2RL," "Cibalan" and "Capracy." These materials do not dye the cellulose acetate so that it is, therefore, necessary to use them in combination with a yellow dispersed cellulose acetate dyestuff where union dyeing is desired. Another suitable type of yellow dyestuff, which has the advantage of being substantive to both the cellulose acetate and the nylon when applied from an acidic medium, is the novel dispersed cellulose acetate dyestuff having the formula:




which is the subject of the copending application of Adams and Salvin, Serial No. 430,409, filed on even date herewith. This dyestuff has the further property of being highly reactive in the fiber with cationic materials, such as melamine-formaldehyde condensates, fixatives for direct dyes, and copper-containing chelating agents, which cationic materials may be employed for improving the washfastness of materials dyed therewith.

The amidogen-formaldehyde condensates used in the practice of this invention are soluble, heat-curable materials of relatively low molecular weight formed by the condensation of formaldehyde and a compound containing a reactive —NH— group, such as urea, melamine, ethylene urea, guanidine, dicyandiamide, guanyl urea or N-methyl urea. As is well known, the formaldehyde reacts at the —NH— group to produce an N-hydroxymethyl, i.e.




In the condensation products employed in the present invention this N-hydroxymethyl radical may be present as such, or may be etherified with a lower aliphatic alcohol such as methanol, ethanol, propanol or butanol, to form an N-alkoxymethyl radical. It is found that the amidogen-formaldehyde condensate is most effective when it is a relatively stable material containing a plurality of N-hydroxymethyl or N-alkoxymethyl radicals and has a cyclic, substantially monomeric structure. Also, it has been found that condensates containing N-methoxymethyl radicals are more effective than the corresponding N-hydroxymethyl compounds. Thus, the best results are obtained by the use of condensation products of monocyclic ureas in which both nitrogens are joined, through carbon to nitrogen bonds, to a divalent aliphatic radical, e.g. ethylene urea, or by the use of condensation products of melamine. Specifically, condensation products such as N,N' - bis(hydroxymethyl)ethylene urea, N,N' - bis-(methoxymethyl)ethylene urea and di- or tri-(methoxymethyl) melamine have given the best results. Very good results, though not as good as those attainable with

the aforementioned condensates, are obtained with such materials as dimethoxymethyl methylene diurea, dimethoxymethyl urea, and di- and trimethylol melamine. Such materials as dimethylolurea, the mixed monomeric methylol compounds resulting from the reaction of 1.3 moles of formaldehyde and 1 mole of urea, i.e. mixed monomethylol and dimethylol urea, and the methyl ethers of such mixed monomeric methylol compounds, are also suitable but less effective. Mixtures of the various amidogen-formaldehyde condensates may be employed if desired.

When blends of regenerated cellulose fibers and cellulose acetate fibers are treated with the aforesaid amidogen-formaldehyde condensates, these condensates tend to be absorbd preferentially on the regenerated cellulose fibers. Accordingly, in this case the process of this invention is somewhat less effective, with respect to the washfastness of the dyed cellulose acetate portion of the blend, than when it is applied to textile materials made entirely of cellulose acetate. It is found that in the treatment of such blends best results are obtained when at least a portion, preferably at least about 30%, of the amidogen-formaldehyde condensate consists of a cyclic urea-formaldehyde condensation product, such as the N,N'-bis-(hydroxymethyl)ethylene urea or its dimethyl ether, or a di- or tri-(alkoxymethyl)melamine. For example, there may be employed a mixture comprising ⅓ of N,N'-bis-(hydroxymethyl)ethylene urea and ⅔ of N,N'-dimethoxymethyl urea or ½ of N,N'-bis(hydroxymethyl)ethylene urea and ½ of N,N'-dimethylolurea or a mixture comprising ½ of N,N'-bis(methoxymethyl)ethylene urea and ½ of the condensation product of urea, stearamide and formaldehyde. By using mixtures of different amidogen-formaldehyde condensates and by changing the proportions in such mixtures the hand and resilience of the finished fabric may be varied, as desired.

The amidogen-formaldehyde condensation product is advantageously applied to the textile material in the form of an aqueous solution thereof. It is preferable to apply this solution at a temperature not above about 30° C. since may of the amidogen-formaldehyde condensates are unstable and tend to polymerize on prolonged exposure to elevated temperatures. However, if desired, the temperature of the solution may be higher, e.g. about 50° C., particularly when the more stable amidogen-formaldehyde condensates are employed and the solution is not subjected to the elevated temperature for long periods of time. The solution may also contain a swelling agent for the cellulose acetate or other organic derivatives of cellulose, such as, for example, the butyl ether of ethylene glycol, acetone or dioxane to improve the uniformity of distribution of the condensate in the textile material. The concentration of the solution and the amount thereof applied to the textile material are desirably such as to incorporate into the textile material about 2 to 15%, preferably about 5 to 10%, by weight of the amidogen-formaldehyde condensate, based on the weight of the textile material.

