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PROCESS OF DYEING

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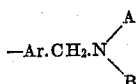
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This invention relates to a process of dyeing in which fixation of dyestuff on textile material is improved. It relates in particular to the fixation of certain dyestuffs by condensing them with formaldehyde and a non-aromatic, primary or secondary amine, impregnating textile material therewith, and subsequently heating the impregnated material to cause the dyestuff condensate to combine with the textile material.

The object of this invention is to improve the fastness of certain dyestuffs, herein called "methylol-forming," on textile materials. It is another object of this invention to provide a process for imparting to dyed fibers, yarns, and fabrics a high degree of resistance to removal of dye from cleaning during laundering and dry cleaning or from wear. It is also an object to provide a process for dyeing which does not require the use of a mordant. It is another object to provide dyestuffs by which color may be imparted to different types of fibers by the same dye. A further object is to provide a universal one-bath dyeing process.

Fixation of certain dyestuffs may be accomplished by processing textile material with a dyestuff possessing the group



in which Ar represents an aromatic nucleus carrying a nuclearly-bound oxygen or sulfur atom, A represents a member of the group consisting of hydrogen, and aliphatic and alicyclic radicals, and B represents a member of the group consisting of aliphatic and alicyclic hydrocarbon groups. A and B may represent, when taken jointly, a divalent hydrocarbon radical or a divalent hetero-radical which jointly with the nitrogen forms a heterocyclic ring, such as found in piperidine, piperazine, pyrrolidine, morpholine, and other cyclic, basic, secondary amines. This essential fixative group may be formed in any dyestuff which is capable of reacting with formaldehyde to form a methylol compound. Aromatic compounds which possess a phenolic hydroxyl or sulfhydryl group with positions available for substitution ortho or para to the hydroxyl or sulfhydryl group are known to react with formaldehyde and are commonly designated "methylol-forming phenols." The term "methylol-forming" dyestuff or dye is used in the same sense and is applied to those dyestuffs which have available for substitution ortho or para positions relative to a nuclearly-bound phenolic hydroxyl or sulfhydryl

group. Such dyes react with formaldehyde and non-aromatic amines possessing at least one hydrogen held by the nitrogen atom and are operable in this process.

Methylol-forming dyestuffs are thus reacted with formaldehyde and amines and used to impregnate fibers, yarn, batting, or fabric by padding, dipping, spraying, or printing according to such well known methods as skein-dyeing, chain-dyeing, raw stock dyeing, package dyeing, piece dyeing, roll printing, screen printing, and the like.

Excess dye liquor may be removed by any suitable means such as squeeze rolls, centrifugal extractor, or the like, when so desired. Then, with or without previous drying, the impregnated material is subjected to a temperature high enough to bring about a reaction of the dyestuff and the textile material. The required temperatures are above 100° C. The temperature used will depend upon the material being dyed, the dyestuff, the process of treating, the presence or absence of catalyst, and the time allowable for completing the reaction. At temperatures of 140 to 150° C. a few minutes usually suffices to fix the dyestuff. At temperatures below 120° C. longer times are necessary, even times up to an hour being sometimes required. After the reaction of organic fiber and modified dye has been effected, it is usually desirable to wash the treated material to remove unreacted excess dye, soluble reaction products, etc., as in the usual soap-off procedure.

The dyes which are amenable to fixation by this process are most conveniently classified according to chemical structure and include azo dyes, such as Tannin Orange R (basic), Resorcin Yellow (acid), Betanaphthol Orange (acid), Para Red (acid), Sudan III (a disazo dye) etc.; nitroso dyes, such as Resorcin Green; indophenol dyes, such as Indophenol Blue (basic); hydroxyketone dyes, such as Alizarine Yellow C, Flavopurpurin, alizarinirisol, etc.; indanthrene dyes, such as Indanthrene Blue 5G; triphenyl methane dyes, such as fluorescein, aurine, xanthene, etc.

The secondary amines which are effective in this process are aliphatic, heterocyclic and alicyclic amines of a wide range of molecular size and structure. Examples of secondary amines which may be used include dimethylamine, diethylamine, dibutylamine, diamylamine, methyl dodecylamine, dicyclohexylamine, morpholine, piperidine, piperazine, pyrrolidine, diethanolamine, triethylene tetramine, and the like.

