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3,023,072

DYEING AND/OR PRINTING

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This invention relates to processes of dyeing and/or printing of materials such as fibers, yarns, films, fabrics and extrusions and more particularly to the pretreatment of such materials to condition them so that they readily and uniformly receive dyes, especially dyes which produce dark and medium shades.

This application is a continuation-in-part of application Serial No. 802,610, filed March 30, 1959, now abandoned.

Materials, including fabrics and yarns constituted wholly or partially of glass fibers are notoriously difficult to dye. Other fibers, films, fabrics and yarns such as those made from olefins, particularly polyethylene and polypropylene, fabrics and yarns, made from or containing (a) at least about 50% by weight of acrylic and related acrylic copolymers (such as Orlon, Creslan, Acrilan, Varel, Zefran, Darvan and Dynel), (b) vinylidene/vinyl chloride copolymer fiber (such as Saran), (c) polyesters (ethylene glycol and terephthalic acid condensation polymers, e.g., Dacron) and (d) polyamide polymers (such as nylon), are also difficult to dye employing commercially available dyes. Fibers, fabrics and yarns of cellulose acetate, cellulose triacetate (Arnel), saponified cellulose acetate (Fortisan), silk, wool and blends of two or more of any of the above enumerated fibers are also difficult to dye with many available dyes; hence, only limited selected dyes can be used requiring involved special dyeing techniques employing either carriers or high-temperature dyeing in enclosed systems.

It is among the objects of the present invention to provide a process of pretreating such materials, particularly fabrics and/or yarns and in the case of the olefins, films also, to condition them so that they will accept and can readily be dyed with commercial dyes, or printed with such dyes.

It is another object of this invention to provide a process of pretreating fabrics and/or yarns of difficultly dyeable fibers to provide a chemical anchor for commercially available dyes and thus permit the thus treated material to be dyed or printed with such dyes in a conventional manner to produce markedly improved dyeings.

It is still another object of this invention to provide a process of pretreating fabrics or yarns containing glass fibers to condition them so that they will accept and can readily be dyed or printed with commercial dyes.

It is still another object of this invention to provide a process of pretreating fabrics or yarns containing polypropylene fibers to condition them so that they will accept and can readily be dyed or printed with commercial dyes.

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 solution of water-soluble deacetylated chitin (acetamino carbohydrate) and a Werner-type reactive chromium complex such as p-aminobenzoate chromic chloride, beta-resorcyloato chromic chloride, glycinato chromic chloride, tannato chromic chloride, glycolato chromic chloride, thioglycolato chromic chloride or sorbato chromic chloride, and the thus treated material is dried and heated to produce a

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film or layer of the resultant reaction product bonded to the base material. This film or layer has a surprising affinity for dyestuffs greater than the sum of the affinities for such dyestuffs of the individual constituents, indicating the presence of synergism.

While the explanation for this phenomena is not fully understood, one probable explanation is given to facilitate a better understanding of the invention. It will be appreciated that this invention is not limited to this explanation.

During the heating of the material treated as above described, the chromium complex polymerizes to form a high molecular weight insoluble polymeric material through the formation of Cr—O—Cr linkages with the p-amino-benzoato, betaresorcyloato, tannato, glycolato, thioglycolato, sorbato or glycinato groups within the polymer, oriented away from the base material, e.g., glass fibers in the case of a glass fiber material. The heated acid salt of deacetylated chitin is converted into an insoluble form due to the partial loss of acid salt forming component and also due to the formation of insoluble amide through dehydration. These two polymeric materials establish strong bonds between themselves and between themselves and the base surface. These bonds are probably due to electrostatic attractions and through covalent chemical bonds; probably the —OH, —NH₂, —CONH— groups present in the polymeric acetamino carbohydrate form strong covalent bonds with the polymerized Werner-type reactive chromium complex. The resultant film or layer firmly bonded to the base surface shows remarkable enhanced dye affinity for commercial dyestuffs due, it is believed, to synergistic action between the two ingredients resulting in the formation of the durable, bonded crosslinked complex polymeric layer or film exceptionally receptive to dyes.

Of the Werner-type chromium complexes mentioned, p-aminobenzoato chromic chloride is preferred because it gives the best results and can be used in producing medium shades as well as dark. The tannato complex is useful chiefly in producing dark shades, i.e., blacks and dark brown. These chromium complexes can be made, for example, by reacting a basic chromium solution with the appropriate acid (p-aminobenzoic, beta-resorcylic, glycine, tannic, glycolic, thioglycolic or sorbic) in the presence of isopropanol following the general procedure disclosed in United States Patent 2,544,667, granted March 13, 1951, or United States Patent 2,683,156, granted July 6, 1954, both assigned to E. I. du Pont de Nemours & Company. All of the chromium complexes, above enumerated, are sold by du Pont as part of the family of chrome complexes offered by it to the trade.

