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PROCESS FOR THE PRODUCTION OF COLORED CELLULOSE TRIACETATE MATERIAL AND BLENDS THEREOF WITH POLYACRYLONITRILE

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No Drawing. Continuation-in-part of application Ser. No. 278,484, May 6, 1963. This application Dec. 11, 1964, Ser. No. 417,762
Claims priority, application Switzerland, Apr. 26, 1963, 5,296/63; May 2, 1963, 5,507/63
15 Claims. (Cl. 8—21)

ABSTRACT OF THE DISCLOSURE

A process is provided for producing colored cellulose acetate fiber material, polyacrylonitrile type fiber material and blended fabrics consisting essentially of these two types of fibers or blends of polyacrylonitrile type fibers with staple rayon. Padding liquors or printing pastes are also provided. The process comprises padding the fiber material with a thickened padding liquor or printing the material with a printing paste which contains at least one water-soluble acid wool dyestuff, at least one mono- or poly-nuclear aromatic compound which is substituted at the aromatic ring by a functional group containing oxygen, an amide of a thiocarbon-derived acid, and thickener, as well as, if desired, other conventional additives, and steaming the resultant impregnated or printed goods.

This is a continuation-in-part of our pending application Serial No. 278,484, filed May 6, 1963, now abandoned.

The present invention concerns a process for the production of colored cellulose acetate fiber material, polyacrylonitrile type fiber material, and blended fabrics consisting essentially of the aforesaid two types of fibers or of blends of polyacrylonitrile type fibers with staple rayon, and the padding liquors or printing pastes used for this purpose as well as, as industrial product, the fabric so dyed or printed.

In a preferred aspect the present invention concerns a process for the pad-dyeing or printing of cellulose triacetate fiber materials.

We have found that hitherto known carriers used in the pad-dyeing and printing of cellulose acetate fibers—by which fibers the art understands secondary cellulose acetate, more exactly 2½-acetate—with water-insoluble dispersion dyestuffs fail when applied to cellulose triacetate.

Up to the present it has been necessary to use water-insoluble dispersion dyestuffs in order to obtain dyeings or prints on cellulose triacetate in sufficiently strongly colored and level shades.

A process has now been found, whereby prints can be obtained on the above-listed textile materials with acid, water-soluble wool dyestuffs. This process has the advantage of giving a much greater choice of dyestuffs, as the class of wool dyestuffs is much more comprehensive than that of dispersion dyestuffs. In addition, the dyeings of prints obtained according to the invention are in no way inferior in their color strength and just as level as those obtained with dispersion dyestuffs. Ineed, some of their fastness properties exceed those of dyeings and prints obtained with dispersion dyestuffs. Among these fastness properties are especially wet fastnesses, i.e. to washing, perspiration, sea water, alkaline media, moreover fastness to sublimation, to many organic solvents and to gas fumes.

The process according to the invention comprises padding the cellulose acetate fiber material or other above-listed textile materials with a thickened padding liquor or printing the aforesaid material with a printing paste which contains at least one water-soluble acid wool dyestuff, at least one mono- or poly-nuclear aromatic compound which is substituted at the aromatic ring by a functional group containing oxygen, an amide of a thiocarbon-derived acid as defined below, and thickener, as well as, if desired, other additives conventional in the textile industry, and steaming the resulting impregnated or printed goods.

The thickened padding liquor or printing paste contains, as aromatic functional oxygen compounds usable as defined, especially, in the preferred mode of carrying out the process according to the invention in practice, either a carbocyclic aryl compound with from one to two preferably unfused six-membered rings, exclusively substituted with at least one substituent, and preferably one to two substituents Y, each Y being, independently, —OH, or —CHO, or —COOH, or a carbocyclic aryl compound with from one to two preferably unfused six-membered rings, exclusively substituted at the same time with at least one substituent defined as Y above, and at least one other substituent Z which is chlorine, bromine, amino, nitro or lower alkyl; for example, aromatic hydroxyl compounds, and more in particular, for use in the coloring of cellulose triacetate staple fibers or stretched filaments, and in the case of polyacrylonitrile fibers, phenols such as phenol, cresols, xylenols, resorcin or p-phenylphenol; aromatic aldehydes, particularly those of the benzene series such as benzaldehyde, chlorobenzaldehyde, salicylaldehyde, cresotinaldehyde or chlorosalicylic aldehyde; and preferably substituted aromatic carboxylic acids such as chlorobenzoic acid, bromobenzoic acid, aminobenzoic acid, nitrobenzoic acid, salicylic acid or cresotinic acid and in the case of cellulose triacetate staple fibers also benzoic acid; or mixtures of these compounds, such mixtures, especially those of one of the above aromatic carboxylic acids with a phenol, especially resorcin, preferably in a ratio of 1:2 to 1:10 affording particularly favorable results.