Primary amines are also effective in our process. Typical compounds include monomethylamine, monoethylamine, t-amylamine, caprylamine, cyclohexylamine, ethylene diamine, monoethanolamine, etc. It is possible with primary amines to use more than one equivalent of formaldehyde for each equivalent of amine to obtain various products of structures which have not been determined.

In general the condensation of a methylol-forming dye with formaldehyde and a primary or a secondary amine is performed under conditions which do not greatly alter the dye or lessen its value as a dyestuff. Reacting proportions of the materials are mixed. It is often advantageous to use an inert solvent, such as alcohol, water, ether, dioxane, or benzene. The mixture may be allowed to stand for twenty-four hours or more at room temperature or the mixture may be heated under reflux or in a closed vessel. If desired, the formaldehyde and amine may be mixed first and the dye added in successive increments. In another procedure dye and amine may be mixed and formaldehyde solution gradually added. The product may be separated by distilling off the solvent. It may sometimes be separated by crystallization. It is also possible to use the dye solution directly without further treatment for purification.

It is necessary to use at least one molecular equivalent of formaldehyde and at least one molecular equivalent of an amine for each molecule of dye. When more than one reactive ortho or para position in a phenolic nucleus is available for substitution, more than one equivalent each of formaldehyde and amine may be used, if desired, to introduce two or more methylene amine groups.

The reacted dye may be applied in the same way as any comparable dyestuff. It may be used in the presence of an acid, such as acetic acid, in which case a salt form is applied. It may, if desired, be used in the presence of an alkaline material, such as soda ash, sodium bicarbonate, borax, or the like. Some dyes are rendered more soluble in alkaline or neutral solution by the conversion to the methylene amine derivative, as herein described, with subsequent conversion to a quaternary ammonium salt by heating the amine condensate with a reactive alkylating agent or aralkylating agent, such as a dialkyl sulfate (dimethyl sulfate), a halide (benzyl chloride, methylallyl bromide) or the like.

In applying the modified dyestuffs small amounts of an acid or an acidic salt seem to provide catalytic action in the reaction of the dye and textile material, but they are not essential in the process.

The dyestuffs bearing a methylene amine group react with a wide variety of organic textile materials, such as wool, silk, cotton, mercerized cotton, rayon, cellulose acetate, paper, linen, kapok, jute, straw, etc. These materials may be in the form of fibers, or raw stock, yarn, woven or knitted cloth, felts, batting, etc. Any of the organic materials which are used in making fabrics, yarns, sheets, battings, and the like, and which are not damaged by treatment in an aqueous bath and by heating above 100° C. may be used in the herein described process. The textile material and the modified dye react, it is believed, through the methylene group, which has been added to the dye, and yield a complex which resists removal of dye by any ordinary means. Another advantage of the introduction of the

methylene amine group in the dye is the improved solubility or dispersibility of many of the treated dyes. Furthermore, any of the dyes obtained by the herein described method may be reacted with practically any natural or artificial fiber which contains reactive groups, such as the hydroxyl groups in cellulosic materials. It does not follow that identical shades result on all types of fibers, but the treatment does allow the use of dyes on fibers which would otherwise not be receptive to a particular dye. Likewise, dyes which are not otherwise fast may be applied.

The following examples illustrate the preparation of dyes used in this process:

15 PREPARATION A.—Dimethylaminomethyl fluorescein

To 16.6 g. of fluorescein in 150 ml. of water was added a solution containing 20 g. of 30% formaldehyde and 36 g. of 25% dimethylamine. This was stirred at 70° C. for 3 hours. The solution became dark red when concentrated, and greenish yellow when very dilute. Acid changed it to green in any concentration. It was concentrated in vacuo at 50° C. to a brittle, light red solid. It was more soluble in water than was fluorescein. Nitrogen analysis was 7.07%, showing it to contain slightly more than two dimethylaminomethyl groups.