The deacetylated chitin may be obtained by heating crude chitin successively with soda ash and hydrochloric acid to remove the lime salts and adherent protein followed by digesting the sodium hydroxide or other alkali at an elevated temperature under conditions excluding oxidation, to produce deacetylated chitin. The deacetylated chitin thus produced is reacted with aqueous acetic acid, producing the water-soluble acetic acid salt. While it is preferred to use the acetic acid salt, other salts may be used, such, for example, as those formed by reacting the purified deacetylated chitin with itaconic, formic, pyruvic, or lactic acid. For a more detailed description of the production of such acid salts of deacetylated chitin, reference may be had to United States Patents 2,040,879 and 2,040,880, granted May 19, 1936.

Particularly preferred is the itaconic acid reaction prod-

uct with the deacetylated chitin. The amount of itaconic acid used is approximately the same by weight as the amount of deacetylated chitin. Shades produced with the chrome complex and the itaconic acid salt of deacetylated chitin have better brightness in general than those resulting from the acetic and other acid salts of the deacetylated chitin. This is due to the fact that on curing the film or layer, itaconic acid reacts with the primary amino groups (in the deacetylated chitin and/or chrome complex when employing a complex containing such groups) converting them into N- substituted γ -lactam, which causes less loss of color during the curing treatment. Moreover, the viscosity of the solution or mix applied to the material is less when the same contains itaconic acid rather than acetic acid. Hence, the material picks up the solution or mix more readily with consequent increased concentration of chrome complex and deacetylated chitin on the material and better development of the color when the dye is applied.

The chrome complex and the deacetylated chitin are mixed in the proportion of 1 to 6 parts water-soluble deacetylated chitin (about one-half of which is the acid required for solubilization) to 1 to 6 parts chrome complex (in the form of an isopropanol solution containing from about 60% to 75% by weight of isopropanol) and 88 to 98 parts water.

The solution may be applied to the material to be colored in any desired manner, for example, by padding, dipping, spraying, etc. The amount applied will, of course, depend on the material treated. A pick up (increase in weight) 10% to 80% by weight will give good results. The temperature of application is not critical; a preferred range is from 50° F. to 110° F.

After application, the treated material is dried and then passed through a curing oven maintained at a temperature of 200° F. to 350° F., preferably 300° F. to 310° F. for glass fiber fabrics, and 240° F. to 290° F. for polyurethane, i.e., at lower temperatures the residence time is from 1 to 5 minutes or longer, depending upon the temperature, i.e., at lower temperatures the residence time is longer and vice versa. Near the upper portion of the range the residence time is about 2 minutes or less. The temperature and residence time should be so chosen as to effect curing of the chrome complex and deacetylated chitin mixture without damage to the base material. This temperature for any desired residence time can readily be determined for each material by subjecting a sample of the material to heat for the time interval under consideration and determining the temperature at which the material begins to pucker or be deformed when so heated.

The thus pretreated material will not hydrolyze readily even when treated with hot water or dilute alkali. Acids, such, for example, as sulfuric, hydrochloric, etc., effect stripping of the anchor layer or film. This feature enables the production of desirable effects by treating films, fabrics and/or yarns before or after the dyeing or printing, with acid in selected areas to remove the anchor film in those areas and thus obtain desired pattern effects.

The dyeing or printing of the pretreated material is accomplished by conventional techniques.

Examples of dye types which can be used are given below; C.I. means Color Index.

REACTIVE DYES

Reactive dyestuffs of the monochloro triazine family, such as Cibacron Yellow R, Cibacron Brilliant Orange G, Cibacron Rubine R, and Cibacron Turquoise Blue G, manufactured by Ciba Company, Inc.; dichloro triazine family, such as Procion Brilliant Red H3B, manufactured by Arnold Hoffman & Company, Inc.; and the vinyl sulfone family, such as Remazol Brilliant Blue R, manufactured by Carbic Colors & Chemical Company, Inc.