The term "amide of a thiocarbon-derived acid" as used herein means amides optionally substituted at the amino-nitrogen atom and, as the case may be, in several tautomeric forms, as well as corresponding hydrazides and imides of organic thiocarboxylic acids, furthermore the corresponding amide derivatives, and tautomers thereof, of mono- and di-thiocarbonic acids inclusive of imides and nitriles derived from hypothetical ortho-acids of this class, in particular of ortho-thiocarbonic acids.

As such amides of a thiocarbon-derived acid, the padding liquor or printing paste contains, for example, thioamides of carboxylic acids such as thioacetamides, N-methyl- or N-ethyl- or N-hydroxyethyl-thioacetamide, or amide-type derivatives of thiocarbonic acid such as thiourea or isothiourea which may be substituted at the nitrogen or sulfur atom, alkyl and hydroxyalkyl groups containing preferably not more than 4 carbon atoms being used in particular as nitrogen or sulfur substituents, or thiosemicarbazide, also optionally N-lower alkyl substituted thiuram mono- and di-sulfides such as tetra-lower alkyl thiuram mono- or di-sulfide or water-soluble salts, in particular alkali metal or ammonium salts and especially lower alkyl-ammonium salts of thiocyanic or thioisocyanic acids. Thiourea is preferred, since particularly deep dyeings or prints on cellulose triacetate are obtained therewith.

Water-insoluble amides such as the above-mentioned tetra-alkyl-thiuram disulfides are preferably used finely

dispersed, as a suspension or emulsion in an inorganic solvent such as ethanol.

The padding liquor or printing paste used according to the invention thus contains the aromatic functional oxygen compounds as defined and the amide of thiocarbon-derived acid in amounts of, together, about 50 to 250 g., preferably in amounts of about 150 g. per kilogram liquor or paste.

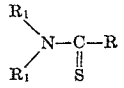
In a preferred mode of carrying out the process according to the invention, padded or printed cellulose triacetate fabrics are produced by

(I) applying to at least a portion of the entire surface, i.e. either by printing or by padding, of a cellulose acetate material or polyacrylonitrile type fiber material, especially of cellulose triacetate fabric, a coloring mixture which consists essentially of

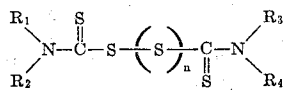
(1) a water-soluble acid wool dyestuff, in amounts of 5 to 120 grams per kilogram (g./kg.) of the mixture;

(2) thickener as defined hereinafter, in amounts of at least about 150 up to about 600 g./kg. of the mixture;

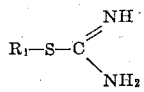
(3) the amido-type compound derived from a thiocarbon-derived acid, namely a member selected from the group consisting of a compound of the formula



a compound of the formula



a compound of the formula



wherein

each of R_1, R_2, R_3 and R_4, independently, is a member selected from the group consisting of lower alkyl and hydroxy-lower alkyl,

R is a member selected from the group consisting of lower alkyl and hydrazino,

n is an integer ranging from 0 to 1; and, preferably, thiourea, in amounts of about 40 to 120 g./kg. of the mixture;

(4) A fixing component which is made up of the following:

(α) the aromatic compound having a functional oxygen-containing substituent or substituents, preferably

a member selected from the group consisting of phenol, pyrocatechol, resorcinol, phloroglucinol, benzaldehyde substituted with a substituent Z, benzoic acid substituted by a substituent Z, and naphthoic acid substituted by a substituent Z, and phenol substituted with a substituent X, wherein X is a member selected from the group consisting of from one to three lower alkyl groups and phenyl, and

Z is a member selected from the group consisting of —OH, —CHO, —Cl, —Br, —NO_2, —NH_2, lower alkyl, but optimally resorcinol; (α) amounting to about one-third to one-half of the fixing component, by weight,

(β) an organic solvent for the aforesaid components (1), (2), (3), and (4) (α), which is a mixed solvent comprising preferably a saturated aliphatic thio-alcohol such as thiodiethylene glycol, amounting to about one third of the fixing component, and the balance of the fixing component, which balance consists of a lower alkanol, preferably ethanol and/or benzyl alcohol, as solvent, the total fixing component amounting to from about 100 to 300 g./kg. of the mixture,

the balance of the coloring mixture consisting of water; and

(II) steaming the resulting colored fabric with saturated steam at 0.2 to maximally about 2 atmospheres excess pressure and corresponding temperatures of about 100° C. and higher for about 5 to 30, and preferably 10 to 20 minutes.

The resulting padded or printed products are then rinsed as described further below and dried.

"Lower" used in connection with an aliphatic radical means that the radical has maximally 4 carbon atoms.

The weight ratio of the aromatic functional oxygen compounds to that of the amides and other thio compounds mentioned is about 4:1 to 1:4 and preferably about 2:1 to 1:2, optimal results being obtained with a ratio of about 1:2.

