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PRINTING AND DYEING OF POLYESTER AND CELLULOSIC FIBERS AND BLENDS THEREOF
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ABSTRACT OF THE DISCLOSURE

Coloring compositions for cellulose and polyesters containing azoic compound and coupling component, a large proportion of urea, and sufficient alkali to provide a pH between 12 and 14, together with optional polyhydric alcohol; printing pastes comprising the foregoing compositions and thickeners; and processes for coloring cellulosic and/or polyester fibers with the foregoing compositions.

The present invention relates to coloring procedures, and it will be particularly described in connection with printing procedures.

The present invention will be especially described in its application to the color printing of fabrics of cellulosic fibers and/or polyester fibers and it will be particularly described in its application to the printing of textile fibers containing polyester fibers, such as Dacron, Kodel, Fortrel and Terylene, which may be combined with cellulosic fibers such as cotton, rayon and linen. Either type of fabric may be printed according to this invention by itself or in various combinations of polyester and cellulosic fibers.

It has been found that it does not give satisfactory results to print blends of polyester fibers and cellulosic fibers with printing pastes, particularly containing diazotized bases stabilized with organic compounds such as methyl taurine or sarcosine together with coupling components, since this requires a subsequent treatment or fixing or developing operation with acid aging with fumes of acetic and/or formic acid to achieve hydrolysis of the stabilized base.

The need to acid age creates an obstacle to the use of azoic printing pastes by themselves or combined with other dyestuffs which cure or fix by other methods and it is difficult to find a suitable way to couple or develop these azoic printing pastes under conditions which would simultaneously induce development and fixation of other dyestuffs and it is a primary achievement of the present invention that printing or coloring of textiles with azoic components may be achieved together with the fixation and application of other dyestuffs thereto.

The acid aging process is not most effective with polyester fibers or cellulosic combinations containing polyester fibers, since uneven effects are obtained and the cotton or cellulosic fiber is colored or affected without any substantial effect upon the polyester fiber.

At the same time it has not been found satisfactory to print cotton or cotton-polyester combinations with insoluble disperse dyestuffs which are not soluble in water and which require organic compounds as carriers, such as benzoic acid, ortho phenyl phenol, methyl salicylate, diphenyl, or the sodium salts of these compounds or various other methyl or ethyl, straight chain or cyclo, alkyl or hexyl phenols. The difficulty here is that the cotton will not be properly colored and there will be considerable unevenness between the polyester fiber and the cotton fiber.

It is a principal object of the present invention to provide a coloring procedure, and preferably a color

printing procedure, in which the color printing may be applied to polyester-cellulosic blends as well as polyester or cellulosic fibers by themselves without changing the formulation for different percentages of these fibers and with the ability to print the separate fibers individually, apart from the blends thereof.

A further object of the present invention is to provide an effective printing composition or printing base which may be readily applied to either cellulosic or cotton fibers on one hand or polyester fibers on the other hand, or blends thereof, with assurance that color effects will be achieved on the resultant fabrics, whether they be woven or knitted, without the necessity of acid fume aging.

Another object is to provide a printing system applicable to cellulosic fibers on one hand or polyester fibers on the other hand, or blends thereof, which may be readily accomplished without multiple fixing treatments and in which a simple, readily controlled printing process may be achieved in commercially available equipment.

Still further objects and advantages will appear in the more detailed description set forth below, it being understood, however, that this more detailed description is given by way of illustration and explanation only and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

It has been surprisingly found that printing pastes are most effective for application to cellulosic or polyester fibers or combinations thereof, whether they contain azoic components alone or with disperse or other dyes, if there is developed after the printing operation at elevated temperature cyanic acid together with ammonia and ammonium carbonate.

These compounds are developed only after the printing paste has been applied and the fabric has been dried, and the exposure and reaction should take place during a period of less than 10 minutes and desirably between 20 seconds to 300 seconds.