30 PREPARATION B.—Benzyl chloride quaternary salt of dimethylaminomethyl fluorescein

To 5 g. of dimethyl aminomethyl fluorescein was added 4 g. of benzyl chloride with thorough mixing. This mixture was heated on the steam bath for 2 hours. It became gummy, then brittle, and yielded a red powder which contained 4.08% nitrogen.

40 PREPARATION C.—Morpholinomethyl 3-amino-4-methylbenzeneazo- α -naphthol

To 9.2 g. of 3-amino-4-methylbenzeneazo- α -naphthol was added a solution containing 7 g. of 15% formaldehyde and 3.4 g. of morpholine and 50 ml. of water. These were stirred together for 3 hours at 70° C. and concentrated in vacuo at 50° C. A red powder resulted, soluble in dilute acids.

50 PREPARATION D.—Product from quinizarin, formaldehyde and monomethylamine

To 24 g. of quinizarin suspended in 150 ml. of water was added 60 g. of 35% aqueous monomethylamine and 20 g. of 30% aqueous formaldehyde. The mixture was stirred at 70° C. for 3 hours. Concentration in vacuo at 50° C. gave a dark brown powder, containing 3.68% nitrogen. It was soluble in amine solutions or other basic solutions and to a limited extent in dilute acids.

Details of various typical applications are given herewith to illustrate the wide application of the new dyeing procedure.

Example 1

Small pieces of cotton, silk, and wool were dipped in a 5% aqueous solution of bis-dimethylaminomethyl fluorescein, squeezed and dried. They were then heated at 130° C. for one-half hour and given a thorough washing. Colors were retained as follows: Cotton, yellow; silk, coral pink; wool, pale orange.

Checks, run with a solution of fluorescein itself, gave no retention of color.

Example 2

Wool and cotton fabrics were treated as in Example No. 1, except that the benzyl chloride

quaternary salt of dimethylaminomethyl fluorescein was used in 5% aqueous solution.

After being heated at about 130° C. and washed, the cotton was permanently dyed a bright yellow-orange, and the wool a pale peach shade.

Example 3

Cotton, silk, and wool fabrics were run through a bath of a 5% aqueous solution of bis-dimethylaminomethyl 3,6-dihydroxy-9-phenyl xanthene containing a trace of acetic acid. They were squeezed, dried, and heated one-half hour at 130° C. After being washed, the cotton and silk were deep rose-red, and the wool was pale rose.

Example 4

Cotton, silk, and wool fabrics were run through a 1% alcoholic solution of dimethylaminomethyl 3-amino-4-methyl benzene-azo- α -naphthol, and subsequently treated as in Example 3. All retained a rich chocolate brown color after thorough washing.

Example 5

The fabrics were treated as in Example 3, except that the dye-bath was a 2% toluene solution of the reaction product of 1 mol of 2,4-dihydroxybenzhydrol, 2 mols of formaldehyde and 2 mols of dimethylamine. Resulting colors were: Cotton, rose pink; silk, coral pink; wool, pale rose.

Example 6

Cotton, linen and wool samples were treated as in Example 3, except that the dye used was a 2% aqueous solution of dimethylaminomethyl quinizarin as the acetate. The colors produced were deep purple on cotton and linen and medium purple on the wool.

Example 7

A viscose rayon fabric was treated with a solution of bisdimethylaminomethyl 3,6-dihydroxy-9-phenyl xanthene as in Example 3. It retained a rose-red color, fast to washing.

Example 8

A cellulose acetate fabric was run through a 1/2% alcoholic solution of dimethylaminomethyl 3-amino-4-methyl benzeneazonaphthol, squeezed, dried, and heated one-half hour at 130° C. After washing, the color was cocoa-tan.

Example 9

Pieces of linen fabric were dipped through an aqueous solution containing 2% of dimethylaminomethyl quinizarin and 2% of acetic acid. They were treated as in Example 8. A deep blue-purple color resulted.

Example 10

A mixed cotton and mohair fabric was dipped through an aqueous solution containing 5% of the dimethylaminomethyl derivative of 3,6-dihydroxy-9-phenol xanthene and 2% of acetic acid. It was squeezed, dried, heated one-half hour at 130° C. and washed. The cotton fibres retained a deep rust shade and the mohair was lightly colored, giving an attractive effect of differential dyeing.