As thickener, the liquor or paste contains, for example, the disaggregated types of gum usual in the textile industry, for example the so-called "crystal gum" or thickeners based on cellulose such as carob bean flour, tragacanth, British gum or alkali metal alginates or cellulose derivatives such as methyl cellulose or soluble salts of carboxymethyl cellulose.

The padding liquor or printing paste can contain, for example, acids, in particular, low fatty acids such as formic, and mainly acetic acid; or organic solvents such as alcohols, e.g. methanol, ethanol, benzyl alcohol, ethylene glycol, thiodiethylene glycol, glycerin; or mixtures of such compounds as further additives usual in the textile industry.

"Acid wool dyestuff" as used in this specification and in the appended claims means dyestuffs, the colored anions of which draw on wool from hot, acid, aqueous solution and comprises also those of the aforesaid dyestuffs which do so already from their neutral solution.

The acid wool dyestuffs in the padding liquor or printing paste used according to the invention can be of the most varied classes of dyestuffs. Advantageously they are the technically proved dyestuff classes of the azo, anthraquinone, phthalocyanine, nitro, formazan or triphenylmethan dyestuffs which may also contain metals such as copper, nickel, chromium or cobalt. As azo dyestuffs, mainly monoazo dyestuffs are used, e.g. those of the type benzene-azo-hydroxy-benzene, benzene-azo-aminobenzene, benzene-azo-hydroxynaphthalene, naphthalene-azo-hydroxy-naphthalene, benzene-azo-amino-naphthalene, benzene-azo-hydroxypyrazole, benzene-azo-aminopyrazole, benzene-azo-acyloacetylarylamide or those of the analogous naphthalene-azo and heterocycle-azo types. By "heterocycle" are meant those having five or six ring members, in particular containing nitrogen such as thiazoles, imidiazoles, triazoles, tetrazoles, oxdiazoles, thiadiazoles, pyridines, pyrimidines, benzthiazoles, benzimidazoles, benztriazoles, indazoles, quinolines. Acid wool dyes from the class of polyazo dyestuffs can also be used. The azo dyestuffs can be metallized, chiefly by chromium or cobalt, the formazan and phthalocyanine dyes preferably by copper or nickel. Particularly favorable results are attained with heavy metal-containing azo dyestuffs, preferably (—SO_3H)-free chromium or cobalt containing monoazo dyestuffs, which contain one metal atom bound to two molecules of azo dyestuffs.

The pH-value of the liquors and pastes according to the invention should be below 7, preferably in the range of 3.5 to 7, depending on the dyestuff used. This pH can be adjusted by adding a corresponding small amount (not more than 1% calculated on the weight of the liquor or bath) of benzoic acid.

As textile materials which can be padded or printed by the process according to the invention, optimal results are obtained on cellulose triacetate fabric which is therefore preferred, which very satisfactory dyeings and prints are also obtained on other cellulose acetate fibers such as cellulose diacetate or cellulose 2½-acetate, and also on polyacrylonitrile type fibers, by which term there are understood polyacrylonitrile fibers and fibers consisting of copolymers obtained from acrylonitrile and up to 30% by weight of another monomer copolymerizable with acrylonitrile, examples of which other monomers are

given, for instance in Canadian Patent 557,597, issued on May 20, 1958, to The Chemstrand Corporation, Decatur, Ala., and in U.S. Patents 2,837,500; 2,837,501 and 3,096,-139. Moreover, blended fabrics as described hereinbefore can also be used with satisfactory results.

It should, however, be borne in mind that the process according to the invention is destined primarily for the dyeing and printing of cellulose triacetate. The strength of the fibers of normal cellulose acetate (2½ acetate) may suffer when such fibers are dyed or printed according to this process.

The cellulose triacetate material is treated with the padding liquor or printing paste by the usual methods. The padded or printed goods are steamed in the known manner and then rinsed, e.g. with cold or warm water which can contain the additives usual in the textile industry, e.g. wetting or wash-active substances. Beautiful dyeings or prints of good color strength are attained.

The following examples serve to illustrate the invention. The temperatures are given in degrees centigrade. Where not otherwise expressly stated, parts and percentages are by weight. The relationship of parts by weight to parts by volume is as that of grams to cubic centimeters. C.I. means "Colour Index," second edition, 1956, published by the Society of Dyers and Colourists, Bradford, England, and The American Association of Textile Chemists and Colorists, Lowell, Mass., U.S.A.

Example 1

80 grams (g). of thiourea are stirred into 500 g. of 25% crystal gum solution (e.g. NAFKAGUM 75, of Scholten, Foxhall, Netherlands) and the mixture is diluted with 260 ml. of water. A 60° warm solution of 50 g. of phenol in 80 g. of thiodiethylene glycol, 20 g. of benzyl alcohol and 30 g. of ethanol is added to this mixture.

