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METHYLATED METHYLOLMELAMINE AS A FIXING AGENT FOR DYED COTTON TEXTILES

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1 Claim. (Cl. 8—74)

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This invention relates to the fixation of dyestuffs on textiles.

One of the major problems of the dyer is the fastness of dyes and particularly with respect to washing. Many attempts have been made to render colors sufficiently fast to withstand hot soaping, especially in the presence of small amounts of alkali under conditions normally encountered in commercial laundries. This is particularly true in the case of direct azo dyestuffs for cotton which generally exhibit relatively poor fastness to washing. Many procedures described in the art yield dyeings which are fast to hot water but not to hot soaping. In other cases, generally involving the use of condensation products of formaldehyde with such amidic substances as urea, dicyandiamide and melamine, dyeings of good fastness are produced. Certain processes (see for example U. S. Patents 2,169,546 and 2,195,357) employ condensation products of formaldehyde with aminotriazines and appear to give partially satisfactory results on dye fixation, but under conditions leading to good dye fixation these treatments seriously weaken or embrittle textile materials and often alter the shade of the color. Since washfastness is generally poorest in the case of cotton and other cellulosic materials which are most easily damaged, such processes leave much to be desired.

This invention has as an object the production of dyeings of the maximum possible fastness to washing and other wet treatments with a minimum of deleterious effects on the fabric. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein the wash fastness of a dyed textile or flexible organic sheet material is improved by treatment with a monomeric nitrogen-containing compound having at least two nitrogen atoms each of which is attached to a methylene (—CH_2—) group which is in turn linked through an ether oxygen to a monovalent hydrocarbon radical.

The preferred materials of the above general classification are monomeric organic compounds, otherwise free from reactive groups, containing a plurality of amidic nitrogens having thereon etherified methylol groups. By amidic nitrogen is meant the nitrogen atom in amides including

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carbonamides, oxoamides, thioamides, iminoamides (amidines) and sulfonamides.

The preferred methods of practicing this invention involve treating a dyed material with a monomeric di- or poly-N-alkoxymethyl compound in the following manner:

The dyed material is wetted with a solution containing the poly(N-alkoxymethyl) compound and is subsequently dried and subjected to an elevated temperature for a time sufficient to cause fixation of the dyestuff. More specifically it is preferred to wet the material with approximately an equal weight of a treating solution which possesses a pH of 3–6.5 and contains 1–20% of the poly(N-alkoxymethyl) compound. After evaporation of the solvent to deposit the impregnant on and within the fibers, the dye is affixed by heating for a short time at 100–170° C. The material is then removed from the oven, rinsed in water and dried. An alternative procedure which is also very effective involves heating dyed cloth in a solution containing from 1–10% of the active agent based on the weight of the cloth employed and in the presence of a mild acidic catalyst, e. g., at a pH below 6.5 and preferably above 3.

The more detailed practice of the invention is illustrated in the following examples, wherein parts given are by weight. There are, of course, many forms of the invention other than these specific embodiments.

EXAMPLE I

This example illustrates the fixation of several representative azo dyestuffs which are thereby rendered fast to hot soap solutions.

A 20% aqueous solution of N,N'-bis(methoxymethyl) adipamide (made by the procedure described in copending application of McGrew, Serial No. 360,835, filed October 11, 1940, now U. S. Patent 2,364,737) was prepared by dissolving 20 parts of the agent in 80 parts of water. There were then wetted in the solution samples of cotton fabric previously dyed in the usual manner with the following representative azo dyestuffs.

1. Pontamine Blue BB (Color Index No. 406).

2. A red azo dyestuff prepared by tetrazotizing the 1-(p-aminobenzoyl) derivative of 2-methyl-

p-phenylenediamine and coupling to two moles of m-aminobenzoyl-J-acid.

3. A yellow azo dyestuff prepared by tetrazotizing N,N'-bis(p-aminobenzoyl)-2-sulfo-p-phenylenediamine and coupling to two molecules of m-aminophenylmethylpyrazolone.

