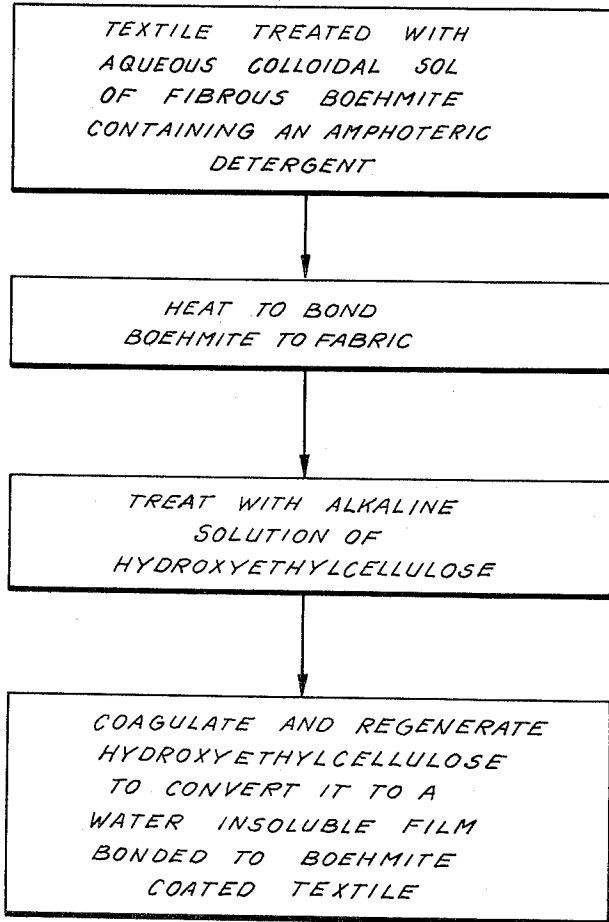


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J. PAUL

3,240,553

PROCESS OF CONDITIONING YARN AND FABRIC MATERIALS TO RENDER THEM
RECEPTIVE TO DYES HAVING AFFINITY FOR CELLULOSIC MATERIALS AND
SUCH CONDITIONED YARN AND FABRIC MATERIALS
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3,240,553

PROCESS OF CONDITIONING YARN AND FABRIC MATERIALS TO RENDER THEM RECEPTIVE TO DYES HAVING AFFINITY FOR CELLULOSIC MATERIALS AND SUCH CONDITIONED YARN AND FABRIC MATERIALS

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9 Claims. (Cl. 8—100)

This invention relates to processes of dyeing and/or printing of textile materials such as yarns and fabrics and, more particularly, to the pretreatment of such materials to condition them so that they readily and uniformly receive dyes, especially dyes for which they normally have little substantivity and/or affinity.

In this specification all percentage values are on a weight basis.

Textile materials such as yarns and fabrics which are normally difficult to dye when composed of one type of fiber and are even more difficult to dye when two or more different fibers are intimately blended to produce a mixed or blended yarn or fabric can be dyed or printed by the process of this invention to produce pleasing effects, including uniformly colored yarns and fabrics.

As is well known, fibers of different chemical compositions require different dyeing and/or printing techniques and in many cases cannot be colored by the same dyestuff and hence require chemically different dyestuffs. This requirement seriously complicates the dyeing and/or printing of blended yarns and fabrics. In many cases it is impossible to attain an identical hue on the fibers of different chemical compositions because the dyestuffs which are suitable for the coloration of one of the fibers will not produce a like hue on the other fiber or fibers in the blended yarn or fabric. One example of this problem is presented by the coloration of mixtures of cotton and cellulose acetate fibers. Any attempt to color such a mixture a bright turquoise shade by heretofore known techniques will result in failure because the acetate portion of the yarn or fabric will always be duller than the cotton. There are no bright turquoise dyestuffs in the dispersed dyestuff range which have to be used to color the cellulose acetate and hence it is not feasible with presently available techniques to produce bright uniform turquoise shades on blends of cotton and cellulose acetate. The difficulty of uniformly coloring such blends is also compounded by the further difficulty of obtaining equal fastness properties with the two ranges of dyestuffs which must be used. The fastness properties of the dyestuffs on each fiber can differ widely with respect to resistance to exposure to light, water, solvents and other such influences. Each fiber can also require a different method for the final fixation of the dyestuff, hence the processing of yarns and fabrics composed of blends of fibers by heretofore known techniques is invariably much more complex than it is for yarns and fabrics composed of fibers all of the same chemical composition.

One method which has been proposed as a solution for these difficulties is the coloration of such fabrics and yarns by applying thereto either an oil-in-water or water-in-oil pigmented emulsions. While this method does produce uniformly colored yarns and fabrics it leaves much

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to be desired. The resulting yarn or fabric is usually stiffened considerably and if the blended yarn or fabric has a high proportion of synthetic fibers it usually has poor fastness to dry cleaning, solvent spotting and rubbing. The range of hues producible by such pigmented printing and dyeing techniques also leaves much to be desired and bright hues, as a general rule, cannot be produced by presently available pigmented emulsions.