The azoic components, with or without added disperse dyes, will effectively react and develop colored insoluble organic pigments in and on the fibers above set forth when the exposure lasts between 15 seconds to about 350 seconds, and at a temperature of between 271° F. to about 425° F. With the blended polyester cellulosic fibers, depending upon the percentage of polyester and cellulosic fibers, the ranges may be from 350° F. to 400° F. and for a period of 15 seconds to 300 seconds.

It has been found most important that the cyanic acid, together with carbon dioxide be generated in situ. Desirably the reaction should have access to air or with an exhaust so as to remove ammonia and ammonia carbonate which are reaction byproducts which retard the rate of reaction. The acid produced by the thermally induced reaction is sufficient to change the initial pH of the printed area from between 12 to 14 down to between 7 to 7.5.

It has been found that the most effective method of achieving the release of these compounds in situ is by the inclusion of a nitrogenous organic compound in the printing composition in the amount of above 5% and desirably between 15 to 35% and the most effective compound has been found to be urea, which has been first dissolved before application.

Urea has been found to be much more satisfactory than melamine, urethane, dicyandiamide, cyanuric acid, acetamide, or alkylated or methylated derivatives thereof. These last mentioned compounds do not produce an effective evolution of the cyanic acid nor of the carbon dioxide to achieve the desired result. Thiourea may be utilized to replace part or all of the urea.

It has been found that the urea in the print paste should be present in an amount varying from above 5% to 35% and desirably from 15% to 30% in a solution containing a polyhydroxy or polyhydric alcohol, such as ethylene glycol, glycerin, propylene glycol, sorbitol, mannitol and pentaerythritol.

In any case, however, in the final print composition it is necessary that the urea never be less than 5% by weight or desirably be not less than 10% by weight. The glycerin or other polyhydric alcohol, when used should be present in not less than 1/2 to 3% by weight.

Desirably the urea in final print paste should not exceed 40% by weight and desirably should not exceed 30 to 35% by weight. The combination may be printed from a composition containing a thickener, such as alginate, starch, modified starch or dextrin, or other thickeners.

The print paste, before application to the fabric, should have a pH of between 8 and 14 and desirably a pH of 12 to 14, and this is most desirably achieved by adding an aqueous caustic alkali solution. Desirably, at a subsequent stage after drying and heating, the resultant developed, colored area should have a pH of between 7.0 and 8.5, and desirably of 7.0 to 7.5.

It is also possible to have present a small amount of alkyl ether of a glycol, such as mono, di or tri methyl, ethyl or propyl ether of ethylene or propylene glycol, which may be present in amount of 1 to 6% by weight and desirably about 4% by weight of the total combination, including the thickener and the water.

The glycol ether serves as a solvent and dispersing agent for the stabilized diazonium compound, the coupling component and the disperse dyestuff, if present.

Where disperse dyes are also used, these may be present in relatively small amounts in the printing paste down to as low as 1/4% and up to 10%.

The preferred diazo amino compounds are sodium or potassium sarcosides or methyl taurides of the diazonium compounds of various amino aromatic compounds, such as amino benzene, amino toluene, or substituted aminobenzenes or amino-toluenes, including benzidine or substituted benzidines.

The preferred substituents are alkyl or alkoxy groups, halogens, nitro groups, or substituted sulfonamides. These stabilized diazonium compounds are combined with naphthalene compounds, such as hydroxy naphthoic acid condensed with aniline or toluidine or substituted compounds of the same character, such as methyl, ethyl, propyl, methoxy or ethoxy substituted compounds or other coupling compounds.

Desirably these coupling compounds are in approximately equimolar proportions with the diazo amino compounds and are present in amount ranging from 1/4 to 5% by weight of the printing paste.

Where both the azoic components and the disperse dyes are present, the total is about 2 to 12% of both of these dyestuffs with about 1 to 6% of the azo dyestuff and 0.25 to 6% of the disperse dyestuff.

It is not preferred to use sodium cyanamide, 5-sulfo 2-butyl amido benzoic acid, diethanolamine and diisopropanolamine. The sarcosides and taurides have been found to be most satisfactory.