4. A scarlet azo dyestuff prepared by tetrazotizing 1,3-di(p-aminophenoxy) propane and coupling to two equivalents of m-aminobenzoyl-J-acid and subsequently tetrazotizing the resulting product and coupling to two molecules of resorcinol.

After impregnation the materials were wrung until the gain in weight was approximately 100% and were then heated for 10 minutes at 125° C. After rinsing, the fastness of the dyeings to washing was ascertained by boiling for 30 minutes in an 0.5% tallow soap solution containing 0.2% sodium carbonate. In every case the treated dyeings were found to be considerably superior to controls, bleeding but slightly and producing no stain on an attached piece of silk. A similar treatment of the same dyeings with an adipamide-formaldehyde condensation product (dimethylol-adipamide) increased the fastness somewhat but the results were in no way comparable with those obtained using the ether, for the dyeings were not rendered sufficiently fast and serious changes in shade and spotting were observed. The results are summarized in the following table.

TABLE I

Effect of agents on fastness of dyeings to boil wash test

	Dyestuff			
	1	2	3	4
(*a*) None (control)	D	D	D	D
(*b*) Dimethyloladipamide	C	C	C+	C+
(*c*) N,N'-bis(methoxymethyl) adipamide	A	B+	A+	A

A=excellent, B=good, C=fair, D=poor (control).

EXAMPLE II

Viscose rayon yarn which had been rendered basic, e. g., by incorporation of a protein or albuminous material, was dyed in the usual manner with the acid dyestuff 1-amino-4 (p-toluidino)-anthraquinonedisulfonic acid and the fastness improved as follows: After dyeing, the skeins were steeped in a 10% solution of N,N'-bis(methoxymethyl) urea (Kadowaki, Bull. Chem. Soc. Japan 11, 248 (1936)) containing 1% ammonium chloride as catalyst and sufficient acetic acid to neutralize the effect of the basifying agent. The yarns were subsequently centrifuged, squeezed, dried at the ordinary temperature and finally baked 5 minutes at 160° C. The dyeings thus produced were fast to treatment with hot soap solution whereas untreated dyeings were markedly inferior in fastness.

Similar treatment of this dyed viscose yarn with a 10% aqueous solution of N,N'-bis(methoxymethyl)adipamide containing 4% acetic acid yielded dyeings likewise fast to hot soaping whereas untreated material was markedly inferior in fastness to hot soaping.

EXAMPLE III

This example illustrates the use of alkoxymethyl derivatives of other amides. The alkoxymethylamides were prepared as described in copending application Serial No. 360,835.

Samples of bleached cotton muslin dyed in the usual manner with a blue azo dye (Color Index No. 406) were impregnated with 5% aqueous solutions of the following reagents:

1. N,N'-bis(methoxymethyl) succinamide.
2. N,N'-bis(methoxymethyl) fumaramide.
3. N,N'-bis(methoxymethyl) sebacamide.

The solutions were then acidified with sufficient amount of acetic acid to produce a pH of 2.5. After impregnation, the samples were wrung out until the gain in weight was approximately 100%, dried at the ordinary temperature and ironed for 30 seconds. The dyeings thus produced possessed excellent fastness to boiling soap solution, the bleeding and loss of color being negligible whereas untreated controls were very poor in both respects.

EXAMPLE IV

This example illustrates the use of the polyalkoxymethyl derivative of a cyclic amidine.

Four samples of cotton fabric dyed with a blue dye (Color Index No. 406) were impregnated in 5% aqueous solutions of N,N',N''-tris(methoxymethyl) melamine, prepared by the procedure described in McGrew copending application Serial No. 387,771, filed April 9, 1941, adjusted to a pH of 3.7–3.9 and wrung to 100% gain in weight. After drying at the ordinary temperature these four samples were heated in an oven for, respectively, (*a*) four minutes at 105° C., (*b*) 30 seconds at 130° C., (*c*) 10 seconds at 165° C., and (*d*) 20 seconds at 165° C. After rinsing in cold water these samples were all found to be substantially unaffected by boiling in 0.5% soap solution containing 0.2% added sodium carbonate. Similar treatments conducted at pH 4.4–4.5 produced essentially the same results. The untreated fabric has very poor fastness.