As stated, a metal-containing chelating agent, preferably a copper-containing chelating agent, may be employed in conjunction with the amine-formaldehyde condensate. While chelating agents which are copper salts, e.g. copper acetate or copper sulfate, may be employed, it is often preferably to use those copper-containing chelating agents which contain copper combined with complex organic compounds, e.g. with reaction products of dicyandiamide and formaldehyde, or combinations such as disclosed in U.S. Patent No. 2,573,489. An example of a very suitable chelating agent is the product sold under the name "Cuprofix 47," which provides only relatively small amounts of free copper ion. Other copper-containing chelating agents, containing larger amounts of copper ions, e.g. those sold under the names "Coprantex B" and "Resofix VF," may be employed advantageously, particularly when fixable direct dyes are present. The chelating agent may contain other metals, e.g. zirconium, nickel or chromium, instead of copper.

When a metal-containing chelating agent is employed it is preferably incorporated into the aqueous solution containing the amidogen-formaldehyde condensate. One convenient method for incorporating this chelating agent is to dissolve it in water and mix the solution with an aqueous solution of the amidogen-formaldehyde condensate. The amount of chelating agent may be, for example, about 1 to 3% by weight based on the weight of the textile material.

As stated, a catalyst should be present during the reaction in the fiber between the amidogen-formaldehyde condensation product and the dyestuff. Suitable catalysts are those which are acidic at the temperature at which this reaction is carried out. A particularly effective catalyst is a mixture prepared by adding formaldehyde to ammonium chloride or to an amine hydrochloride in aqueous medium. The addition of the formaldehyde increases the acidity, i.e. it causes the pH of the aqueous mixture to drop sharply, e.g. from an initial value of 5.5 down to a value of 2.0. A very suitable catalytic mixture of this type is the one known as "Catalyst G–8." Ammonium chloride, per se, is also a good catalyst. Other suitable catalysts are ammonium sulfate and the amine hydrochloride known as "Aerotex Accelerator 187." Other catalysts which may be used but which are less effective than those mentioned above are oxalic acid and the alkanolamine hydrochloride known as "Accelerator UTX." Advantageously, the catalyst is mixed into the aqueous solution of the amidogen-formaldehyde condensate. For example, a dilute aqueous solution of the catalyst may be mixed with the aqueous solution of the amine-formaldehyde condensate just before the mixture is applied to the textile material. Suitable proportions of the catalyst are about 2 to 10%, preferably about 5 to 10%, by weight based on the weight of the amidogen-formaldehyde condensate. Of course, if the dyed textile material carries an alkaline material, e.g. as an impurity, such alkaline material will react with all or part of the catalyst thereby reducing the effective amount of catalyst present. Accordingly, in such a case the amount of catalyst actually applied to the textile material must be increased to provide the desired effective amount thereof.

It is also found that the addition of formaldehyde to the aqueous bath containing the amidogen-formaldehyde resin effects a significant improvement in the washfastness of the resulting treated dyed textile material. This is surprising since treatment of the dyed material with aqueous formaldehyde, together with an acidic catalyst but without the amidogen-formaldehyde condensate, causes no improvement in washfastness. The effect of added formaldehyde is particularly pronounced when the aqueous treating bath contains a less reactive amidogen-formaldehyde condensate, e.g. a condensate of urea and less than two moles of formaldehyde. However, a definite improvement is obtained by the addition of formaldehyde to baths containing the more reactive of the condensates, e.g. N,N'-bis(hydroxymethyl)ethylene urea. Advantageously, the concentration of formaldehyde in the aqueous treating bath, containing the amidogen-formaldehyde condensate, is about ½ to 5%. The formaldehyde is conveniently added to the treating bath in the form of an aqueous solution thereof, e.g as a solution containing about 40% of formaldehyde by weight.