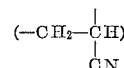
Among the textile materials which can be treated by the process of this invention are fabrics and yarns manufactured wholly or in mixtures with others of—

- (A) Cellulosic Fibers:
 - (1) Cotton
 - (2) Rayon
- (B) Cellulose Diacetate:
 - (1) Celanese
- (C) Cellulose Triacetate:
 - (1) Arnel
 - (2) Tricel
- (D) Polyamide:
 - (1) Nylon
 - (2) Perlon
 - (3) Rislán
- (E) Polyester:
 - (1) Dacron (ethylene glycol-terephthalic acid condensation polymer)
 - (2) Fortrel
 - (3) Terylene
 - (4) Kodel
 - (5) Tergal
 - (6) Diolen
 - (7) Vycron

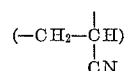
The fibers Fortrel, Terylene, Kodel, Tergal, Doilen and Vycron are long chain synthetic polymers composed of at least 85% by weight of an ester of a dihydric alcohol and terephthalic acid.

- (F) Acrylic:
 - (1) Acrilan
 - (2) Creslan
 - (3) Dynel
 - (4) Orlon
 - (5) Verel
 - (6) Zefran

The fibers Acrilan, Creslan, Orlon and Zefran are long chain synthetic polymers composed of at least 85% by weight of acrylonitrile units



The fibers Dynel and Verel are known in the art as modacrylic, which are long chain synthetic polymers composed of less than 85% but at least 35% by weight of acrylonitrile units



- (G) Olefins:
 - (1) Polypropylene
- (H) Nitril:
 - (1) Darvan

The nitril fibers including Darvan contain at least 85% of a long chain polymer of vinylidene dinitrile ($-\text{CH}_2-\text{C}(\text{CN})_2-$) where the vinylidene dinitrile content is no less than every other unit in the polymer chain.

(I) Mineral:

(1) Glass

While the present invention finds its major use in dyeing and/or printing the more difficultly dyeable fibers, B to I inclusive and blends thereof with or without the cellulosic fibers of A above, it can be used to treat fabrics consisting wholly of cellulosic fibers producing novel attractive colorations.

It is a principal object of this invention to provide a process for conditioning the surface of yarns and fabrics composed of the fibers hereinabove disclosed so that they can be uniformly and readily dyed and/or printed to produce pleasing effects including bright hues heretofore not obtainable.

It is another object of this invention to provide such process in which one and the same dyebath or print paste can be used notwithstanding the fabric or yarn contains blends of two or more different fibers.

Still another object of this invention is to provide such process which permits dyeing and/or printing of the conditioned yarns and fabrics without requiring the use of special processing techniques, carriers, or high temperatures but enables the dyeing or printing to be accomplished with readily available dyestuffs, particularly readily available dyes for cellulosic materials, in accordance with the customary procedures for applying such dyestuffs.

A further object of this invention is to provide such process which enables the dyeing or printing of the conditioned yarns and fabrics with greater uniformity and brilliance than has heretofore been obtainable and permits the yarns or fabrics to be colored with dyestuffs for which they normally have little or no affinity.

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

In accordance with this invention the material to be colored, whether by dyeing or printing, is treated before dyeing or printing with an aqueous colloidal sol of fibrous alumina monohydrate having the boehmite crystal lattice and which is hereinafter referred to as fibrous boehmite. The properties and manner of producing fibrous boehmite is disclosed in U.S. Patent 2,915,475 granted December 1, 1959, and this product is sold by E. I. Du Pont de Nemours and Company, assignee of this patent under its trademark "Baymal" which is identified as a colloidal alumina, the surface of the fibrils of which are modified by adsorbed acetate ions or other acid radicals which is generally associated with an aluminum ion or a basic aluminum ion. The dispersible boehmite powder, for example, can contain about 70% Al_2O_3 and about 10% acetate radical (expressed as acetic acid). It can be made by heating an aqueous dispersion of alumina in the presence of an acid radical under the conditions disclosed in said patent, 2,915,475.

The fibrous boehmite sol produced by the addition of the dry product to water has a pH of about 4 and the particle charge in the sol is positive. The average fibril length is from 25 to 1,500 millimicrons and the ratio of the length of the fibrils to their width is at least about 20 to 1.

The fibrous boehmite sol applied contains a surface active agent, the alkali metal salt of a C_{10} to C_{18} aliphatic imidazoline carboxylic acid which conditions the boehmite so that it is compatible with the hydroxyethylcellulose subsequently applied. The coating of sol thus applied is cured to bond the fibrous boehmite to the fibers. The thus treated textile materials are then coated with an aqueous alkali solution of hydroxyethylcellulose and the coating thus produced coagulated to form a water-insoluble hydroxyethylcellulose firmly bonded to the alu-

mina coated fibers, which water-insoluble hydroxyethylcellulose has surprisingly good substantivity and/or affinity for readily available dyestuffs such as the reactive dyes, vat dyes, azoic dyes, naphthol shades, chrome dyes, direct dyes and sulfur dyes, applied by conventional dyeing techniques. Textile blends containing fibers of markedly different dye characteristics when treated by the process of this invention are dyed or printed with uniform coloration in bright colors, and the colorations possess good fastness properties to light, heat, water, solvents, abrasion, etc.

The preliminary deposition of fibrous boehmite sol containing the mentioned surface active agent greatly and surprisingly improves the bond or adhesion between the hydroxyethylcellulose and the fibers. This improvement in the bond or adhesion is responsible for the high resistance to abrasion of the dyed textile.

The coagulated and regenerated hydroxyethylcellulose provides a cellulosic surface over the yarn or fabric which is receptive of dyes used in dyeing or printing cellulosic materials. The hydroxyethylcellulose used is produced by reacting alkali cellulose with ethylene oxide so that from 2% to 10% advantageously from about 2% to about 5% of ethylene oxide is actually combined with the alkali cellulose as disclosed more fully in U.S. Patent 2,847,411 granted August 12, 1958. The preferred hydroxyethylcellulose is that sold commercially under the trademark "Ethylose" which has an ethylene oxide content of about 4.0% and has the hydroxy groups evenly distributed along the cellulose chain and evenly substituted with ethyl substituents, the degree of substitution being about 0.15. Films produced as herein described are remarkably resistant to swelling in water, have good affinity for dyestuffs and result in colored products which are fast to washing, sun, abrasion, and dry cleaning.