Chrome dyes:

- Printing Chrome Brown D.S.
- Chromocitronine R—
 - Part I, C.I. Mordant Yellow 26
 - Part II, C.I. 22880
- Chrome Fast Red NL
- Chrome Fast Orange RL—
 - Part I, C.I. Mordant Orange 37
 - Part II, C.I. 18730
- Chrome Luxine Green S—Part I, C.I. Mordant Green 3
- Panduran Turquoise
- Panduran Blue B
- Novochrome Fast Grey N
- Chrome Luxine Yellow 5G
- Panduran Green G

Acid dyes:

- Neolan Black WA Ex. conc.—
 - Part I, New C.I. 52;
 - Part II, New C.I. 15711
- Neolan Blue 2G conc.—
 - Part I, New C.I. 158A;
 - Part II, New C.I. 15050
- Neolan Orange R—
 - Part I, New C.I. 76;
 - Part II, New C.I. 11870
- Neolan Red 3B—Part I, New C.I. 191
- Neolan Green BL conc.—
 - Part I, New C.I. 12;
 - Part II, New C.I. 131125
- Neolan Yellow GR conc.—
 - Part I, New C.I. 99;
 - Part II, New C.I. 13900
- Neolan Violet 7R—Part I, New C.I. 59
- Neolan Blue 2R—Part I, New C.I. 154
- Cibalan Brilliant Yellow 3GL—Part I, New C.I. 714

Direct dyes:

- Lumicrease Yellow EFUL
- Lumicrease Navy Blue GLA 35%
- Lumicrease Green 3LB conc. 160%—Part I, New C.I. 31
- Pyrazol Fast Turquoise GLL
 - Part I, New C.I. 86;
 - Part II, New C.I. 74180

Liquid sulfur dyes:

- So-Dye-Sul. Liquid Black 2RCF—
 - Part I, New C.I. 2;
 - Part II, New C.I. 53195
- So-Dye-Sul. Liquid Black R
 - Part I, New C.I. 1;
 - Part II, New C.I. 53185
- So-Dye-Sul. Liquid Brown HFCF
- So-Dye-Sul. Liquid Brown AFCF
- So-Dye-Sul. Liquid Brown FCF—Part I, New C.I. 37
- So-Dye-Sul. Liquid Olive Yellow YCF—Part I, New C.I. 3
- So-Dye-Sul. Liquid Green G—
 - Part I, New C.I. 2;
 - Part II, New C.I. 53571
- So-Dye-Sul. Liquid Green BGCR—Part I, New C.I. 16
- So-Dye-Sul. Liquid Navy—
 - Part I, New C.I. 7;
 - Part II, New C.I. 53440

Indigosol dyes:

- Algisol Golden Yellow 1RK—Part II, New C.I. 59106
- Algisol Brilliant Violet 14R—CF—
 - Part I, New C.I. 1;
 - Part II, New C.I. 60011

Basic dyes:

- Rhodamine GGDN Ex. conc.—
 - Part I, New C.I. 1;
 - Part II, New C.I. 45160

Disperse, acetate dyes:

- Interchem. Direct Acetate Black N.C.

Vat dyes:

- Indanthrene Blue BFP
Caloloid Navy Blue NTC
Part I, New C.I. 18;
Part II, New C.I. 59815
Calcoloid Jade Green NC Supra
Part I, New C.I. 1;
Part II, New C.I. 59825
Calcoloid Yellow GC
Part I, New C.I. 2;
Part II, New C.I. 67300
Calcoloid Brown R
Part I, New C.I. 3;
Part II, New C.I. 69015
Liquid vat dyes (Hydron type):
So-Dye-Vat Liquid Blue GS
So-Dye-Vat Liquid Blue FER—
Part I, New C.I. 43;
Part II, New C.I. 53630
Sulfur dyes (powders):
Sulfogene Brilliant Green J—Part I, New C.I. 14
Sulfogene Brilliant Blue BGL—
Part I, New C.I. 13;
Part II, New C.I. 53450
Naphthol shades:
Naphthol AS-RL—
Part 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
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
Naphthol AS-L3G—
Part I, New C.I. 33;
Part II, New C.I. 37620, and
Fast Red AL Salt—
Part I, New C.I. 36;
Part II, New C.I. 37275
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
Naphthol AS-RL—G.I. given above, and
Fast Red RL Salt—
Part I, New C.I. 34;
Part II, New C.I. 37100
Naphthol AS-PH—
Part I, New C.I. 14;
Part II, New C.I. 37558, and
Fast Red AL Salt—C.I. given above
Naphthol AS-PH—C.I. given above, and
Fast Orange RD Salt—Part I, New C.I. 49
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

The liquid sulfur colors and chrome colors have been found particularly effective in the coloration of polypropylene, particularly polypropylene fabrics and yarns. Polypropylene, it is noted, is a material which is unusually difficult to dye and can not be dyed satisfactorily by most heretofore known dyeing procedures.