The superiority of the tris(methoxymethyl)-melamine over the melamine-formaldehyde condensation products may be seen in the following table which shows the effect on tensile strength of treatment at various temperatures for a time sufficient to obtain substantially the same excellent fixation of the color.

TABLE II

	Agent	pH of solution	Treatment	Per cent loss tensile strength
1	N,N',N''-tris(methoxymethyl) melamine.	4.3	105° C./4 min.	9.4
	do	4.4	130° C./30 secs.	7.4
	do	4.4	165° C./10 secs.	None
	do	4.4	165° C./20 secs.	6.2
	do	3.9	165° C./10 secs.	6.0
2	Trimethylol melamine	5.2	100° C./4 min.	23.0
	do	5.2	120° C./5 min.	23.2
3	Dimethylol melamine	4.5	120° C./4 min.	18.3

EXAMPLE V

This example illustrates the use of an ethyl ether.

The compound N,N',N''-tris(ethoxymethyl)-melamine was prepared from trimethylol melamine according to the procedure of copending application Serial No. 387,771. A 5% solution of this reagent in 1:1 ethanol-water was then divided into 3 portions to which were added, respectively, sufficient glacial acetic acid to produce pH's of 3 and 4, and sufficient sodium acetate to produce a pH of 8.4. Samples of bleached cotton muslin dyed in the usual manner with a blue dye (Color Index No. 406) were then wetted in each of these solutions until the gain in weight

was approximately 100%, passed through a nip and dried at the ordinary temperature. These dried samples were then held in an ironing machine for 30 seconds, rinsed, dried and tested by immersing in boiling soap solution for 30 minutes. The following results were obtained.

TABLE III

Wash fastness to dyeings of Pontamine Blue BB aftertreated with N,N',N''-tris(ethoxymethyl)-melamine

Control (no agent)	Treatment with agent at—		
	pH 3	pH 4	pH 8.4
D	A+	A+	A

Ratings: A=excellent, B=good, C=fair, D=poor.

In contrast with the excellent results obtained with the monomeric N,N',N''-tris(ethoxymethyl)-melamine, unsatisfactory results were obtained with the syrupy material obtained by condensing melamine, and formaldehyde in absolute ethanol at elevated temperatures with hydrochloric acid as a catalyst. This condensation product was insoluble in water. In alcohol or dimethylformamide solutions (10%) either neutral or acidified with acetic acid up to 10% these syrupy materials gave stiff boardy fabrics, color spotting and shade change. When treated with 4% solutions the fabrics were somewhat boardy, had a stiff feel, and the color had changed and was in addition spotty. The fixation of the dye was only fair.

The monomeric ethers of trimethylolmelamine are prepared by stirring trimethylolmelamine in anhydrous liquid medium with 2 to 5 parts of a monohydric alcohol, preferably of not more than four carbons, e. g., methanol or ethanol, at a temperature of not more than 50° C. and preferably at 0° C. to 25° C., in the presence of an anhydrous acid condensing agent, until the suspended trimethylolmelamine disappears, neutralizing with the sodium alcoholate of the alcohol used, filtering off the sodium salt of the condensing agent and isolating the ether from the filtrate.

EXAMPLE VI

This example illustrates the use of N-alkoxymethyl derivatives of cyclic compounds containing the substituted nitrogen atoms in the ring.