Desirably a printing paste composed of a stabilized diazonium compound and a coupling component in approximately equimolar ratio, a polyhydric alcohol, 10 to 35% urea, a glycol ether, sodium or potassium hydroxide, water and a suitable thickening agent, with or without a disperse dye is applied to the fabric by any of several means, as for example with engraved rollers, machine screens, hand screens or block printing. The printed fabric may then be dried at normal operating temperatures ranging from 180° to 250° F.

Color development and fixation are obtained by subjecting the printed, dried fabric to dry heat without steaming in excess of 271° F. for up to 300 seconds. The opti-

mum range on cotton is from 300°-400° F. for 15 to 60 seconds. The optimum range on a mixed fiber fabric such as a 65% Dacron/35% cotton shirting is from 350°-425° F. for 60 to 300 seconds.

Finally, the fabric is washed, and it has been found that there is a most satisfactory fixation and development of the color upon the cotton or other cellulosic and polyester fibers, single and combined, with the color being of uniform appearance and reproducible on a specific fabric.

EXAMPLE I

	Preferred	Range
Urea	25	15 to 35.
Azoic components	10	5 to 20.
Monoethyl ether of ethylene glycol	4	1 to 6.
Glycerin	2	1/2 to 4.
Thickener	59	50 to 70.

The azoic components may include 10 parts of a composition made of 17.5 parts of sodium sarcoside of the diazo of 4 chlor 2 amino toluene, 18.3 parts of condensation product of 2-hydroxy 3-naphthoic acid with o-toluidine, 10 parts of ethylene glycol, 10 parts of methanol, and 4.1 parts of potassium hydroxide and sufficient water to make up 100 parts.

A disperse dye may be present in amounts of 1/4 to 10 parts.

EXAMPLE II

	Preferred parts
Stabilized Red TR Sarcoside	44.5% amine molecular weight 141.5
Naphthol ASD molecular weight 277	5.25
NaOH 50% solution	4.575
Monoethyl ether of ethylene glycol	1.5
Glycerin	10.0
Urea	5.0
Water	62.5
	11.175

In the above example, the first component is sodium sarcoside of diazonium compound of 5-chlor-2-amino toluene, and the second component is the condensation product of o-toluidine with 2,3 oxynaphthoic acid.

EXAMPLE III

	Preferred parts
Stabilized Red PT Sarcoside	41% amine molecular weight 107
Naphthol ASD molecular weight 277	4.375
NaOH 50% solution	4.625
Monoethyl ether of ethylene glycol	1.5
Glycerin	10.0
Urea	5.0
Water	62.5
	12.0

The first component is the sodium sarcoside of diazonium compound of paratoluidine.

EXAMPLE IV

	Preferred parts
1-amino 4-azobenzene	7-naphthol
Anilide of 2,3 oxynaphthoic acid	3.5
Sodium methyl tauride of tetrazotized o-dianisidine	.5
NaOH 50% solution	4.0
Monoethyl ether of ethylene glycol	1.5
Glycerin	10.0
Urea	5.0
Ester Scarlet 2GH a disperse dye produced by Harshaw Chemical Co.	45.0
Ester Blue BLH a disperse dye produced by Harshaw Chemical Co.	2.5
Water	7.5
	20.5

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EXAMPLE V

	Preferred parts
Naphthol ASG (4,4' - bi - ortho - aceto-acetotoluidine) -----	2.200
NaOH 50% -----	1.100
Stabilized Red KB sarcoside 53.4% amine molecular weight 141.5 -----	3.075
Monoethyl ether of ethylene glycol -----	10.000
Glycerin -----	5.000
Urea -----	62.500
Water -----	16.125

The first component is the condensation product of ethylacetacetate and o-tolidine, the third component is the sodium sarcoside of the diazo compound of 4-chlor-2-amino toluene.

The above composition may be combined with a disperse dye by substituting for the 16.125 parts of water, 5.0 parts of Ester Yellow YLH, a disperse dye produced by Harshaw Chemical Co. and 11.125 parts of water.