The amount of dyestuff applied will, of course, depend on the color or shade desired. For those dyestuffs which require oxidation to develop the color, it is preferred to

use either hydrogen peroxide or sodium perborate at about 120° F.

Acids appear to adversely affect the anchor film or layer and hence sodium bichromate and acetic acid are not recommended; nor is the application of dyestuffs in strongly acid media, such as sulfuric acid, recommended. In developing the Indigosols the use of a mixture of 2% sodium nitrite and 4% chloracetic acid at 100° F. for one-half minute gave good results.

- 10 The following examples are given for illustrative purposes; it will be understood this invention is not confined to these examples. In these examples all parts and percentages are on a weight basis, unless otherwise indicated.

Example I

This example involved the use of a pretreating solution containing

	Percent
20 Deacetylated chitin -----	1.8
Concentrated acetic acid -----	1.6
p-Aminobenzoato chromic chloride (containing about 65% isopropyl alcohol) -----	2.6
Water -----	94

- 25 Swatches of two heat cleaned glass fiber fabrics, namely, bouclé and casement weave, and a glass fiber yarn were immersed in this pretreating solution. The bouclé wet pick up was 40%, the casement weave 19%, and the yarn 12%–15%. Thereafter the wet swatches and yarn were dried on a drying can and heated for two minutes at 300° F. to 310° F.

The thus treated cloth was immersed in plain water at 180° F. for ¾ hour, and in 1% caustic soda at 180° F. for ¾ hour, without noticeable hydrolysis taking place.

- 35 Dyeing of the pretreated cloth and yarn was effected by immersing the pretreated swatches and yarn in beakers containing the indicated dyestuffs in the amount stated.

A. REACTIVE DYES

In this series of dyeings 10% urea was added to the dye baths containing the dyes noted below to dissolve the color. The dyeing was carried out by immersing the swatches and yarns in the dye baths for about 1 hour at 200° F. No alkali is needed for color fixation; evidently the anchor film is self-fixing to this class of dyes. The use of alkali in dyeing or printing the pretreated material with reactive dyes actually reduces the color value.

	Percent
50 Cibacron Yellow R -----	1
Cibacron Brilliant Orange G -----	1
Procion Brilliant Red H3B -----	1
Cibacron Rubine R -----	1
55 Remazol Brilliant Blue R -----	1

All samples were dyed evenly; the color exhausted well from the dye bath.

B. CHROME COLORS

60 5% urea was used to dissolve the color; the dyeing was carried out by immersing the swatches and yarn for one hour in the dye bath at a temperature of about 180° F. The colors thus applied were:

	Percent
65 Printing Chrome Brown D.S. -----	1
Chromocitronine R -----	1
Chrome Fast Red NL -----	1
Chrome Fast Orange RL -----	1

70 The results in all cases were excellent. The dye was evenly and uniformly applied.

C. NEOLAN COLORS

75 These colors were applied at about 180° F. with the

swatches and yarn immersed in the dye bath for one hour. No assistants were required.

	Percent
Neolan Red 3B	1
Neolan Orange R	1
Neolan Yellow GR conc.	1
Neolan Blue 2G conc.	1
Neolan Black WA Ex. conc.	1
Neolan Green BL conc.	1

The results were excellent. Uniform dyeing was obtained in every case.

D. LIQUID SULPHUR COLORS

	Percent
So-Dye-Sul. Liquid Black 2RCF	5
So-Dye-Sul. Liquid Brown HPCF	3

These colors were applied with the aid of 1% So-Dye Fide B (aqueous mixture of sodium sulfide and sodium polysulfides) for one hour at 160°–170° F. They were developed in a 1% by weight H₂O₂ solution (35% by weight concentrations). The results were excellent; uniform even dyeings were obtained in every case.

E. INDIGOSOLS

	Percent
Indigosol Yellow IRK	1
Algol Brilliant Violet 14R-CF	1

These colors were applied by immersing the material in the bath at 140°–150° F. and maintaining them therein for one hour. The color was developed by treatment of the dye samples with an aqueous solution containing 2% NaNO₂ and 4% chloroacetic acid at 100° F. for one-half minute. Good results were thus obtained.

F. CIBALAN COLORS

1% Cibalan Brilliant Yellow 3GL was applied at a temperature of 180° F., the material being immersed in the dye solution for about one hour. Excellent dyeing resulted.