As stated, the process of this invention may be applied to textile materials comprising blends of cellulose acetate and regenerated cellulose fibers. It is well known that the application of amidogen-formaldehyde condensates to fibers of regenerated cellulose increases the resilience and resistance to shrinkage of the fibers but has the disadvantages of reducing their abrasion resistance and tear strength. In the process of this invention the latter dis-

advantages may be overcome in large part by the application of certain finishing agents, such as the silicones, e.g. those methyl hydrogen polysiloxanes known as "De Cetex" 102, 104, 108, or "Hydropruf," or long aliphatic chain melamine compounds, such as the condensation products of stearamide or stearylamine with melamine and formaldehyde. These finishing agents are advantageously incorporated into the aqueous solution containing the amidogen-formaldehyde condensate and in proportions sufficient to provide 0.5 to 2% or more of such materials based on the weight of fabric. The use of these finishing agents also imparts durable water repellency to the textile material and results in a fabric which has a higher safe ironing point and an improved resistance to shrinkage on pressing in the presence of moist steam. The aliphatic melamine derivatives also improve the resistance of the dyed material to gas fading.

In one convenient method of practicing this invention a fabric comprising yarns of cellulose acetate is dyed in an aqueous dyebath containing one or more of the dyestuffs described above. The amounts of the dyestuffs present in the dyebath are, of course, dependent on the type and depth of shade desired on the fabric. Thus, the total amount of dyestuff applied may be about 0.2 to 6%, by weight, based on the weight of the fabric. In order to carry out the dyeing operation at a relatively rapid rate the aqueous dyebath should be maintained at an elevated temperature, e.g. at least about 75° C., preferably about 80 to 90° C. Such elevated temperatures are particularly desirable since many of the dispersed cellulose acetate dyestuffs suitable for use in this invention are of the high temperature slow dyeing type, which have a slow rate of dyeing onto cellulose acetate at lower temperatures. If desired, the aqueous dyebath may be maintained under superatmospheric pressure so that the dyeing may be conducted at temperatures above the normal boiling point of said dyebath, particularly when fabrics of acetone-insoluble cellulose acetate of higher acetyl value are employed. The dyestuffs should be well dispersed in the dyebath, e.g. in the conventional manner, by the use of a suitable surface active agent, so that a level and well penetrated dyeing is obtained. The dyeing operation may be carried out in any suitable apparatus, such as a winch or a jig. After dyeing the fabric should be rinsed thoroughly to remove any residual alkali, surface active agent or unbound dyestuff and should be dried quickly to avoid any tendency for migration of the colors.

After drying, the dyed fabric is advantageously brought into contact with an aqueous bath containing the amine-formaldehyde condensate, the chelating or fixative agent, the catalyst and the finishing agent. This bath may be conveniently applied to the fabric by padding, for example by passing the fabric through the bath and then through the lower nip of a bank of three pressure rolls, then again through said bath and through the upper nip of said bank of rolls. The amount of the aqueous bath picked up by the fabric in the padder may be varied, e.g. from about 60 to 125% based on the weight of the fabric.

After the padding operation the textile material is dried and then cured. Conveniently the drying is carried out in a tenter at a temperature of, for example, 240 to 280° F., preferably using some overfeed to the tenter to permit the textile material to relax. The dried fabric is then cured, e.g. at a temperature of about 285° F. to 340° F. for a period of about 2 to 15 minutes. After the curing operation the fabric is desirably washed, preferably in the presence of a mild detergent, to remove any residual acidity and prevent the development of odor. If desired, the fabric may be subjected to any suitable mechanical treatment, such as calendering or button-breaking, to prevent mark-off and to modify the hand of the fabric.

The process of this invention is preferably applied to a fabric, e.g. a woven or knitted fabric. However, it is also applicable to textile material in any other desired form, e. g. staple fibers, yarn or tow.

The following examples are given to illustrate the invention further.