30 g. of the dyestuff 2:1 chromium complex of 2-aminophenol-5-sulfonic acid amide→1-(4'-chlorophenyl)-3-methyl-5-pyrazolone are sprinkled into this so-called "stock thickener" while stirring well. The mixture obtained is made up to 1000 g. with water.

A fabric made of cellulose triacetate staple fiber is printed with the paste so obtained in the usual way and then steamed and washed.

A strongly colored brilliant red pattern is obtained on the fabric.

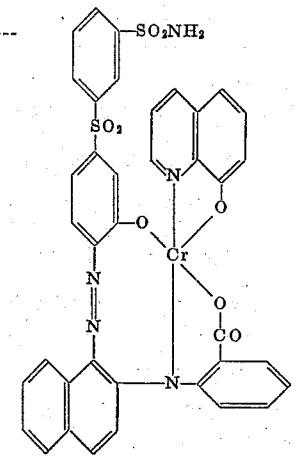
By using in the above example instead of the cellulose triacetate staple fabric another fabric, for example, of cellulose triacetate filament, or an acrylic fiber containing a blend of copolymers comprising 88 parts of a copolymer of 94% by weight of acrylonitrile and 6% by weight of vinyl acetate blended with 12 parts of a copolymer of 50% by weight of acrylonitrile and 50% by weight of methylvinylpyridine, similar satisfactory red prints are obtained.

Prints having similar properties are obtained when the above example is repeated but using, instead of the 80 g. of thiourea and the 50 g. of phenol, the combination of components given below (in amounts of g. per kg. of printing paste):

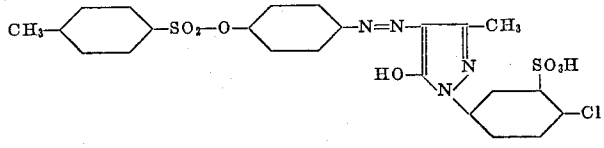
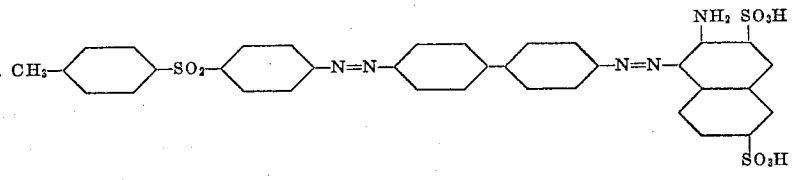
Example	Aromatic functional oxygen compound	Amide of thiocarbon-derived acid
2	50 g. resorcinol dissolved in 50 g. of water.	80 g. thiourea.
3	50 g. pyrocatechol	100 g. thiourea.
4	50 g. phloroglucinol	Do.
5	50 g. p-chloro-benzoic acid	Do.
6	50 g. o-amino-benzoic acid	Do.
7	50 g. p-phenyl-phenol	Do.
8	50 g. resorcinol dissolved in 50 g. water.	100 g. tetramethylthiuram-disulfide.
9	do	100 g. thioacetamide.
10	60 g. o-nitro-benzoic acid	Do.
11	60 g. salicylic acid	100 g. thiourea.
12	50 g. benzaldehyde	Do.
13	50 g. resorcinol dissolved in 50 g. water.	80 g. ethyl isothiourea (for dyestuff see following table).
14	do	90 g. thiosemicarbazide (for dyestuff see following table).

When Example 1 is repeated, but instead of the dyestuff mentioned therein, the same amounts of the dyestuffs given in column II of the following table are used, then colored patterns of similar quality are obtained on cellulose triacetate fabric which have the shades given in column III below:

TABLE

I Example No.	II Dyestuff used	III Shade on cellulose triacetate
15	The anthraquinone dyestuff described in Example 8 of German Patent 631,518	Blue.
16	The monoazo dyestuff: 2-diazo-benzene-1-sulfonic acid phenol ester→2-amino-8-hydroxy-naphthalene-6-sulfonic acid.	Red.
17	The 2:1 chromium complex described in Example 2 of U.S. Patent 2,714,102	Yellow.
18	The 2:1 cobalt complex described in Example 2 of U.S. Patent 2,738,345	Do.
19	The 2:1 chromium complex described in Example 2 of U.S. Patent 2,730,522	Orange.
20	The mixed 2:1 chromium complex described in Example 4 of U.S. Patent 2,826,572	Red.
21	The 2:1 cobalt complex described in the Table No. 14 of U.S. Patent 2,817,655	Ruby.
22	The 2:1 cobalt complex dyestuff: 2-diazo-4-propylsulfonyl-phenol→2-hydroxy-naphthalene	Bordeaux.
23	The 2:1 chromium complex described in the Table No. 13 of U.S. Patent 2,817,655	Violet.
24	The 2:1 chromium complex described in Example 1 of the U.S. Patent 2,723,263	Blue.
25	The 2:1 chromium complex dyestuff: 2-aminophenol-4-sulphonic acid amide→1-hydroxy-5,8-dichloro-naphthalene.	Navy blue.
26	The 2:1 chromium complex described in Example 1 of the U.S. Patent 2,551,056	Golden yellow.
27		Green.