APPLICATION OF FIBROUS BOEHMITE

The concentration of fibrous boehmite in the sol applied to the textile material can be from 1% to 10%. A preferred concentration is about 4%. As noted, sols of the fibrous boehmite are normally acidic in nature exhibiting a pH of about 4. It is important that this acidity be neutralized so that the subsequent alkaline treatment with hydroxyethylcellulose is not impaired. The neutralization to a pH of 7 of a 4% sol with sodium or other alkali metal hydroxide however raises the viscosity at 25° C. from approximately 10 centipoises to approximately 10,000 centipoises. This increase produces a sol which is much too viscous to be applied by normal padding techniques and results in poor penetration and distribution in and around the fibers of the textile material.

In accordance with this invention from about 0.2% to 1%, preferably about 0.25% of an amphoteric surface active agent consisting of the alkali metal, e.g., sodium or potassium salt of a C_{10} to C_{18} aliphatic imidazoline carboxylic acid is incorporated in the boehmite sol. This amphoteric surfactant is available commercially under the trade name "Uniterge K" from the Universal Chemical Corporation of Central Falls, Rhode Island. It has the surprising property of neutralizing the acidity of the sol and yet prevents the change in pH from increasing the viscosity of the sol so that it cannot be handled and applied to the textile material effectively. This amphoteric detergent actually promotes the penetration and distribution of the fibrous boehmite into and around the fibers of the textile materials.

The compositions initially applied to the textile material should contain from 1% to 10%, preferably about 4%, of fibrous boehmite, from 0.2% to 1%, preferably about 0.25%, of the amphoteric detergent and the rest water. A preferred composition contains 4.0% fibrous boehmite, 0.25% amphoteric detergent ("Uniterge K") and 95.75% water.

The sol is prepared by dissolving the "Uniterge K" in the required amount of water with suitable mechanical agitation, adding the required amount of boehmite and

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continuing the agitation for 10-15 minutes or until a good smooth dispersion is obtained. This dispersion is stable and can be stored for use when desired.

Application of the sol to the textile material can be made in any conventional manner such as by coating, spraying or padding. The amount of sol deposited on the textile material can vary between 10% to 100% of the textile material's weight. A preferred amount is approximately 80%, i.e., the amount of sol applied is such as to increase the weight of the textile by about 80% based on the dry weight of the textile.

After the sol has been applied the textile material containing the sol is dried in any conventional manner such as on drying cylinders or in a loop dryer or on a tenter frame. Drying can be effected at temperatures of from 200° F. to 500° F. for a time period sufficient to effect removal of substantially all of the water. The dried textile material is then heat treated at a temperature of 250° F. to 450° F. for a dwell or residence time of from 30 seconds to 600 seconds. A preferred temperature and time of heating is approximately 400° F. for about 60 seconds. This heat treatment conditions the fibrous boehmite so that it no longer tends to swell and disintegrate upon exposure to water and firmly bonds the boehmite to the textile. The drying and curing can be carried out in one and the same oven, if desired.

After this heat treatment the textile is ready for the deposition of the hydroxyethylcellulose, which can be applied immediately to the heat treated textile or after batching the heat treated textile and at such future time as may be convenient.

APPLICATION OF HYDROXYETHYLCELLULOSE

The concentration of hydroxyethylcellulose in the solution applied to the textile can be varied from 2% to 8%. A preferred concentration for this solution is about 5%. The amount of alkali metal, e.g., sodium or potassium hydroxide, in this solution to obtain proper solubility of the hydroxyethylcellulose is from 5% to 9%, preferably about 6.25%.

Thus the hydroxyethylcellulose solution contains from 2% to 8% hydroxyethylcellulose, from 5% to 9% alkali metal hydroxide, and the rest water, although a small amount, say from 0.1% to 1% amphoteric detergent can also be incorporated. A preferred solution contains:

	Percent	
Hydroxyethylcellulose	5	
Sodium hydroxide	6.25	
Amphoteric detergent ("Uniterge K")	0.25	
Water	88.5	
Total	100	

The solution is prepared at temperatures below 77° F. A portion of the water can be added as ice to facilitate production of the solution. Lower temperatures facilitates dissolution of the hydroxyethylcellulose. At temperatures above 77° F. there is a tendency for gelation to take place. The amphoteric detergent is dissolved in water while agitating. The amphoteric nature of this surfactant insures good stability in the alkaline medium necessary to dissolve the hydroxyethylcellulose and provides for a good wetting action of the hydroxyethylcellulose on the textile material. It also facilitates the dispersion of the hydroxyethylcellulose when added to the water containing the amphoteric detergent. After a good dispersion is obtained the sodium hydroxide is added followed by the addition of about one-fifth the water content as ice. The use of ice accelerates solution and also improves the filterability of the solution. After filtration the solution can be used but it is preferred to allow it to age for about 24 hours. Such aging lowers the viscosity of the solution thereby making it easier to apply to the textile material.

The hydroxyethylcellulose solution thus prepared can

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be applied in any conventional manner such as by spraying, coating or padding. The amount of hydroxyethylcellulose solution deposited on the textile can vary between 10% to 100% of the textile material's weight. A preferred amount is approximately 80% based on the dry weight of the textile.