G. NAPHTHOL SHADES

Three mixtures were applied by pad naphtholating at 180° F., drying, pad coupling cold, rinsing and subjecting the thus treated material to a soaping treatment. The three mixtures were as follows:

	Ounces per gallon
Naphthol AS-BS	½
F. Scarlet RN Salt	2
Naphthol AS-ITR	½
F. Red ITR Salt	1.2
Naphthol AS-RL	½
F. Red B Salt	1.8

Excellent results were obtained; the dyeings were even and uniform in every case.

H. BASIC COLORS

1% Rhodamine 6GDN Ex. conc. was applied to the sample materials by immersing them for one hour at 180° F. Evenly dyed fabrics and yarn resulted.

I. VAT COLORS

	Percent
Calcoloid Navy Blue NTC Single Paste	2
Calcoloid Jade Green NC Supra Double Paste	2
Calcoloid Yellow Single Paste	2
Calcoloid Brown R Double Paste	2
Indanthrene Brilliant Blue BFP	2

These colors were reduced at 140° F. with 1.5% caustic soda solution (25% concentration) and 0.75% of sodium hydrosulfite; the thus treated cloth was immersed in the reduced dye solution at 140°–160° F. for about one hour, then developed with 1% H₂O₂ at 120° F.

Excellent results were obtained; the dyeings were even and uniform.

Fastness tests were run on sample dyeings obtained as above described. These tests involved subjecting specimens to Fade-ometer light exposure for 10, 20, 30 and

40 hours. The tests also involved hand washing of samples in a solution containing 0.2% soap (cleate flakes) at 100° F. for five minutes each cycle, and for five consecutive cycles. These tests showed that the samples had good color fastness, particularly in the case of the vat colors, the sulphur colors, the naphthols, the chrome colors, the reactive colors and the Neolan colors.

Examples II to VIII, inclusive

10 This series of examples involved the use of a pretreating solution containing in each case 2% deacetylated chitin, 2% acetic acid (84% concentration) and 93% water. The pretreating solution of these examples contained, respectively, 3% of paraminobenzoato chromic chloride (Example II), beta-resorcyloato chromic chloride (Example III), glycinate chromic chloride (Example IV), tannato chromic chloride (Example V), glycolato chromic chloride (Example VI), thioglycolato chromic chloride (Example VII), sorbato chromic chloride (Example VIII.)

Heat cleaned glass fiber fabric was padded with each of the above solutions. The wet pick up was from 22% to 24%. The thus treated fabrics were dried and cured at 320° F. for two minutes.

25 The fabrics were then dyed by immersing in the following dye baths:

(A)

	Percent
Anthracene Brown S (chrome dyestuff)	2
30 Urea	8

The fabrics were dyed for one hour at 180° F.

(B)

	Percent
35 So-Dye-Sul. Liquid Green (Sulfur color)	6
So-Dye-Fide B	4

The fabrics were dyed at 180°–200° F. for one hour. After one-half hour of dyeing, 30% (based on the weight of the bath) sodium chloride was added to the dye bath. 40 The dyed fabrics were then oxidized with 1% sodium perborate at 120° F.

(C)

	Percent
Metrovat Jade Green Dbl. Paste (Vat color)	1.5
45 Sodium hydroxide (25%)	1.5
Hydrosulfite	.75

The fabrics were dyed for one hour at 150°–160° F. Thereafter the fabric was oxidized with 1% sodium perborate at 120° F.

(D)

	Percent
Procion Brilliant Red H3B (Reactive Dye)	2
50 Urea	8

55 The fabrics were dyed for one hour at 200° F. Uniform dyeings were obtained in every case.

Examples IX to XV, inclusive

This group of examples differed from II to VIII, inclusive, in that the pretreating solution of Examples II to VIII, inclusive, were applied to a pre-scoured polypropylene fabric (100% polypropylene). The wet pick up was from 38% to 40%. The polypropylene fabrics, after drying, were cured at 275° F. for 5 minutes. The dyeing procedures were the same with the respective dye applications. Uniform dyeings were obtained in each case.

Examples XVI, XVII and XVIII

70 In this group of examples the pretreating solution contained

	Percent
Deacetylated chitin	2
Acetic acid (84%)	2
Para-aminobenzoato chromic chloride	3
75 Water	93

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Example XVI involved the padding of this solution on a saponified cellulose acetate (Fortisan) fabric. The wet pick up was 81%. The fabric was then dried and cured for 2 minutes at 320° F.

Example XVII involved the padding of this solution on a white polyethylene fabric. The wet pick up was 70%. The polyethylene fabric was dried, cured on a hot can (temperature 225° F.) for 20 minutes. This method of curing was used to avoid fusion of the material.