EXAMPLE VI

	Preferred parts
Condensation product of 2-hydroxy-3-naphthoic acid with aniline -----	5.240
Sodium methyl tauride of tetrazotized o-dianisidine -----	7.460
NaOH 50% solution -----	1.832
Ester Blue GSH a disperse dye produced by Harshaw Chemical Co. -----	9.370
Mono ethyl ether of ethylene glycol -----	12.500
Glycerin -----	6.250
Urea -----	47.150
Water -----	10.198

EXAMPLE VII

The preferred composition before addition of a thickener may be prepared as follows:

Ingredient	Preferred, parts	Range, parts
Azoic components -----	5 to 12	3 to 15.
Alkali -----	$\frac{3}{4}$ to $1\frac{1}{4}$	$\frac{1}{2}$ to 2.
Polyhydric alcohol -----	5 to 6	0 to 9.
Disperse dye -----	5 to 10	0 to 15.
Urea -----	45 to 65	35 to 80.
Glycol ether -----	10 to 12	0 to 15.
Water -----	Sufficient to make a thick paste.	

NOTE.—Normally the water should make up the composition up to 100 parts by weight.

In Examples I to VII all parts are by weight. In Examples II to VII there are given compositions in parts by weight which may be prepared for use with a suitable thickener in amounts ranging from 20 to 50 parts by weight of the composition to 50 to 80 parts by weight of the thickener. Example I is an example of a printing paste ready for use.

The essential feature of the present invention is the inclusion of sufficient urea, ranging from above 5 to 35% by weight of the thickened printing paste which, when applied to the fabric of cellulosic or polyester fibers or blends thereof and subsequently dried and heat-treated at from 271° to 425° F. for 15 to 300 seconds, surprisingly produces the hydrolysis of a stabilized azo base and subsequent coupling thereof with coupling components, with fixation to the fiber to give a satisfactory degree of fastness and a uniform color, whether the polyester be used by itself, the cellulosic fiber be used by itself, or whether blends be used ranging from 0% of one to 100% of the other.

An important feature of the present invention resides in the fact that the printed material after drying is heated in a non-acidic dry or low moisture atmosphere, preferably with sufficient air currents to carry off any evolved gases.

The polyester fibers above referred to are usually condensation products of ethylene glycol and terephthalic acid.

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In connection with the azo components the first component desirably includes a readily hydrolyzable diazo amino aromatic compound which may be substituted with alkyl, alkoxy, halogen, nitro, substituted sulfonamide and amino groups.

The second azoic components are usually selected from the following groups:

- (a) anilides of betaoxynaphthoic acid;
- (b) acetoacetarylides of aromatic amines;
- (c) carbazoles;
- (d) pyrazolones.

The preferred stabilizers are sarcosine and methyl-taurine.

Less preferably propyl glycine, methyl glucamine, 4-sulfanthranilic acid, N-substituted anthranilic acid, piperolic acid are used as stabilizers.

Although sodium and potassium hydroxide are the preferred alkalies, other alkaline materials such as alkaline salts may be employed to give a pH of above 8.

The present invention may be applied from an emulsion print paste of the oil in water or water in oil type. In this case the thickener is the emulsion.

Essentially the invention resides in a composition of azoic components with or without other coloring components and urea together with a glycol ether, polyhydric alcohol and an alkali for combination with a thickener which will make a printing paste. Such paste will contain when prepared an aromatic diazo amino compound with a coupling component such as an anilid of beta oxynaphthoic acid containing 5 to 35% of urea based upon the final weight of the print preparation which may be applied to a substrate such as cotton or polyester fibers or blended cotton and polyester fibers, followed by drying and then heating in a non-acidic low moisture or dry atmosphere without steaming in excess of 271° F. and usually from 3 seconds at 425° F. to about 45 seconds at 284° F.

The times indicated are the elapsed times until color appears and does not include time required for more complete fixation.

In dyeing procedures the thickener may be eliminated.