After the application of the hydroxyethylcellulose solution to the boehmite treated textile material, the latter is treated to convert the hydroxyethylcellulose to water-insoluble form. Preferably, but not necessarily, the regeneration is preceded by a steaming treatment. Such steaming is effected by introducing the textile material impregnated with the hydroxyethylcellulose into a steaming chamber maintained at a temperature of 220° F. to 250° F. and exposing it to this atmosphere for approximately 10 seconds to 50 seconds. Preferred steaming conditions are about 240° F. with a dwell time of 30 seconds. This steaming causes the hydroxyethylcellulose solution to more thoroughly penetrate into the boehmite treated textile material. At the steaming temperatures, the viscosity of the hydroxyethylcellulose decreases by approximately 2,000 centipoises to 3,000 centipoises, probably followed by some gelation of the deposited hydroxyethylcellulose. Such gelation at this stage is not determined but is advantageous in preventing loss of hydroxyethylcellulose during the subsequent coagulating and regenerating treatment.

COAGULATION AND REGENERATION

The deposited hydroxyethylcellulose, whether or not subjected to a steaming treatment, can be coagulated and regenerated by a number of methods. The regeneration can be accomplished through the removal of the alkali metal hydroxide either through neutralization, dehydration, gelation through heating, followed by washing, or a combination of any of the foregoing. Coagulants and regenerants which can be used are as follows:

(A) Alkaline Coagulants:

- (1) Sodium hydroxide solution of mercerizing strength, i.e., 20% to 30%
- (2) Solutions of Sodium Carbonate
- (3) Solutions of Sodium Bicarbonate
- (4) Solutions of Ammonium Sulfate
- (5) Solutions of Borax
- (6) Solutions of Trisodium Phosphate
- (7) Solutions of Disodium Phosphate
- (8) Solutions of Sodium Silicate

(B) Acid Coagulants:

- (1) Solutions of water soluble acids such as:
 - (a) Sulfuric Acid
 - (b) Phosphoric Acid
 - (c) Acetic Acid
 - (d) Formic Acid
- (2) Solutions of acid salts or salts and acid such as:
 - (a) Sodium Sulfate and Sulfuric Acid
 - (b) Sodium Phosphate and Phosphoric Acid
 - (c) Aluminum Sulfate and Sulfuric Acid
- (3) Vapors of various acids such as:
 - (a) Carbon Dioxide Gas
 - (b) Acetic Acid Vapor
 - (c) Formic Acid Vapor

Treatment with acid media effects neutralization of the alkali metal hydroxide with consequent precipitation of the hydroxyethylcellulose in water-insoluble form.

(C) Neutral Coagulants:

- (1) Solutions of Ammonium Salts—
 - (a) Ammonium Sulfate Solution
 - (b) Ammonium Sulfate and Sodium Sulfate Solution

(D) Heat:

- (1) Hot Air
- (2) Infra Red
- (3) Steam

Except for coagulating and regeneration procedures described in class D, all of the procedures are best conducted at temperatures of from 40° C. to 60° C. Class D procedures are carried out at any convenient temperature controlled by the heating medium used. In all cases the coagulation and regeneration procedure effects precipitation of the hydroxyethylcellulose in a form which bonds with the boehmite and fibers of the textile material.

Coagulation and regeneration should in all cases be followed by rinsing with water or by neutralizing or acidifying, and rinsing to remove by-products such as salts and excess acid or alkaline materials.

A preferred neutralization procedure is the use of a solution of ammonium sulfate and sodium sulfate at a temperature of 50° C. Equally good results can be obtained using a solution of 10% sulfuric acid and 15% sodium sulfate at 50° C. Such solutions produce hydroxyethylcellulose films on the fibers of the textile materials with the least amount of stiffening and with a minimum tendency to re-swell upon subsequent exposure to water.

The thus treated textile materials can be dyed with commercially available dyestuffs used for cellulosic materials, employing conventional dyeing and/or printing techniques used with such dyestuffs and with the production of uniform colorations fast to washing, dry cleaning, solvent spotting and rubbing on the textile materials, including yarns and fabrics composed of blends of different fibers having markedly different dye affinities. Typical suitable dyestuffs are listed below:

(A) Reactive dyes:	Part I C.I.
Procion Yellow 6 G -----	C.I. Reactive Yellow 1.
Cibacron Brilliant Yellow 3 G -----	C.I. Reactive Yellow 2.
Levafix Yellow 4 G -----	C.I. Reactive Yellow 10.
Drimarene Yellow Z-3 GL -----	C.I. Reactive Yellow 11.
Remazol Golden Yellow Y -----	C.I. Reactive Yellow 17.
Procion Brilliant Orange G -----	C.I. Reactive Orange 1.
Cibacron Brilliant Orange G -----	C.I. Reactive Orange 2.
Drimarene Orange 2-G -----	C.I. Reactive Orange 6.
Remazol Brilliant Orange RR -----	C.I. Reactive Orange 7.
Procion Brilliant Red 2 B -----	C.I. Reactive Red 1.
Cibacron Brilliant Red 3 B -----	C.I. Reactive Red 4.
Reactone Red 2 B -----	C.I. Reactive Red 17.
Remazol Brilliant Red BB -----	C.I. Reactive Red 21.
Procion Purple H 3 RS -----	C.I. Reactive Violet 1.
Cibacron Violet 2 R -----	C.I. Reactive Violet 2.
Remazol Red Violet R -----	C.I. Reactive Violet 4.
Drimarene Violet Z-RL -----	C.I. Reactive Violet 3.
Procion Blue 3 G -----	C.I. Reactive Blue 1.
Procion Brilliant H 7 G -----	C.I. Reactive Blue 3.
Cibacron Brilliant Blue BR -----	C.I. Reactive Blue 5.
Drimarene Blue ZGL -----	C.I. Reactive Blue 16.
Remazol Brilliant Blue R -----	C.I. Reactive Blue 19.
Levafix Brilliant Blue RR -----	C.I. Reactive Blue 12.
Levafix Brilliant Green IB -----	C.I. Reactive Green 1.
Procion Brilliant Green 2 B -----	No Color Index No.
Cibacron Brown 3 GR -----	C.I. Reactive Brown 1.
Procion Brown H 4R -----	No Color Index No.
Procion Black HN -----	No Color Index No.
Cibacron Black BG -----	C.I. Reactive Black 1.
Remazol Black B -----	C.I. Reactive Black 5.
Drimarene Black Z BL -----	C.I. Reactive Black 4.
Levafix Grey IG -----	C.I. Reactive Black 2.