TABLE—Continued

I Example No.	II Dyestuff used	III Shade on cellulose triacetate
28	The mixed 2:1 chromium complex described in Example 1 of the U.S. Patent 2,711,404	Brown.
29	The 2:1 chromium complex described in Example 1 of the U.S. Patent 2,829, 140	Dark brown.
30	The 2:1 chromium complex described in Example 8 of the U.S. Patent 2,551,056	Grey.
31	4,4'-bis-(o-diazophenyl-sulphonyloxy)-diphenyl-methane→1-phenyl-3-methyl-5-aminopyrazole-4'-sulphonic acid (2 equivalents).	Yellow.
32	4,4'-bis-(o-diazophenyl-sulphonyloxy)-diphenyl-methane→2-aminonapthalene-5-sulphonic acid (2 equivalents).	Orange.
33	4,4'-bis-(o-diazophenyl-sulphonyloxy)-diphenyl-methane→2-amino-5-hydroxynaphthalene-6-sulphonic acid (2 equivalents, acid coupling).	Red.
34	The 2:1 chromium complex described in Example 4 of the U.S. Patent 2,830,980	Yellowish red.
35	The 2:1 chromium complex described in Example 1 of the English Patent 823,945	Blue.
36	The 2:1 chromium complex described in Example 2 of the Swiss Patent 330,129	Green.
37	The 2:1 chromium complex described in Example 2 of the U.S. Patent 2,891,939	Dark green.
38	The 2:1 cobalt complex described in Example 2 of the U.S. Patent 2,829,140	Reddish brown.
39	C.I. Acid Black 48 (No. 65'005)	Bluish grey.
40	The 2:1 chromium complex described in Example 11 of U.S. Patent 2,551,056	Black.
41	The monoazo and disazo chromium mixed complex described in Example 5 of the Canadian Patent 579,201	Do.
42	The monoazo dyestuff described in Example 2 of the U.S. Patent 2,773,055	Yellow.
43	The disazo dyestuff described in Example 5 of the French Patent 1,150,719	Orange.
44	The disazo dyestuff: 2,2'-bis-diazo-4,4'-dichloro-diphenyl-sulfide→2-amino-8-hydroxy naphthalene sulfonic acid.	Red.
45	C.I. Acid Yellow 117 (No. 24'820)	Yellow.
46	C.I. Acid Yellow 40 (No. 18'950)	Do.
47	The monoazo dyestuff: 	Do.
48	C.I. Acid Red 155 (No. 18'130)	Red.
49		Orange.
50	C.I. Acid Red 114 (No. 23'635)	Red.
51	C.I. Acid Blue 150 (No. 61'130)	Blue.
52	C.I. Acid Blue 127 (No. 61'135)	Brilliant blue.
53	C.I. Acid Black 47 (No. 56'055)	Grey.
54	C.I. Acid Orange 3 (No. 10'385)	Orange.
55	The monozao dyestuff: 2-diazo-benzoic acid→1-(2',5'-dichloro-3'-sulfophenyl)-3-methyl-5-pyrazolone	Yellow.
56	C.I. Acid Orange 7 (No. 15'510)	Orange.
57	C.I. Acid Red 52 (No. 45'100)	Brilliant red.
58	C.I. Acid Violet 24 (No. 44'055)	Reddish blue.
59	C.I. Acid Violet 15 (No. 43'525)	Blue.
60	C.I. Acid Blue 47 (No. 62'085)	Do.
61	C.I. Acid Blue 41 (No. 62'130)	Do.
62	C.I. Acid Blue 62 (No. 62'045)	Do.
63	C.I. Acid Red 73 (No. 27'290)	Scarlet.
64	C.I. Acid Blue 59 (No. 50'315)	Blue.
65	C.I. Acid Blue 102 (No. 50'320)	Do.
66	C.I. Acid Yellow 65 (No. 14'170)	Yellow.
67	C.I. Acid Red 88 (No. 15'620)	Red.
68	C.I. Acid Brown 6 (No. 14'625)	Reddish brown.
69	C.I. Acid Blue 9 (No. 42'090)	Blue.
70	C.I. Acid Green 9 (No. 42'100)	Green.
71	The first cupriferous formazane dye-stuff described in Example 2 of Belgian Patent 603,740	Blue.
72	The first cupriferous formazane dye-stuff described in Example 6 of Belgian Patent 603,740	Do.
73	The fourth cupriferous formazane dye-stuff described in Example 7 of Belgian Patent 603,740	Do.
74	The nickeliferous formazane dye-stuff described in Table II, No. 4 of Belgian Patent 603,740	Violet-brown.
75	C.I. Acid Blue 25 (No. 62'055)	Blue.
76	Copper phthalocyanine disulfonic acid	Turquoise.
77	Nickel phthalocyanine disulfonic acid	Turquoise blue.
78	The second 2:1 chromium complex dyestuff described in Example 5 of U.S. Patent 2,551,056	Bluish red.
79	The monoazo dyestuff:2-diazo-diphenyl-sulfone-3'-sulfonic acid→5-amino-3-methyl-1-(3'-chlorophenyl)-pyrazole.	Yellow.
80	The monoazo dyestuff:2-diazo-1-hydroxy-benzene-4,6-disulfonic acid→1,3-diamino benzene (after-treated with chromium).	Brown.