Example XVIII involved dipping a polypropylene yarn in the solution and squeezing through low pressure pad nip to about 90% wet pick up. The yarn was then dried and cured at 280° F. for 5 minutes.

The thus treated fabrics and yarn were then dyed, with the following dyes:

- (1) 6% So-Dye-Sul. Liquid Green BGCF
- (2) 2% Anthracene Brown S
- (3) 3% Metrovat Jade Green Dbl. Pste.
- (4) 2% Neolan Violet 7R
- (5) 2% Procion Brill. Red H3B
- (6) 1.5% Lumicrease Green 3LB

Uniform dyeings were obtained in each case.

Example XIX

This example involved the dyeing of a polypropylene-rayon blended fabric. The pretreating solution was the same as in Example XVI. The wet pick up was 85%. The fabric was then dried and cured at 320° F. for 2 minutes.

Swatches of the thus treated fabric were then beaker dyed with the following dyes:

(A)

	Percent
So-Dye-Sul. Liquid Brown AFCF	5
So-Dye-Fide B	5

Dyed for one hour at 160°-170° F., 50% sodium chloride added after one-half hour dyeing and the dyed fabric oxidized with 1% sodium perborate at 120° F.

(B)

	Percent
Colcosol Jade Green NP Supra Dbl. Paste	2
Hydrosulfite	.75
Sodium Hydroxide (50%)	1.5

Dyed for one hour at 150°-160° F. and then oxidized with sodium perborate at 120° F.

(C)

	Percent
Chromocitronine R	2
Urea	8

Dyed for one hour at 170°-180° F.

(D)

	Percent
Procion Red H3B	2
Urea	8

Dyed for one hour at 190°-200° F.

Uniform dyeings were obtained in each case.

Example XX

An acrylic fabric (Orlon) was pretreated with the pretreating solution employed in Example I, and the thus treated fabric cured for 2 minutes at 300°-310° F. It was then dyed with Procion Brilliant Red H3B by immersing swatches in a 1% dye solution.

Another sample was dyed with So-Dye-Sul., Liquid Brown HFCF. The results were good; uniform dyeings were produced of good color fastness.

Example XXI

An acrylic fabric (Orlon, about 3 yards per pound) was pretreated as in Example I and dyed with the reactive dyes Remazol Black B, Remazol Red Violet R,

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Cibacron Brilliant Orange G and Procion Brilliant Red H3B as in Example I under the heading "A. Reactive Dyes." Thereafter a white dischargeable paste (sodium formaldehyde sulfoxylate, suitably thickened) was printed on the dyed fabric. The printed goods were then dried and steamed, producing attractive pattern effects in which the ground color was removed and contrasting discharge effects in the printed areas.

Similar effects were obtained by dyeing with chrome colors Chromocitronine R, Panduran Green G, Novochrome Blue CW, Novochrome Brilliant Orange GW, Panduran Blue B, printing with a discharge paste, drying, and steaming.

Example XXII

- 15 Polyester yarn (Dacron) was immersed in a bath of the pretreating solution described in Example I, cured for 2 minutes at about 310° F., and then dyed with Calcoloid Jade Green NC (a vat dye); another pretreated sample of the yarn was dyed with the reactive dye 20 Cibacron Yellow R. In both cases uniform dyeings of good color fastness resulted.

Example XXIII

- 25 A fabric consisting of 65% Dacron and 35% cotton (about 4 yards per pound) was pretreated as in Example I. It was then dyed at 180° F. on a conventional jig containing 1% Chromocitronine R (chrome color) for one and a half hours, and thereafter dried by passage 30 over steam cans. A uniform fast yellow fabric resulted.

Example XXIV

A glass-fiber fabric (5 ounces per square yard) was pretreated with the pretreating solution employed in Example I and the thus treated fabric dried and cured for 2 minutes at about 300° F. It was then printed in a conventional fabric printing machine using a printing paste containing 1% Remazol Black R (reactive dye, 1 ounce per gallon), water (20 ounces per gallon) and emulsion thickener (the rest of the paste). The goods were then dried, steamed, washed with soap solution, and dried. The color was uniform, well defined and fixed in the printed areas.

Example XXV

This example involved the dyeing of a heat cleaned glass fiber fabric which was pretreated with a solution containing

	Percent
Deacetylated chitin	2
Itaconic acid	2.5
Paraaminobenzoato chromic chloride	3
Water	92.5

The wet pick up was about 20%. The wet swatches were dried in a drying can and cured for two minutes at 300° to 310° F.