Six samples of cotton cloth dyed in the usual manner with the blue dye (Color Index No. 406) were impregnated with the following six solutions which with the exception of 3 had acidities in the pH range 3.5 to 4:

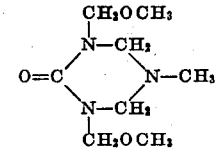
1. An aqueous solution containing 10 parts by weight of N,N'-bis(methoxymethyl)uron (Bull. Soc. Chem. Japan 11, 248 (1936)), 90 parts of water and 5 parts of glacial acetic acid.

2. A similar solution containing 2 parts of glacial acetic acid.

3. A similar solution buffered at ph 5.5 by use of acetic acid and potassium acetate.

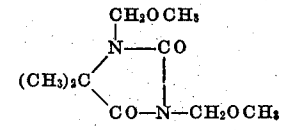
4. An aqueous solution containing 10 parts N,N'-bis(methoxymethyl)ethyleneurea (prepared by applying the procedure described in application Serial No. 426,905, filed January 15, 1942, to cause the reaction of dimethylolethyleneurea with methanol), 90 parts of water and 2 parts of glacial acetic acid.

5. An aqueous solution containing 10 parts by weight of 1,3-bis(methoxymethyl)-5-methyl-s-triazone(2)



90 parts water and 2 parts of glacial acetic acid (prepared by the procedure described in application Serial No. 426,905, filed January 15, 1942).

6. An aqueous solution containing 10 parts of N,N'-bis(methoxymethyl)-5,5-dimethylhydantoin



prepared by similar reaction of 5,5-dimethylhydantoin with formaldehyde and then with dry methanol in the presence of dry hydrogen chloride.

The samples were then passed through a nip until the gain in weight was approximately 100% and were finally baked in an oven at 125° C. for 5 minutes. Dyeings thus produced were all found to be considerably improved in fastness to boiling 0.5% soap solution.

EXAMPLE VII

This example illustrates fixation of dyestuff with an N-alkoxymethyl derivative in aqueous solution.

Two hundred and fifty parts of a 20% sodium chloride solution was acidified with 1 part of formic acid. The resulting solution was divided into two equal parts which were heated to 80 and 100° C., respectively, when there was added to each 10 cc. of a 5% aqueous solution of N,N',N''-tris(methoxymethyl)melamine. A portion of bleached cotton muslin (15 parts by weight) dyed in the usual manner with a blue dye (Color Index No. 406) was then placed in each solution and the solutions maintained at 80 and 100° C., respectively, for 15 minutes, when the cloth was removed and dried. The dyeings thus obtained possessed good fastness to boiling soap solution whereas untreated controls had poor fastness. Analogous treatments with melamineformaldehyde condensation products had virtually no effect on the fastness of the dyeing, for resin precipitated.

EXAMPLE VIII

In this example a number of typical cotton dyestuffs are affixed to the fabric with N,N',N''-tris(methoxymethyl)melamine.

Samples of bleached cotton muslin were dyed in the usual manner with the following colors:

1. The blue azo dyestuff prepared by tetrazotizing dianisidine and coupling to 2 equivalents of 1-amino-8-naphthol-2,4-disulfonic acid and subsequently coppering.

2. The red azo dyestuff prepared by coupling 2 mols of diazotized p-phenylenediamine to 2,2'-imino-bis(5-naphthol-7-sulfonic acid), (di-J-acid).

3. The orange azo dyestuff prepared by coupling tetrazotized 3,3'-diaminoazoxybenzene to 2 mols of 2-amino-5-naphthol-7-sulfonic acid.

4. The red azo dyestuff prepared by coupling diazotized m-aminobenzoyl-p-toluylenediamine to 2 mols of N-(m-aminobenzoyl)-2-amino-5-naphthol-7-sulfonic acid.

5. The green-blue sulfonated copper phthalo-

cyanine color containing 2 sulfonic acid groups for each phthalocyanine nucleus.