Example 81

20 g. of the dyestuff 2:1 chromium complex of 2-amino-1-hydroxybenzene-4-sulfonic acid amide→1-(4'-chlorophenyl)-3-methyl-5-pyrazolone are mixed with 10 g. of benzoic acid and 80 g. of thiourea; the mixture is pasted with 70 g. of a solution consisting of 35 g. of thiodiethylene glycol, 14 g. of benzyl alcohol and 21 g. of ethanol. The mixture is then dissolved in 250 g. of hot water and then stirred into 350 g. of a ready-for-use 5%-alginate thickener prepared by dissolving 50 g. of sodium alginate powder in 1 liter of water. A solution of 50 g. resorcinol in 50 g. of water is then added to this paste and finally the whole is made up to 1000 g. with water.

A fabric made from cellulose triacetate stretched filament is printed in a conventional manner with the paste thus prepared, dried at about 100° and then steamed with dry saturated steam in a continuous steaming apparatus of the Mather-Platt type for 8 to 16 minutes or in a star steamer at 0.2 to 0.8 atmospheres gauge pressure for 10 to 15 minutes.

After steaming, the fabric is rinsed first in cold and then in hot water, then soaped at the boil with an aqueous solution of 1 to 2 g. liter of a non-ionogenic washing agent and finally dried.

A strongly colored golden yellow print is obtained which is fast to washing at the boil, sublimation and light.

Example 82

20 g. of the dyestuff 2:1 chromium complex of 2-amino - 1 - hydroxybenzene-5-ethyl sulfone→1-phenyl-3-

methyl-5-pyrazolone are thoroughly mixed with 80 g. of thiourea and 10 g. of benzoic acid and the mixture is pasted with 70 g. of a solution consisting of 35 g. of thiodiethylene glycol, 14 g. of benzyl alcohol and 21 g. of ethanol. The mixture is then dissolved in 250 g. of hot water and the solution is stirred into 350 g. of a previously prepared, ready-for-use 5%-sodium alginate thickener. A mixture of 35 g. of resorcinol in 35 g. of water is then added to this paste which is finally made up to 1000 g. with water while stirring.

A fabric of cellulose tri-acetate staple fiber is printed in a conventional manner with the paste so prepared, dried at 100° and then steamed with dry saturated steam in a continuous steaming apparatus of the Mather-Platt type for 8 to 10 minutes.

After steaming, the fabric is rinsed first in cold and then in hot water, then soaped at 40 to 50° with an aqueous solution of 1 to 2 g./liter of a non-ionogenic washing agent and dried.

A strongly colored red print is obtained which is fast to washing and sublimation.

Similarly good results are obtained when employing in the above example a blended fabric consisting of 50% by weight of the polyacrylonitrile type fibers used in the second part of Example I and 50% by weight of cellulose triacetate fibers.

Example 83

30 g. of the dyestuff 4-(2',4'-dinitro-1-anilino)-1,1'-diphenylamine-2-sulfonic acid are mixed with 80 g. of thiourea and 10 g. of benzoic acid and the mixture is pasted with 70 g. of a solution consisting of 35 g. of thiodiethylene glycol, 14 g. of benzyl alcohol and 21 g. of ethanol. The mixture is then dissolved in 250 g. of hot water and stirred into 350 g. of a previously prepared, ready-for-use 5%-sodium alginate thickener. A mixture of 50 g. of resorcinol in 50 g. of water is then added to this paste which is finally made up to 1000 g. with water.

Polyacrylonitrile fabric is printed in the usual way with the paste so prepared, dried and then steamed with dry saturated steam in a continuous steaming apparatus of the Mather-Platt type for 8 to 16 minutes or in a star steamer at 0.2 to 0.3 atmospheres gauge pressure for 10 to 15 minutes. After steaming, the fabric is rinsed in cold and then in warm water, soaped at 60° with an aqueous solution of 1 to 2 g./liter of a non-ionogenic washing agent and then dried.

A strongly colored dark golden yellow print is obtained which is fast to washing and sublimation.

Similarly good results are obtained when employing in the above example a blended fabric consisting of 70% by weight of the polyacrylonitrile type fibers used in the second part of Example 1 and 30% by weight of staple rayon.