The thus treated swatches were then dyed with

- (A) 6% So-Dye-Sulfur Liquid Brown AFCF (Sulfur Dye)
 60 (B) 3% Metrovat Jade Green Dbl. Paste (Vat Dye)
 (D) 2% Novochrome Brill. Orange (Chrome Dye)
 (D) 1.5% Lumicrease Green 3LB Con. (100% Direct Dye Color)
 (E) 2% Neolan Violet 7R (Acid Dye)
 65 (F) 2% Procin Red H3B (Reactive Dye)

Uniform dyeings were obtained in each case.

- In example I and Examples XVI to XXV, the substitution of beta-resorcyloato, glycinato, tannato (where dark colors are desired), glycolato, thioglycolato, or sorbato chromic chloride for the p-aminobenzoato chromic chloride gives good results although not as good as is obtained by the use of the pretreating solution containing the p-aminobenzoato chromic chloride. The combination 70 of these other chromic chlorides with the acid salts of

deacetylated chitin gives far better dyeing and printing results than were obtainable by prior known techniques.

The substitution of other water-soluble salts of the deacetylated chitin, particularly the itaconic acid salt, for the acetic acid salt used in Examples I to XXV, inclusive, gives good, fast, uniform dyeings and printings.

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 film, fabric, yarn and fiber materials to render them dye receptive, which process comprises treating said material with an aqueous solution of a Werner-type reactive chromium complex and a water-soluble deacetylated chitin in the proportions of from 1 to 6 parts by weight of said water-soluble deacetylated chitin to 1 to 6 parts by weight of the chromium complex, and heating the thus treated material to produce a layer of the reaction product of said Werner-type reactive chromium complex and the deacetylated chitin on said material.

2. The process of conditioning film, fabric, yarn and fiber materials to render them dye receptive, which process comprises treating said material with an aqueous solution of a chromium chloride complex from the group consisting of p-aminobenzoato, beta-resorcylo, glycinato, tannato, glycolato, thioglycolato, and sorbato chromium chlorides and a water-soluble deacetylated chitin in the proportions of from 1 to 6 parts by weight of said water-soluble deacetylated chitin to 1 to 6 parts by weight of the chromium complex, drying and thereafter heating the thus treated material to produce a layer of the reaction product of said chromium chloride complex and said deacetylated chitin on said material.

3. The process as set forth in claim 2, in which the material after application of said solution is dried, heated to a temperature of from 200° F. to 350° F. for 1 to 5 minutes and the dye is applied to the heated material.

4. The process of conditioning difficultly dyeable fabrics for reception of dyes, which comprises applying to said fabrics an aqueous solution containing a chromium chloride complex from the group consisting of p-aminobenzoato, beta-resorcylo, glycinato, tannato, glycolato, thioglycolato, and sorbato chromium chlorides and a water-soluble deacetylated chitin in the proportions of from 1 to 6 parts chromium complex to 1 to 6 parts of the water-soluble deacetylated chitin followed by drying and heating the thus treated fabric to a temperature of from 200° F. to 350° F.

5. The process as defined in claim 4, in which the chromium complex is p-aminobenzoato chromic chloride.

6. The process as defined in claim 4, in which the chromium complex is p-aminobenzoato chromic chloride, the water-soluble deacetylated chitin is the acetic acid salt of deacetylated chitin, and the treated fabric is heated to a temperature of from 300° F. to 310° F. for about 2 minutes.

7. The process as defined in claim 4, in which the chromium complex is p-aminobenzoato chromic chloride, and the water-soluble deacetylated chitin is the itaconic acid salt of deacetylated chitin.

8. The process of conditioning difficultly dyeable yarns for dyeing, which comprises applying to said yarns an aqueous solution containing a chromium complex from the group consisting of p-aminobenzoato, beta-resorcylo, glycinato, tannato, glycolato, thioglycolato, and sorbato chromium chlorides and a water-soluble deacetylated chitin in the proportion of 1 to 6 parts chromium complex to 1 to 6 parts of the water-soluble deacetylated chitin followed by drying and heating the thus treated yarn to produce a layer of the reaction product of said chromium chloride complex and the deacetylated chitin on said yarn.

9. The process as defined in claim 8, in which the chromium complex is p-aminobenzoato chromic chloride.

10. The process as defined in claim 8, in which the chromium complex is p-aminobenzoato chromic chloride, and the water-soluble deacetylated chitin is the acetic acid salt of deacetylated chitin.

11. The process as defined in claim 8, in which the chromium complex is p-aminobenzoato chromic chloride, and the water-soluble deacetylated chitin is the itaconic acid salt of deacetylated chitin.