(B) Vat dyes:

	Part I	Part II
5 Ponsol Flavone GC -----	C.I. Vat Yellow 2 -----	67300
Algol Orange RFN -----	C.I. Vat Orange 5 -----	73335
Ciba Brilliant Pink R -----	C.I. Vat Red 1 -----	73300
Indanthrene Scarlet 2G -----	C.I. Vat Red 14 -----	71110
Sandothrene Violet N4R -----	C.I. Vat Violet 1 -----	60010
Ciba Blue 2B -----	C.I. Vat Blue 5 -----	73065
Indanthrene Brilliant Green B -----	C.I. Vat Green 1 -----	59825

(C) Azoic dyes:

	Part I	Part II
15 Rapidogen Yellow G -----	C.I. Azoic Yellow 1 -----	37610/37090
Rapidogen Orange RFN -----	C.I. Azoic Orange 3 -----	37558/37010
Rapidogen Red G -----	C.I. Azoic Red 6 -----	37520/37090
Rapidogen Violet B -----	C.I. Azoic Violet 1 -----	37505/37165
Rapidogen Blue B -----	C.I. Azoic Blue 6 -----	37505/37175
Rapidogen Green B -----	C.I. Azoic Green 1 -----	37585/37175
20 Rapidogen Black Brown T -----	C.I. Azoic Brown 16 -----	37605/37120
Rapidogen Black 3G -----	C.I. Azoic Black 4 -----	None

(D) Naphthol shades:

25 Naphthol AS-RL -----	Par I New C.I. 11; Part II New C.I. 37535, and
Fast Red B Salt -----	Part I New C.I. 5; Part II New C.I. 37125.
30 Naphthol AS-ITR -----	Part I New C.I. 12; Part II New C.I. 37550, and
Fast Red ITR Salt -----	Part I New C.I. 42; Part II New C.I. 37150.
35 Naphthol AS-L3G -----	Part I New C.I. 33; Part II New C.I. 37620;
Fast Red AL Salt -----	Part I New C.I. 36; Part II New C.I. 37275.
40 Naphthol HB -----	Part I New C. I. 16; Part II New C.I. 37605, and
Fast Orange GC Salt -----	Part I New C.I. 2; Part II New C.I. 37005.
45 Naphthol AS-RL -----	C.I. given above, and
Fast Red RL Salt -----	Part I New C.I. 34; Part II New C. I. 37100.
50 Naphthol AS-PH -----	Part I New C.I. 14; Part II New C.I. 37558, and
Fast Red AL Salt -----	C.I. given above.
55 Naphthol AS-PH -----	C.I. given above, and
Fast Orange RD Salt -----	Part I New C.I. 49.
60 Naphthol AS-BS -----	Part I New C.I. 17; Part II New C.I. 37515, and
Fast Scarlet RN Salt -----	Part I New C.I. 13; Part II New C. I. 37130.

(E) Chrome dyes:

	Part I	Part II
65 (1) Chrome Luxine Yellow 5G -----	None -----	None
(2) Chromocitronine R -----	C.I. Mordant Yellow 26 -----	22880
(3) Chrome Fast Orange RL -----	C.I. Mordant Orange 37 -----	18730
70 (4) Chrome Fast Red NL -----	None -----	None
(5) Printing Chrome Brown DS -----	None -----	None
(6) Panduran Blue B -----	None -----	None
(7) Panduran Turquoise -----	None -----	None
(8) Panduran Green G -----	None -----	None
(9) Chrome Luxine Green S -----	Mordant Green 3 -----	None
75 (10) Novochrome Fast Grey N -----	None -----	None

(F) Direct dyes:

	Part I	Part II
Fastusol Orange L8 GL-CF.....	C.I. Direct Orange 59.	None
Fastusol Red L4 BL-CF.....	C.I. Direct Red 79.	29065
Pontamine Fast Blue 4GL.....	C.I. Direct Blue 78.	34200

(G) Sulphur dyes:

	Part I	Part II
Sodyesul Liquid Yellow E-CF....	C.I. Solubilized Sulfur Yellow 4.	53125
Sodyesul Liquid Green BG-CF....	C.I. Solubilized Sulfur Green 16.	None
Sodyesul Liquid Black 4G-CF....	C.I. Solubilized Sulfur Black 1.	53185

TYPICAL APPLICATION PROCEDURE USED IN CONDITIONING THE FABRICS OF THE EXAMPLES

Step (1).—Impregnate the textile material with a sol consisting of 5% fibrous boehmite, 0.25% "Uniterge K," and 94.75% water, using a conventional two bowl textile padder. The impregnation is carried out at room temperature and the expression of the padder is regulated so that the textile materials absorbs approximately 80% of its dry weight of the sol.