*Example I*

A woven fabric comprising a blend of 50% by weight of cellulose acetate fibers and 50% by weight of viscose rayon fibers is treated to remove any starch adhering thereto and is then thoroughly scoured. Thereafter it is dyed in a brown shade on a winch, using an aqueous dyebath comprising 0.51% of disperse powder comprising the blue dye 1-hydroxy-4-p-(β-hydroxyethyl)anilido-8-hydroxy-5-nitro anthraquinone, 0.51% of disperse powder comprising 4-nitro-2,6-dichlorophenylazo 4'-bis (β-hydroxyethyl)amino-2'-chlorobenzene, 0.14% of disperse powder comprising about 40% of the azo red dye 4-nitro-2-methoxy phenyl azo 4'-bis(β-hydroxyethyl) amino-2'-acetylamino benzene and about 60% of sodium lignosulfonate, 0.58% of "Resofix Blue GL," a fixable blue direct dyestuff, 1.08% of "Cuprofix Yellow GL," a fixable yellow direct dyestuff, 2.30% of "Risofix Rubine BLN," a fixable red direct dyestuff, all proportions being based on the weight of the fabric. The dyebath also contains 3% of "Igepon AP" (the sodium salt of isethionic acid), 2% of tetra sodium pyrophosphate, and 10% of Glauber's salt, based on the weight of the fabric. At the start of dyeing the temperature of the dyebath is 50° C. Dyeing is continued for one hour during which time the temperature is raised to 82° C. After dyeing, the fabric is rinsed well, dried immediately on a tenter frame, cooled, allowed to relax in a scutching pan, and then padded with a mixture comprising 15% of "Sandoz Resin EN" (comprising as the active ingredient 50% of dimethylolurea), 10% of Rhonite R–1 (comprising as the active ingredient 50% of N,N'-dihydroxymethyl ethylene urea), 3% of "Cuprofix 47" (a copper-containing chelating agent), 1.5% of Catalyst G–8 (a mixture of an organic amine hydrochloride with formaldehyde), 1% of "Softener H" (a cationic type of softening agent) and the balance water. The padding bath is prepared by dissolving "Sandoz Resin EN" and "Rhonite R–1" in water at room temperature; dissolving the "Cuprofix 47" in water at 60 to 65° C. and then cooling the resulting solution to room temperature; mixing these two solutions together with the softener and finally adding the catalyst. The fabric picks up 78% of its weight of this padding bath. The padded fabric is dried on a pin dryer at 275° F. for 4 minutes and is then cured with relaxation for 7 minutes at 320° F. Thereafter the fabric is scoured at 75° C. for 10 minutes, rinsed in hot water at 60° C. and rinsed in cold water and then dried.

*Example II*

Example I is repeated except that in place of the 10% of "Rhonite R–1" there are used 6% of a mixture comprising as the active ingredient 80% of N,N'-dimethoxymethyl ethylene urea.

*Example III*

Examples I and II are repeated with the following exceptions: The blue and red disperse powders are used in the amounts of 0.26% and 0.07%, respectively while the orange dyestuff is replaced by 0.17% of a mixture disperse yellow powder comprising about 40% of 2-nitrodiphenylamine-4-sulfonanilide and about 60% of sodium lignosulfonate. The amounts of the blue, yellow and red direct dyestuffs are changed to 0.19%, 0.19% and 0.21%, respectively. The fabric is dyed gray.

*Example IV*

Examples I, II and III are repeated except that the curing of the padded fabric is carried out at 340° F. for 2 minutes.

*Example V*

Another very suitable padding recipe contains 7.50% of "Aerotex Resin 801" (N,N'-dimethoxymethyl urea),

15% of "Rhonite R–1," 3% of "Cuprofix 52" (a copper-containing cationic fixative agent), 4% of "Hydropruf" (a silicone finishing agent), 1.5% of "Cobelfix" (zinc octoate which acts to catalyze the curing of the "Hydropruf"), 1.5% of "Catalyst G–8," and the balance water.

*Example VI*

Another very suitable padding recipe is similar to that of Example V except that 3% of "Permel" is substituted for the "Cobelfix" and "Hydropruf" and ammonium sulfate is substituted for the "Catalyst G–8."

*Example VII*

Example III is repeated except that the yellow dyestuff 2 - nitro - diphenylamine - 4 - sulfon(N - β - hydroxyethyl)-anilide is substituted for the 2-nitro-diphenylamine-4-sulfonanilide.

The fabrics produced according to the foregoing examples are subjected to the #2 A.A.T.C.C. washfastness test, involving washing at 120° F. After five washings the fabrics showed practically no change in shade.

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 treatment of textile materials comprising fibers of an organic derivative of cellulose, which comprises dyeing said textile material with a dispersed cellulose acetate dyestuff containing a plurality of radicals selected from the group consisting of an $NH_2$ group, an alcoholic hydroxyl group and a phenolic hydroxyl group, then applying to the dyed textile material a mixture of formaldehyde and a soluble heat-curable condensation product of formaldehyde and a compound containing a reactive —NH— group, said condensation product containing a plurality of radicals selected from the group consisting of N-hydroxymethyl and N-lower alkoxymethyl radicals, and then heating said textile material to effect a reaction between said dyestuff and said condensation product in said fibers.

2. Process as set forth in claim 1 in which said condensation product is selected from the group consisting of N,N'-dimethoxymethyl ethylene urea, N,N'-dihydroxymethyl ethylene urea, trimethoxymethyl melamine and dimethoxymethyl melamine.

3. Process as set forth in claim 1 in which said dyestuff contains a phenolic hydroxyl group and an alcoholic hydroxyl group.

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