The dyed fabrics were then impregnated in a 10% aqueous solution of N,N',N''-tris(methoxymethyl) melamine containing sufficient acetic acid to produce a pH of 4.4. After impregnation the materials were wrung until the gain in weight was approximately 100% and were dried in a current of air. The dyed fabrics were baked in an oven at 164° C. for 1 minute and the fastness to washing ascertained in the usual manner in boiling 0.5% tallow soap solution containing 0.2% of sodium carbonate. In every case the treated dyes were found to be considerably superior to controls, bleeding but slightly. A similar treatment of the same dyeings with a 5% solution of this reagent at a pH of 4.4 produced essentially the same result.

EXAMPLE IX

This example illustrates the fixation of dyestuffs to rayon.

Viscose rayon fabric was dyed in the standard manner with the following colors:

1. The blue azo dyestuff prepared by coupling diazotized p-phenylenediamine to 1-naphthylamine-6-sulfonic acid, diazotizing and coupling to 2-amino-7-naphthol-3-sulfonic acid and finally diazotizing and coupling to 1-naphthylamine-6-sulfonic acid.

2. The scarlet azo dyestuff prepared by coupling aniline and p-aminoacetanilide to N,N'-2(5-hydroxy-7-sulfonaphthyl) urea (urea-J-acid).

The dyed rayon samples were wetted in the usual manner in 5 and 10% solutions respectively of N,N',N''-tris(methoxymethyl) melamine containing sufficient acetic acid to produce a pH of 4.3. After air drying and baking in an oven at 165° C. for 1 minute dyeings were produced which were substantially unaffected by boiling soap solution.

The treated examples are markedly superior in fastness to untreated controls.

EXAMPLE X

This example illustrates the fixation of two representative colors on cellulose acetate.

Samples of cellulose acetate fabric were dyed by orthodox procedures with the following colors:

1. The yellow azo dyestuff prepared by coupling p-aminoacetanilide to p-cresol.

2. The orange azo dyestuff prepared by coupling diazotized p-nitroaniline to aniline.

The dyed fabric was impregnated as usual with a 10% solution of N,N',N''-tris(methoxymethyl) melamine, acidified with acetic acid to pH of 4.4 air dried and subsequently baked for 1 minute at 165° C. In this manner the fastness of the dyes to hot or boiling soap solutions was markedly improved.

On dyeing nylon (a synthetic fiber-forming polyamide) with the same colors and subsequently treating as described above, dyeings were obtained which exhibited considerably greater fastness to boiling soap solution than the untreated controls.

Example XI

This example illustrates the fixation of dyestuffs on wool and leather.

Samples of woven wool and of leather were dyed in the customary manner with the following colors:

1. The violet azo dyestuff prepared by coupling diazotized p-phenylenediamine to 1,8-dihydroxynaphthalene-3,6-disulfonic acid.

2. The azo dyestuff prepared by tetrazotizing benzidine and coupling to 1 mol of 2-naphthylamine-3,6-disulfonic acid and 1 mol of phenol (p-toluene sulfonated). The wool and leather samples were then wetted in both 5 and 10% solutions of N,N',N''-tris(methoxymethyl) melamine acidified with acetic acid to a pH of 4.2. After wringing to 100% gain in weight and drying in a current of air, the samples were placed in an oven at 165° C. for 1 minute to insolubilize the color. The woolen dyeings thus produced were very markedly improved and were substantially unaffected by boiling soap solution. In the case of leather the samples were slightly stiffened but the dyeings were markedly improved in fastness.

The present invention is generic to the use in the fixation of dyestuffs to organic textile materials and flexible organic sheet materials of monomeric ethers of poly-(N-methylol) compounds. These are compounds having at least two nitrogen atoms, each of which is in turn attached to a methylene group which is in turn attached through an ether oxygen to a monovalent hydrocarbon radical.

A preferred class are monomeric organic compounds, otherwise free from reactive groups, containing a plurality of amidic nitrogens having thereon etherified methylol groups. By amidic nitrogen is meant the nitrogen atom in carbonamides, oxoamides, thioamides, amidines, guanidines, cyclic amides, cyclic amidines, cyclic ureas, sulfonamides, phosphonamides, etc.