By azoic components is included an azoic compound and a coupling component. By polyhydroxy or polyhydric alcohol or compound is included aliphatic alcohols having more than one hydroxy group. The coloring composition before addition to the thickener is desirably in the form of a paste containing 10 to 25% of water and containing 35 to 75% of urea. By azoic coloring or printing compositions is included compounds containing such components.

The advantages of the present invention are not achieved where small quantities of urea are employed in amounts less than 5% on the printing paste as an anti-freeze or as a solubilizing agent, as applied to azoic components and disperse dyes. Moreover, urea is not effective for the purposes of the present invention at temperatures less than 271° F.

It has been clear that the inclusion of small amounts of urea is not at all effective with azoic compositions and combination thereof with disperse dyes when developed and fixed by heat treatment only since only poor and non-commercial color values will be achieved and neither dyestuff would be properly fixed and during washing the major proportion of the dyestuffs would be washed away.

Although the present invention particularly contemplates coloring or printing blends of cellulosic and polyester fibers with azoic compositions and disperse dyes without disadvantageously affecting either coloring compounds or the color effect on the fibers, other dyes may also be included such as acid dyes or direct cotton dyes.

As many changes could be made in the above printing and dyeing of polyester, cellulosic fibers and blends thereof, and many widely different embodiments of this invention could be made without departure from the scope of the claims it is intended that all matter contained

in the above description shall be interpreted as illustrative and not in a limiting sense.

Having now particularly described and ascertained the nature of the invention, and in what manner the same is to be performed, What is claimed is:

1. A method of coloring cotton and polyester fibers singly and in combination which comprises applying to them a coloring composition containing an azoic compound and a coupling component, a large proportion of urea, alkali and a polyhydric alcohol said composition having a pH between 12 and 14.

2. A method of coloring cellulosic and polyester fibers and blends thereof which comprises applying thereto a urea-containing azoic composition having a pH of between 12 and 14 and then drying and heating to above 270° F. without steaming the fibers, said composition containing urea in large proportion.

3. The process of claim 2 wherein the composition contains a thickener.

4. A method of coloring cellulosic and polyester fibers and blends thereof which comprises applying thereto azoic coloring composition containing caustic alkali and polyhydric alcohol and having a pH of between 12 and 14, said composition containing urea in large proportion, and then drying and heating to above 270° F. without steaming the fibers.

5. A coloring composition containing azoic compound and coupling component, a large proportion of urea, and caustic alkali, said composition having a pH between 12 and 14.

6. A coloring composition according to claim 5 wherein the alkali is sodium hydroxide or potassium hydroxide.

7. A coloring composition containing azoic compound and coupling component, a large proportion of urea, polyhydric alcohol, and caustic alkali, said composition having a pH between 12 and 14.

8. A composition according to claim 7 wherein the alkali is sodium hydroxide or potassium hydroxide.

9. A coloring composition containing 35 to 80 parts of urea, 3 to 15 parts of azoic components, 2 to 9 parts of polyhydroxy alcohol, and 5 to 15 parts of an alkyl ether of a glycol and also ½ to 2 parts alkali, in parts by weight.

10. A printing paste comprising 25 parts of urea, 10 parts of azoic components, 2 parts of polyhydric alcohol, 4 parts of an alkyl ether of a glycol and 40 to 60 parts of a thickener having a pH between 12 and 14.

11. A coloring composition containing an azoic compound and a coupling component, a disperse dye, a glycol ether, a polyhydric alcohol, and an alkali said composition having a pH between 12 and 14.

12. A printing composition containing 15 to 35 parts of urea, 5 to 20 parts of azoic components, 1 to 6 parts of a glycol ether, ½ to 4 parts of a polyhydric alcohol and 50 to 70 parts of a thickener.

13. A printing composition containing 15 to 35 parts of urea, 5 to 20 parts of azoic components, 1 to 6 parts of a glycol ether, ½ to 4 parts of a polyhydric alcohol and 50 to 70 parts of a thickener, and ¼ to 10 parts of a disperse dye.

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