Step (2).—Immediately following Step (1) the material is dried to width utilizing an enclosed heated tenter frame. Heating can be accomplished by any conventional means such as gas, hot air or steam.

Step (3).—Thereafter the textile material is exposed to a temperature of 400° F. for 30 seconds utilizing a conventional textile curing oven heated by any suitable means such as gas, hot air or steam.

Step (4).—The thus treated textile material is thereafter impregnated with a solution of 5% hydroxyethylcellulose, .25% "Uniterge K," 6.25% sodium hydroxide and 88.50% water. This impregnating step can be conducted in a conventional two bowl textile padder, at room temperature. The expression of the padder is set so that the textile material absorbs approximately 80% of its dry weight of the impregnating solution.

Step (5).—This optional, but preferred, step consists of steaming the textile material from Step (4) in a continuous horizontal steamer at 250° F. for 30 seconds.

Step (6).—In this step the regeneration and coagulation of the hydroxyethylcellulose film is conducted in a conventional 8-compartment open washer. Each compartment is filled with solutions in accordance with the descriptions which follows:

Compartment 1:

15% Ammonium Sulfate
5% Sodium Sulfate
80% Water
(Temperature 122° F.)

This provides a neutral bath.

Compartment 2: Overflowing cold water.

Compartment 3:

5% Sulfuric Acid conc.
10% Sodium Sulfate
85% Water
(Temperature 122° F.)

In this compartment neutralization of the caustic soda employed in Step (4) is effected to convert the hydroxyethylcellulose to an insoluble form.

Compartment 4: Overflowing cold water.

Compartment 5: 0.25% Sodium Carbonate (Temperature 180° F.)

Compartment 6: 0.25% Sodium Carbonate (Temperature 180° F.)

In compartments 5 and 6 excess acid used in compartment 3 is neutralized.

Compartment 7: Overflowing cold water.

Compartment 8: Hot water (Temperature 180° F.)

Step (7).—After completion of Step (6) the textile material has a pH of about 7 and is dried in any conventional manner such as through the use of drying cylinders, and enclosed tenter frame or a loop dryer.

The textile material is now ready for printing or dyeing with dyestuffs normally used for cellulose, such as those above disclosed, by use of any conventional application techniques. The following examples are given to illustrate this invention. It will be appreciated this invention is not limited to these examples.

Example I

A textile material consisting of 50% cellulose acetate and 50% cotton was pretreated according to the methods of this invention as has been previously described. It was then printed by conventional methods using a roller printing machine and an intaglio engraved roller with a paste of the following composition:

5% Procion Brilliant Blue H7GS
15% Urea
35% Sodium Alginate Thickening
1% Sodium Meta Nitro Benzene Sulfonate
1.5% Sodium Bicarbonate
62.5% Water

After printing the textile material was steamed for five minutes, rinsed, soaped and dried. A uniform turquoise blue print was obtained on both the cotton and cellulose acetate portions of the textile material. This shade was fast to washing and was commercially acceptable. A comparison print made on the untreated textile material was much inferior in appearance and the cellulose acetate portion was completely white. The procion dye used in the print paste is a derivative of cyanuric chloride, manufactured by Imperial Chemical Industries Ltd., and requires the presence of hydroxyl groups on the fiber for fixation of the dye to occur.

Example II

The textile material used in Example I was dyed by impregnating on a two bowl padder with the following solution containing a cibacron dye, manufactured by Ciba, and possessing one reactive group:

2% Cibacron Brilliant Orange G
10% Urea
10% Sodium Alginate Thickening
1% Sodium Meta Nitro Benzene Sulfonate
1.5% Sodium Carbonate
75.5% Water

After impregnation the textile material was dried and fixation of the dye was carried out by heat treating, in a conventional textile curing oven, for three minutes at a temperature of 230° F. The material was then washed and dried. The textile material thus processed was dyed a bright uniform orange shade. A textile material not pretreated, on the other hand, when dyed in the same manner had only the cotton fibers dyed with the cellulose acetate fibers substantially free of color.

Example III

4% Remazol Red Violet R was printed as in Example I on the same textile material. After fixation by steaming and following rinsing, washing and drying, an examination indicated that the fabric was uniformly colored in the printed areas.

Example IV

A textile fabric whose construction consisted of 65% "Dacron" and 35% cotton was treated in accordance with this invention, as hereinabove described. It was then printed on a conventional printing machine with a paste of the following composition:

6% Procion Blue H7GS
15% Urea
1% Ludigol (Sodium Meta Nitrobenzene Sulfonate)
35% Keltex (3% Solution of Sodium Alginate)
1.5% Sodium Bicarbonate
41.5% Water

After printing the fabric was steamed in a continuous ager and soaped to remove any unfixed dyestuff. A very uniform turquoise blue print was obtained whereas when the above composition was printed on a control fabric of the same construction which was not pretreated the results were much inferior as the dyestuff was fixed only to the cotton portion of the fabric and gave an uneven appearance.