Because of the favorable results obtained the preferred specific classes of monomeric ethers of poly-(N-methylol) amidic substances are the monomeric ethers of poly-(N-methylol) amides, including amidines and thioamides, of polybasic organic acids otherwise free from reactive groups. The etherified poly-(N-methylol) carbonic acid amides, i. e., amides of carbonic acid such as melamine, urea, and substituted ureas, are particularly preferred.

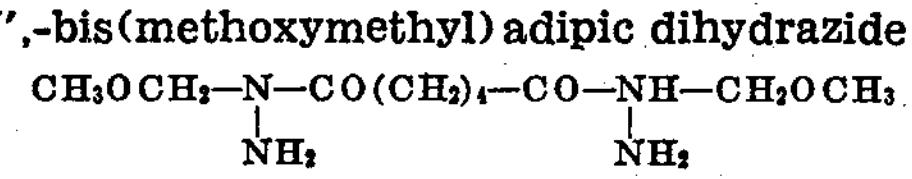
Because of the ease of preparation it is preferred to use monomeric poly-(N-methylol) compounds etherified with an alkanol of from 1–5 carbon atoms and having at least one hydrogen on the carbinol atom. The N-methoxy-methyl compounds of amides are particularly preferred.

Illustrative poly-(N-methylol) ethers in addition to those employed in the examples are:

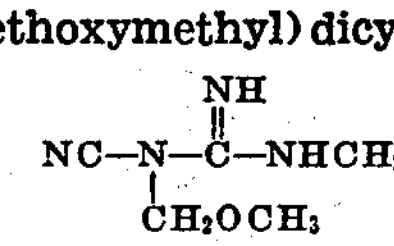
N,N'-bis(phenoxymethyl) adipamide
N,N'-bis(alpha-naphthoxymethyl) urea
N,N',N''-tris(cyclohexyloxymethyl) melamine
N.N,N''-tris(allyloxymethyl) melamine
N N'-bis(butoxymethyl) adipamide
N,N',N''-tris(methoxymethyl) tricarballylamide
N.N'-bis(isopropoxymethyl) urea
N,N',N'',N''' - tetrakis(methoxymethyl) methylenediurea
N,N'-bis(methoxymethyl) biuret

$CH_3OCH_2NHCONHCONHCH_2OCH_3$

N,N',-bis(methoxymethyl) adipic dihydrazide

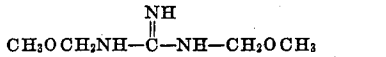


N,N'-bis(methoxymethyl) dicyandiamide

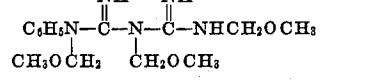


N,N'-bis(benzyloxymethyl) urea
N,N'-bis(methoxymethyl) terephthalamide

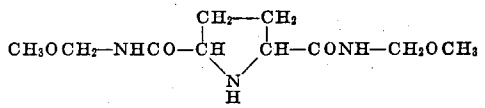
N,N'-bis(methoxymethyl) hydantoin
N,N'-bis(ethoxymethyl) thiourea
N,N'-bis(methoxymethyl) adipohydroxamic acid
N,N'-bis(methoxymethyl) guanidine



N,N',N''-tris(methoxymethyl) phenylbiguanide



N,N'-bis(methoxymethyl) diketopiperazine
N,N',N''-tris(methoxymethyl) cyanuric acid
N,N'-bis(ethoxymethyl) uracil
N,N' - bis(methoxymethyl) pyrrolidinedicarbonamide



N,N'-bis(methoxymethyl) dithiooxamide

The useful compounds of this invention possess the properties of homogeneity, and constancy of composition and molecular weight. When solid, they are generally crystalline materials of definite molecular weight or distillable liquids. They differ from the resinous or syrupy materials, indefinite in chemical composition and physical properties, frequently described in the art as being obtainable by heating in alcohol the condensation products of aldehydes with amidic substances. The products employed in the process of this invention are highly reactive materials which are harmed by such treatment. They are best prepared by reaction of a dry methylol compound with an absolute alcohol in the presence of a dry acidic catalyst at low or moderate temperatures.