What we claim is:

1. A process for the production of a colored textile material comprising:

(I) applying to at least a portion of the entire surface of a fabric consisting essentially of a member of the group of cellulose triacetate stretched filament, cellulose triacetate staple fiber, a blend of cellulose triacetate fibers and polyacrylonitrile-type fibers, and a blend of staple rayon and polyacrylonitrile-type fibers, a mixture consisting essentially of

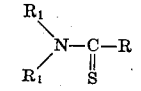
(a) an acid, water-soluble wool dyestuff;

(b) a member selected from the group consisting of phenol, pyrocatechol, resorcinol, phloroglucinol, benzaldehyde, benzaldehyde substituted with a substituent Z, benzoic acid substituted by a substituent Z, naphthoic acid substituted by a substituent Z, and phenol substituted with a substituent X, wherein

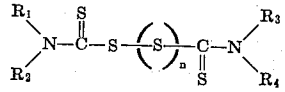
X is a member selected from the group consisting of from one to three lower alkyl groups and phenyl, and

Z is a member selected from the group consisting of —OH, —CHO, —Cl, —Br, —NO_2, —NH_2, lower alkyl;

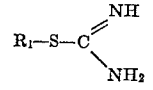
(c) a member selected from the group consisting of a compound of the formula



a compound of the formula



a compound of the formula



and thiourea; wherein

each of R_1, R_2, R_3 and R_4, independently, is a member selected from the group consisting of lower alkyl and hydroxy-lower alkyl,

R is a member selected from the group consisting of lower alkyl and hydrazino, and

n is an integer ranging from 0 to 1; and

(d) a thickener; and

(II) steaming the resulting colored fabric.

2. A process as described in claim 1, wherein step II is carried out under an excess pressure of about 0.2 to 2 atmospheres.

3. A process as described in claim 1, wherein steaming is carried out for from about 5 to 30 minutes.

4. A process as described in claim 1, wherein the entire surface of said fabric is colored by padding the same with said mixture.

5. A process as described in claim 1, wherein a part of the surface of said fabric is colored by printing the same with said mixture in a pattern.

6. A process as described in claim 1, wherein the member under (b) is p-chloro-benzoic acid.

7. A process as described in claim 1, wherein the member under (c) is thiourea.

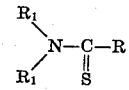
8. A process for the production of a colored textile material comprising:

(I) applying to at least a portion of the entire surface of a fabric consisting of a member of the group of cellulose triacetate stretched filament, cellulose triacetate staple fiber, a blend of cellulose triacetate fibers and polyacrylonitrile-type fibers, and a blend of staple rayon and polyacrylonitrile-type fibers, a mixture consisting essentially of

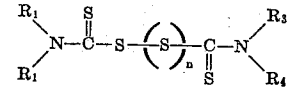
(a) an acid, water-soluble wool dyestuff,

(b) a mixture of benzoic acid and resorcinol in a weight ratio of about 1:2 to 1:5, the content of benzoic acid in said coloring mixture not exceeding substantially an amount of 1% by weight,

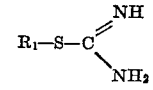
(c) a member selected from the group consisting of a compound of the formula



a compound of the formula



a compound of the formula



and thiourea; wherein

each of I_1, R_2, R_3 and R_4, independently, is a member selected from the group consisting of lower alkyl and hydroxy-lower alkyl,

R is a member selected from the group consisting of lower alkyl and hydrazino, and

n is an integer ranging from 0 to 1; and

(d) a thickener; and

(II) steaming the resulting colored fabric.

9. A mixture for padding and printing fabrics consisting essentially of

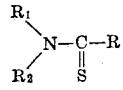
(a) an acid, water-soluble wool dyestuff;

(b) a member selected from the group consisting of phenol, pyrocatechol, resorcinol, phloroglucinol, benzaldehyde, benzaldehyde substituted with a substituent Z, benzoic acid substituted by a substituent Z and naphthoic acid substituted by a substituent Z, and phenol substituted with a substituent X, wherein

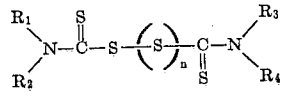
X is a member selected from the group consisting of from one to three lower alkyl groups and phenyl, and

Z is a member selected from the group consisting of —Cl, —Br, —NO_2, —NH_2 and lower alkyl;

(c) a member selected from the group consisting of a compound of the formula

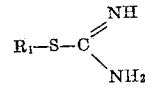


a compound of the formula



thiourea and

a compound of the formula



wherein

each of R_1, R_2, R_3 and R_4, independently, is a member selected from the group consisting of hydrogen, lower alkyl and hydroxy-lower alkyl,

R is a member selected from the group consisting of lower alkyl and hydrazino, and

n is an integer ranging from 0 to 1; and

(d) a thickener.