Example 11

A cotton sheeting was dipped through a solution containing 10% of acetic acid and about 1/2% of the product from the reaction of quinizarin with 2 mols of aqueous formaldehyde and 6

mols of aqueous monomethylamine. It was dried, heated one-half hour at 130° C., and washed. A deep purple color was retained.

In the case of various dyes which are ordinarily sulfonated to render them soluble, the process of this application may be substituted for the sulfonation. In this way the dye is obtained in a soluble form and at the same time the new method of fixing the dye may be used. However, sulfonated dyes can be used in the process.

By condensing a methylol-forming dye with formaldehyde and a non-aromatic amine having at least one hydrogen on each nitrogen atom, there is obtained a dyestuff which may be fixed to an organic textile material by the application of heat. Certain dyes not previously retained by fibres may thus be applied without the use of mordants or precipitating agents. Dyes which were heretofore retained only by one type of fibre may be used with other types as well. Only a single dye-bath is required in processing and the process of fixation of dyes herein described may be carried out with the equipment available in practically any finishing and dyeing plant. Phenolic dyestuffs which have been avoided because of sensitivity to alkaline soaps may be used in our new process of dyeing. This is particularly true of vat dyes containing phenolic hydroxyl groups. The treatment usually improves solubility and dispersion of dyes and thus increase their effectiveness in application.

We claim:

1. The process of fixing on organic textile material a phenolic dyestuff having available for substitution at least one hydrogen atom in the positions ortho and para to the aromatically-bound hydroxyl group, which comprises condensing said dyestuff with formaldehyde and a non-aromatic amine, having at least one hydrogen atom held by the nitrogen atom, to form a methylene amine condensate with the dyestuff, applying said condensate to textile material, and heating the treated textile material until the modified dyestuff is fast thereto.

2. The process of fixing on organic textile material a phenolic dyestuff having available for substitution at least one hydrogen atom in the positions ortho and para to the aromatically-bound hydroxyl group, which comprises condensing said dyestuff with formaldehyde and a non-aromatic, strongly basic, secondary amine to form a methylene amine condensate, applying the dyestuff bearing a methylene amine group to textile material, and subsequently heating the treated textile material until the modified dyestuff is fast thereto.

3. The process of fixing on organic textile material a phenolic dye having available for substitution at least one hydrogen atom in the positions ortho and para to the aromatically-bound hydroxyl group, which comprises condensing said dye with at least one mol equivalent each of formaldehyde and of a non-aromatic, strongly basic, secondary amine, applying the condensate thus formed to textile material, and subsequently heating the textile material carrying the condensate above 100° C.

4. The process of fixing on organic textile material a dyestuff, possessing a hydrogen atom in a position ortho or para to a nuclear-bound hydroxyl group, which comprises condensing said dyestuff with at least equivalent proportions each of formaldehyde and of a non-aromatic, strongly basic, secondary amine, to form a meth-

ylene amine condensate with the dyestuff, applying said condensate to textile material, and subsequently heating the treated textile material until the modified dyestuff is fast thereto.

5. The process of fixing on organic textile material a phenolic dye having available for substitution at least one hydrogen atom in the positions ortho and para to the aromatically-bound hydroxyl group, which comprises condensing said dye with at least one mol equivalent of formaldehyde and at least one mol equivalent of dimethylamine, applying the condensate thus formed to textile material and heating the treated textile material above 100° C.

6. The process of fixing on organic textile material a phenolic dye having available for substitution at least one hydrogen atom in the positions ortho and para to the aromatically-bound hydroxyl group, which comprises con-

densing said dye with at least one mol equivalent of formaldehyde and at least one mol equivalent of monomethylamine, applying the condensate thus formed to textile material and heating the treated textile material above 100° C.

7. The process of fixing on organic textile material a phenolic dye having available for substitution at least one hydrogen atom in the positions ortho and para to the aromatically-bound hydroxyl group, which comprises condensing said dye with formaldehyde and a non-aromatic, secondary amine to form a methylene amine condensate, alkylating said amine condensate to form a quaternary ammonium salt, applying said salt to dye said textile material, and heating the dyed textile material until the modified dyestuff is fast thereto.

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