A further advantage of the ethers of poly-(N-methylol) compounds over the resinous materials described in the art and over the methylol compounds themselves is the surprising fact that the desired dye fixation reaction is much more readily controlled and superior effects obtained. Fundamentally, two reactions may be visualized, a dye fixation reaction and resinification, the latter a disadvantageous side reaction which competes with the dye fixation for active groups. Dye fixation proceds much more smoothly with less attendant side reactions with etherified N-methylol compounds than with the methylol compounds themselves or the resinous condensation products, both of which either by resinification or by being already resinous give rise to other undesirable effects. Furthermore, the monomeric ethers possess a greater number of active groups per unit weight than the resinous materials, since none of the potentially active substituents are dissipated in formation of the condensation product prior to dye fixation.

The present invention is generic to the fixation, by ethers of poly-(N-alkylol) compounds, of soluble dyestuffs, including soluble derivatives of insoluble dyestuffs and dyestuff intermediates. Dyestuffs intermediate products may also be affixed. In this manner, materials normally possessing little or no affinity for the dyeing agent may be colored by the process of this invention. Suitable dyestuffs whose fastness to wet treatments is improved by this treatment include dyestuffs in all groups, such as, acid dyestuffs, direct dyestuffs, basic dyestuffs, pigment dyestuffs, sulfur or vat dyestuffs. These dyestuffs may belong

to the azo, anthraquinone, indigo, or thioindigo, azine or oxazine, azothine, nitro, stilbene, or triphenyl methane series. The treatment of direct dyes is of particular importance because of the generally poor fastness of these dyes as a class.

If it is desired, instead of the finished dyestuff, intermediate products in solubilized form (including true or colloidal solutions) may be fixed on the fiber. Among such dyestuff intermediate products are materials which may be converted into dyestuffs by known reactions. These materials are coupling components, diazotization components, compounds which form colors by condensation reactions, etc. While it is possible to improve the washfastness of any dyestuff soluble or dispersible in aqueous solutions by treatment with ethers of poly-(N-alkylol) compounds, it is preferred that the dyestuff or intermediate contain active groups such as OH SH, NH_2, NHR, CONH, CONHR, SO_2NH_2, SO_2NHR or active positions, e. g., nuclear hydrogens activated by OH, OCH_3, NH_2, NHR, NR_2, etc., or methylene groups rendered active by being adjacent to a negative substituent such as carbonyl, sulfonyl, or nitro groups.

The invention embraces the fixation of the dyestuff to any organic textile material or flexible organic sheet material. There may be employed textiles in any form including single filaments, yarns or fabrics and textiles from either staple or continuous fibers. Suitable textile materials and natural fibrous materials include wood pulp, cotton, linen, ramie, hemp, jute, wool, silk, and hair and synthetic organic fibers such as are derived from superpolyamides, vinyl polymers, casein, zein, soya protein, cellulose ethers, cellulose esters, e. g., cellulose acetate, and cellulose. Regenerated cellulose rayons produced by any process, e. g., viscose, cuprammonium, etc. are included.

The process is not limited to any particular method of impregnation or treatment. Thus, the textile may be wetted with a solution of the agent and the dyestuff fixed by subsequent heating. In addition, it is generally possible to conduct the impregnation and fixation as a simultaneous operation by heating the textile in a solution of the reagent. In some cases it is possible to treat the textiles with a melt of the poly-(N-alkoxymethyl) compound containing no solvent. However, it is generally most convenient and preferred to use a solution of the impregnating agent, conducting the finishing treatment at the same time or in a later operation. The most effective solvents comprise water, alkanols of from 1-4 carbon atoms and their ether substituted derivatives. Where cellulosic materials are treated, water is an especially preferred solvent since its capacity for swelling cellulose probably facilitates introduction of the N-alkoxymethyl compound into the cellulose fiber.