Example V

A fabric whose construction consisted of 65% "Dacron" and 35% cotton was treated as hereinabove described. It was then dyed by impregnating it on a conventional textile padder with a solution of the following composition:

2% Procion Brilliant Orange G
20% Urea
5% Keltex (3% Solution of Sodium Alginate)
1% Ludigol (Sodium Meta Nitrobenzene Sulfonate)
1.5% Sodium Bicarbonate
70.5 Water

The fabric was then dried and the fixation of the dyestuff was carried out by heating the fabric at 250° F. for 3 minutes. The fabric was then rinsed and soaped to remove any unfixed dyestuff. A uniform orange shade resulted in which both the "Dacron" and cotton portions of the fabric were colored, whereas in an untreated fabric which was dyed at the same time, as a control, only the cotton was colored.

Example VI

Three different fabrics consisting of 100% "Dacron," 100% nylon, and 100% cellulose acetate were dyed according to the procedure of Example V after having been treated according to the methods of this invention. Untreated pieces of the same fabrics were also dyed in the same manner as controls. The treated fabrics were dyed a medium shade of orange while the untreated fabrics were each almost colorless.

Example VII

The fabric dyed in Example V was printed on a conventional roller printing machine with a paste of the following composition:

15% Indanthrene Printing Green B
85% Vat Dyestuff Printing Thickener as described in U.S. Patent 2,894,801, Example III.

The printed and dyed fabric was then finished by aging in a horizontal vat ager for 10 minutes at a temperature of 214° F. to 218° F., oxidizing with a solution of hydrogen peroxide, washing and finally drying. The final effect consisted of a uniform green print on an orange background.

The single figure of the drawing shows by self-descriptive legends the important steps of the process.

It will be noted that the newer fiber-reactive dyestuffs derived, for example, from cyanuric chloride, vinyl sulphone and tri and tetrachloro pyrimidine can be used with excellent results in dyeing and/or printing materials pretreated in accordance with this invention. These

dyes are not suitable for application to non-cellulosic fibers but can be used when such fibers are pretreated as herein disclosed. These dyestuffs require the presence of hydroxyl groups within the fiber for fixation of the dyestuff to occur through the formation of a covalent bond. Unless the fiber dyestuff reaction occurs, these dyes will have no acceptable fastness properties and will be easily removed from the fiber during washing, as invariably carried out following the dyeing or printing of the textiles. The fixation of these dyestuffs on fibers, containing no hydroxyl groups, or on fibers containing relatively few hydroxyl groups, which are not capable of reaction because of inaccessibility through steric hindrance, is of great commercial importance. Through the use of these dyestuffs on textile materials of a non-cellulosic character but treated in accordance with this invention, it is possible to obtain shades on fibers and on mixtures of fibers which heretofore had not been attainable. The fixing of these dyestuffs on normally non-reactive fibers is an important unobvious advance achieved by this invention.

The fabrics and yarns thus produced which in the case of blends are composed of cellulosic fibers blended with one or more of the fibers disclosed above, namely, cellulose diacetate, cellulose triacetate, polyamides, polyesters, acrylic, saponified diacetate, olefins, dinitriles and mineral fibers, have bonded to the surface colloidal fibrous boehmite in amount of from .8% to 8%, preferably 3.2%, based on the weight of the fabric or yarn and a continuous film of water-insoluble hydroxyethylcellulose which overlies the fibrous boehmite and along with the boehmite is firmly bonded to the surface. The boehmite aids in effecting a firm bond between the hydroxyethylcellulose film and the fibrous components of the yarns and fabrics; without the fibrous boehmite, proper bonding between the hydroxyethylcellulose film and the fibers would not be attained. Surprisingly, the successive application of the colloidal sol of fibrous boehmite, containing the amphoteric detergent and the alkaline solution of hydroxyethylcellulose followed by coagulation and regeneration of the hydroxyethylcellulose, results in a firm bond of the water-insoluble hydroxyethylcellulose film with the fibers, which, upon dyeing and/or printing with dyestuffs used for cellulosic materials, gives colorations having good fastness to dry cleaning, washing, solvent spotting and rubbing. The amount of hydroxyethylcellulose film on the material is from 4% to about 7%, preferably about 5%.

It will be understood that this invention is not to be limited by the above examples or the disclosure herein except as defined by the appended claims.

What is claimed is:

1. The process of conditioning yarn and fabric materials constituted of a blend of non-cellulosic and cellulosic fibers to render them receptive to dyes for cellulosic materials, which process comprises applying to said materials a colloidal sol containing about 4% fibrous boehmite, about 0.25% of the sodium salt of a C₁₀ to C₁₈ aliphatic imidazoline carboxylic acid, and the rest water in amount to supply to the said materials about 80% by weight of said sol, drying and then curing the thus treated material at a temperature of 250° F. to 450° F. for from 30 seconds to 600 seconds to bond the fibrous boehmite to the materials, thereafter applying to the fibrous boehmite-containing materials an alkaline solution of hydroxyethylcellulose, containing about 5% of hydroxyethylcellulose produced by reacting alkali cellulose with ethylene oxide so that from about 2% to 10% ethylene oxide is combined with the alkali cellulose, about 6.25% sodium hydroxide, and about 0.25% of the sodium salt of a C₁₀ to C₁₈ aliphatic imidazoline carboxylic acid in amount to apply to said fibrous boehmite-containing material about 80% by weight of said hydroxyethylcellulose solution, steaming the thus treated materials at a tem-

perature of 220° F. to 250° F. for from 10 seconds to 50 seconds, and thereafter coagulating and regenerating the hydroxyethylcellulose thus applied to each material to convert it to water-insoluble hydroxyethylcellulose film bonded to the boehmite-containing material.