12. The process of conditioning a material from the group consisting of fabrics and yarns containing glass fibers for dyeing or printing, which process comprises applying to said material an aqueous solution of a chromium complex from the group consisting of p-aminobenzoato, beta-resorcylo, glycinato, tannato, glycolato, thioglycolato, and sorbato chromium chlorides and a water-soluble deacetylated chitin in the proportions of from 1 to 6 parts of the chromium complex to 1 to 6 parts of the water-soluble deacetylated chitin, and thereafter drying and heating the thus treated material at a temperature of 200° F. to 350° F.

13. The process as defined in claim 12, in which the chromium complex is p-aminobenzoato chromic chloride.

14. The process as defined in claim 12, in which the chromium complex is p-aminobenzoato chromic chloride, the water-soluble deacetylated chitin is the acetic acid salt of deacetylated chitin, and the thus treated material is heated to a temperature of 300° F. to 310° F. for about 2 minutes.

15. The process as defined in claim 12, in which the chromium complex is p-aminobenzoato chromic chloride, the water-soluble deacetylated chitin is the itaconic acid salt of deacetylated chitin, and the thus treated material is heated to a temperature of 300° F. to 310° F. for about 2 minutes.

16. The process of conditioning polypropylene for dyeing or printing, which process comprises applying to the polypropylene an aqueous solution of a chromium complex from the group consisting of p-aminobenzoato, beta-resorcylo, glycinato, tannato, glycolato, thioglycolato, and sorbato chromium chlorides and a water-soluble deacetylated chitin in the proportions of from 1 to 6 parts of the chromium complex to 1 to 6 parts of the water-soluble deacetylated chitin, and thereafter drying and heating the thus treated polypropylene at a temperature of 240° F. to 290° F.

17. The process as defined in claim 16, in which the chromium complex is p-aminobenzoato chromic chloride.

18. The process as defined in claim 16, in which the chromium complex is p-aminobenzoato chromic chloride, the water-soluble deacetylated chitin is the acetic acid salt of deacetylated chitin, and the thus treated material is heated to a temperature of 240° F. to 290° F. for 1 to 5 minutes.

19. A material from the group consisting of films, fabrics, yarns and fibers, said material having bonded to its surface a reaction product of a Werner-type reactive chromium complex and a water-soluble deacetylated chitin in the proportions of from 1 to 6 parts by weight of said water-soluble deacetylated chitin to 1 to 6 parts by weight of the chromium complex, whereby the so-bonded material has an affinity for dyestuffs.

20. The material specified in claim 19 in which the reaction product is the reaction product of p-aminobenzoato chromic chloride and the acetic acid salt of deacetylated chitin.

21. A glass fiber material having bonded to its surface the reaction product of a Werner-type reactive chromium complex and a water-soluble deacetylated chitin in the proportions of from 1 to 6 parts by weight of said water-soluble deacetylated chitin to 1 to 6 parts by weight of the chromium complex, whereby the so-bonded glass fiber material has an affinity for dyestuffs.

22. A glass fiber material as defined in claim 21 in which the reaction product is the reaction product of

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p-aminobenzoato chromic chloride and the acetic acid salt of deacetylated chitin.

23. Polypropylene having bonded to its surface the reaction product of a Werner-type reactive chromium complex and a water-soluble deacetylated chitin in the proportions of from 1 to 6 parts by weight of said water-soluble deacetylated chitin to 1 to 6 parts by weight of the

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chromium complex, whereby the so-bonded polypropylene has an affinity for dyestuffs.

24. Polypropylene as defined in claim 23 in which the reaction product is the reaction product of p-aminobenzoato chromic chloride and the acetic acid salt of deacetylated chitin.

No references cited.

UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 3,023,072

February 27, 1962

Jan Dabrowski

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, lines 37 and 38, strike out "polyperature, i.e., at lower temperatures" and insert instead -- propylene fabrics, at a rate such that --; column 4, line 59, for "Liquid Green BGCR" read -- Liquid Green BGCF --; column 5, line 3, for "Caloloid" read -- Calcoloid --; line 50, for "AS-RL-G.I." read -- AS-RL-C.I. --; column 7, line 21, for "concentrations" read -- concentration --; line 63, after "Yellow" insert -- CCD --; column 8, line 2, for "cleate" read -- oleate --; column 10, line 1, for "Brililant" read -- Brilliant --; line 39, before "water" insert -- urea (10 ounces per gallon), --; line 61, for "(D)" read -- (C) --; line 65, for "Procin" read -- Procion --.

Signed and sealed this 26th day of June 1962.

(SEAL)

Attest:

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