10. A mixture for padding and printing fabrics consisting essentially of, per kilogram of mixture,

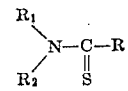
(a) from about 5 to 120 grams of an acid, water-soluble wool dyestuff,

(b) from about 30 to 150 grams of a member selected from the group consisting of phenol, pyrocatechol, resorcinol, phloroglucinol, benzaldehyde substituted with a substituent Z, benzoic acid substituted by a substituent Z and naphthoic acid substituted by a substituent Z, and phenol substituted with a substituent X, wherein

X is a member selected from the group consisting of from one to three lower alkyl groups and phenyl, and

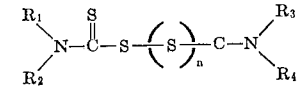
Z is a member selected from the group consisting of —Cl, —Br, —NO_2, —NH_2 and lower alkyl,

(c) from about 40 to 120 grams of a member selected from the group consisting of a compound of the formula

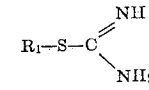


thiourea,

a compound of the formula



and a compound of the formula



wherein

each of R_1, R_2, R_3 and R_4, independently, is a member selected from the group consisting of hydrogen, lower alkyl and hydroxy-lower alkyl,

R is a member selected from the group consisting of lower alkyl and hydrazino, and

n is an integer ranging from 0 to 1; and

(d) from about 150 to 600 grams of a thickener, the balance being aqueous solvent.

11. A composition as defined in claim **10**, wherein component (b) is resorcinol and component (c) is thiourea.

12. Colored fabric of cellulose triacetate produced by the process defined in claim **1**.

13. A process for the production of a colored textile material selected from the group consisting of a padded and a printed polyacrylonitrile type fiber material, comprising:

(I) applying to at least a portion of the entire surface of a polyacrylonitrile fabric a mixture consisting essentially of

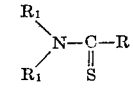
(a) an acid, water-soluble wool dyestuff,

(b) a member selected from the group consisting of phenol, pyrocatechol, resorcinol, phloroglucinol, benzaldehyde substituted with a substituent Z, benzoic acid substituted by a substituent Z and naphthoic acid substituted by a substituent Z, and phenol substituted with a substituent X, wherein

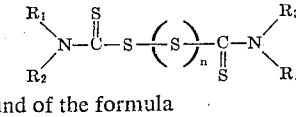
X is a member selected from the group consisting of from one to three lower alkyl groups and phenyl, and

Z is a member selected from the group consisting of —Cl, —Br, —NO_2, —NH_2 and lower alkyl,

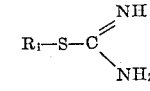
(c) a member selected from the group consisting of a compound of the formula



a compound of the formula



a compound of the formula



and thiourea, wherein

each of R_1, R_2, R_3 and R_4, independently, is a member selected from the group consisting of hydrogen, lower alkyl and hydroxy-lower alkyl,

R is a member selected from the group consisting of lower alkyl and hydrazino, and

n is an integer ranging from 0 to 1; and

(d) a thickener; and

(II) steaming the resulting colored fabric.

14. A mixture for padding and printing fabrics consisting essentially of, per kilogram of mixture,

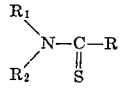
(a) from about 5 to 120 grams of an acid, water-soluble wool dyestuff,

(b) from about 30 to 150 grams of a mixture of

(i) a phenol selected from the group of phenol, pyrocatechol, resorcinol, phloroglucinol, and phenol substituted with a substituent X, wherein X is a member selected from the group consisting of from one to three lower alkyl groups and phenyl and

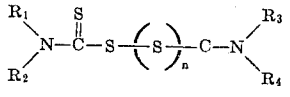
(ii) an aromatic carboxylic acid selected from benzoic acid, chlorobenzoic acid, bromobenzoic acid, aminobenzoic acid, nitrobenzoic acid, salicylic acid and cresotinic acid, the weight ratio of said phenol to said aromatic carboxylic acid ranging from 1:2 to 1:10,

(c) from about 40 to 120 grams of a member selected from the group consisting of a compound of the

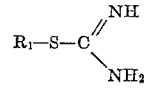


thiourea,

a compound of the formula



and a compound of the formula



wherein

each of R_1, R_2, R_3 and R_4, independently, is a member selected from the group consisting of hydrogen, lower alkyl and hydroxy-lower alkyl,

R is a member selected from the group consisting of lower alkyl and hydrazino, and

n is an integer ranging from 0 to 1; and

(d) from about 150 to 600 grams of a thickener, the balance being aqueous solvent.

15. A composition as defined in claim **14**, wherein said phenol is resorcinol, said aromatic carboxylic acid is benzoic acid, and the component (c) is thiourea.

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NORMAN G. TORCHIN, *Primary Examiner.*

T. J. HERBERT, *Examiner.*