The concentration of the impregnant in the treating solution may vary widely. As may be seen from the examples, it is possible to achieve useful effects by employing solutions whose concentration of N-alkoxymethyl compound is 1% or less. Conversely, the upper limit of concentration which may be employed is determined solely by the solubility of the agent in the medium. In general, it is preferred to use treating solutions containing from 1 to 20% by weight of the impregnant.

Although it is generally most convenient to carry out the impregnation at the ordinary temperatures, the operation may be performed at any

temperature between the freezing point and boiling point of the impregnating solution. It is not necessary to prolong the impregnation step greatly. In fact, it is usually sufficient to merely wet the textile material with the impregnating solution. With materials which are difficultly wetted, e. g., non-cellulosic textiles, it may be desirable to use a relatively high temperature of impregnation and to prolong the process somewhat to facilitate swelling of the fibers and the diffusion of the modifying agents into them. Added substances such as wetting, softening and swelling agents may, of course, be used to obtain this effect.

Although the process of this invention may be carried out under acidic neutral or basic conditions, e. g., a pH of 2–9, it is generally preferable to operate in the presence of an acidic material. A wide variety of substances producing a pH in the range from 2 to 6.5 are particularly effective. If the pH is too low, e. g., below 2, damage to the textile may ensue, especially if the latter is of cellulosic nature. For best results with regard to rate of reaction and subsequent condition of the textile, it is preferred to operate in a pH range between 3 and 6.5. The acidic catalyst need not be present in the impregnating solution but may be introduced separately, for example by (1) impregnating the textile with acid before employing the poly-(N-alkoxymethyl) compound, (2) introducing the acidic material from a second bath subsequent to the application of the impregnant, (3) introducing the acid in the anhydrous form as by exposing the textile to acidic vapors. It is also possible to employ catalysts which are not actively acidic but are potentially so, for example, operable catalysts include nearly neutral ammonium salts such as ammonium chloride and ammonium acetate which become acidic at the higher temperatures encountered during the dye fixation.

The fixation of various types of dyestuffs with poly-(N-alkoxymethyl) compounds usually occurs at temperatures above 40 C., the exact rate being determined by the particular substance employed and to a large extent by the pH of the material. Thus, at pH's as low as 3 to 4 the dye fixation reaction occurs with practicable rapidity at temperatures between 40 and 100° C. At less acidic pH's, e. g., 5 to 6.5, it is usually desirable to use temperatures above 100° C. preferably from 100–165° C. Naturally the highest temperature which may be used is that just below which the textile itself suffers damage by heat. This temperature varies with the nature of the fiber, for example from about 180° C. for cellulose ester fibers to about 230° C. for superpolyamide fibers. At the temperature usually employed, e. g., 100–150° C., durations of from 10 seconds to 5 minutes are usually sufficient for the heat treatment, although longer periods may be employed. In general, more prolonged treatments are desirable or necessary only when the fixation is carried out at temperatures below 100° C. For example, when the dye fixation is conducted entirely in solution at 80–100° C. it is usually necessary to heat for 3 to 20 minutes.

The utility of this invention lies in the production of colored textile materials possessing superior fastness to wet treatments which are therefore useful in a wide variety of applications, e. g., in garments where such properties are very desirable.

The treatment of textiles per se with monomeric ethers of polymethylolcarbonamido compounds forms the subject matter of copending McGrew application Serial No. 410,484, filed September 11, 1941.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claim.

What is claimed is:

Process for increasing the wash fastness of a dyed cotton textile material which comprises heating the dyed material with monomeric N,N',N''-tris(methoxymethyl) melamine, said cotton textile material being dyed with blue dye Colour Index No. 406.

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