2. The process as defined in claim 1, in which the coagulation and regeneration of the hydroxyethylcellulose is effected by treatment with an alkaline solution of sufficient strength to precipitate the hydroxyethylcellulose in a water-insoluble form on the boehmite-containing material.

3. The process as defined in claim 1, in which the coagulation and regeneration of the hydroxyethylcellulose is effected by treatment with an acid to neutralize the alkalinity of the hydroxyethylcellulose solution applied to the boehmite-containing materials and thus precipitate the hydroxyethylcellulose in a water-insoluble form.

4. The process as defined in claim 1, in which the coagulation and regeneration of the hydroxyethylcellulose is effected by heating the said materials containing the hydroxyethylcellulose solution applied to the boehmite-containing materials to effect precipitation of the hydroxyethylcellulose in a water-insoluble form.

5. The process of conditioning fabrics and yarns consisting of blends of cellulosic fibers, with at least one fiber from the group consisting of cellulose diacetate, cellulose triacetate, polyamides, polyesters, acrylic, olefins, nitril and mineral fibers, which process comprises treating said materials with an aqueous colloidal sol containing about 4% fibrous boehmite, about .25% of the sodium salt of a C₁₀ to C₁₈ aliphatic imidazoline carboxylic acid and the rest water, said sol being applied in amount to deposit on the materials about 80% by weight of the sol, drying the thus treated materials, heating the dried materials at a temperature of 250° F. to 450° F. for 30 seconds to 600 seconds to bond the fibrous boehmite thereto, applying to the fibrous boehmite-containing materials an alkaline solution of hydroxyethylcellulose produced by reacting alkali cellulose with ethylene oxide so that about 2% to 5% ethylene oxide is combined with the alkali cellulose, such solution of hydroxyethylcellulose containing about 5% hydroxyethylcellulose, about 6.25% sodium hydroxide, about 0.25% of a sodium salt of a C₁₀ to C₁₈ aliphatic imidazoline carboxylic acid, the amount of hydroxyethylcellulose solution applied to the boehmite-containing materials being about 80% by weight, and thereafter coagulating and regenerating the hydroxyethylcellulose to convert it to a water-insoluble form bonded to the boehmite-containing materials.

6. The process of conditioning yarn and fabric materials to render them receptive to dyes for cellulosic fibers, which process comprises applying to said materials an aqueous colloidal sol containing from 1% to 10% fibrous boehmite, from 0.2% to 1% alkali metal salt of a C₁₀ to C₁₈ aliphatic imidazoline carboxylic acid, and the rest water in amount to apply to the said materials from 10% to 100% by weight of said sol, curing the thus treated materials at a temperature of 250° F. to 450° F. for from 30 seconds to 600 seconds to bond the fibrous boehmite to the materials, thereafter applying to the fibrous boehmite-containing materials an alkaline solution of hydroxyethylcellulose containing from 2% to 8% of hydroxyethylcellulose produced by reacting alkali cellulose with ethylene oxide so that from about 2% to 10% ethylene oxide is combined with the alkali cellulose, from 5% to 9% of alkali metal hydroxide, and from 0.2% to 1% of an amphoteric detergent in amount to apply to said fibrous boehmite-containing materials from 10% to

100% of hydroxyethylcellulose solution, and thereafter coagulating and regenerating the hydroxyethylcellulose thus applied to each material to convert it to a water-insoluble hydroxyethylcellulose film bonded to the boehmite-containing material.

7. The process of conditioning fabrics and yarns consisting of blends of cellulosic fibers, with at least one fiber from the group consisting of cellulose diacetate, cellulose triacetate, polyamides, polyesters, acrylic, olefins, nitril and mineral fibers, which process comprises treating said materials with an aqueous colloidal sol containing about 4% fibrous boehmite, about .25% of the sodium salt of C₁₀ to C₁₈ aliphatic imidazoline carboxylic acid and the rest water, said sol being applied in amount to deposit on the materials about 80% by weight of the sol, drying the thus treated materials, heating the dried materials at a temperature of 250° F. to 450° F. for 30 seconds to 600 seconds to bond the fibrous boehmite thereto, applying to the fibrous boehmite-containing materials an alkaline solution of hydroxyethylcellulose produced by reacting alkali cellulose with ethylene oxide so that about 2% to 5% ethylene oxide is combined with the alkali cellulose, such solution of hydroxyethylcellulose containing about 5% hydroxyethylcellulose, about 6.25% sodium hydroxide, about 0.25% of a sodium salt of a C₁₀ to C₁₈ aliphatic imidazoline carboxylic acid, the amount of hydroxyethylcellulose solution applied to the boehmite-containing materials being about 80% by weight, thereafter steaming the resultant materials at a temperature of 220° F. to 250° F. for 10 seconds to 50 seconds, and thereafter coagulating and regenerating the hydroxyethylcellulose to convert it to a water-insoluble form bonded to the boehmite-containing materials.

8. The process of conditioning yarn and fabric materials to render them receptive to dyes having affinity for cellulosic materials, which process comprises treating said materials with an aqueous colloidal sol of fibrous boehmite containing an alkali metal salt of a C₁₀ to C₁₈ aliphatic imidazoline carboxylic acid, thereafter heating the thus treated materials to bond the fibrous boehmite to the materials, then applying to the thus treated materials an alkaline solution of hydroxyethylcellulose and thereafter coagulating and regenerating the hydroxyethylcellulose to convert it to a water-insoluble form bonded to the boehmite-containing material.

9. Yarn and fabric materials conditioned to render them receptive to dyes having affinity for cellulosic fibers, produced by the process of claim 8.

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