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PHOTOGRAPHIC PROCESS FOR DYEING OF TEXTILE MATERIALS

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No Drawing. Original application August 18, 1945, Serial No. 611,440. Divided and this application October 24, 1946, Serial No. 705,501

1 Claim. (Cl. 95—2)

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The present invention relates to an improved process for the printing of designs upon textile materials and the like and to the product thus obtained. This application is a division of my copending application, Serial No. 611,440, filed August 18, 1945, now Patent No. 2,537,097, January 9, 1951.

Ordinarily, textile materials are printed from an intaglio roller carrying a dyestuff paste, which transfers the paste in the design to be reproduced to the cloth which is then suitably treated to develop or fix the dye. The printing of textiles in this manner involves the expense of preparing the intaglio roller, usually from a drawing, by an electroplating or etching process, which is slow, requires great skill and is costly. Furthermore, the production of gradated designs in this manner or by other mechanical means is limited because of the practical difficulty in preparing a printing roll and the properties of the dye preparations employed. Another disadvantage of this method of printing resides in the fixed dimension of the roll, which limits the spacing or reproduction frequency of the design upon the cloth.

Heretofore, it has been proposed to produce photographic images upon paper impregnated or coated with certain light sensitive diazo compounds and couplers. While such processes have been reasonably satisfactory when applied to coated paper, when applied to textile materials, the prints show poor gradation, poor density and frequently have poor contrast, poor wash fastness and poor color fastness, and have not been sufficiently satisfactory to compete with the intaglio printing of designs upon textiles.

It is an object of the present invention to provide a process of dyeing and printing textile materials and the like to produce designs having good gradation and good wash fastness.

Another object is the provision of a textile material treated with a light sensitive composition upon which may be reproduced photographically various designs and pictures by a simple process.

Another object of the invention is the provision of a process for the production of colored designs upon textile materials which does not require the use of engraved printing rolls and the like for applying the design to the fabric.

Still another object of the invention is the production of designs upon textile fibers in colored patterns having good wash fastness.

Another object is the provision of a process for overall dyeing of textile materials with the production of a light discharged pattern or design.

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In accordance with the present invention, textile material of natural or synthetic fibers or materials impregnated with a light sensitive composition comprising a light sensitive diazonium compound of an aromatic amine decomposable by light to form a non-coupling compound, an organic compound coupling in alkaline medium, precoupling preventive compound or compounds and zinc chloride, is exposed to light under a pattern, design or photographic film to be reproduced and is then developed by a suitable alkaline treatment. There is thus reproduced on the textile material a positive image showing excellent gradation and density.

The presence of zinc chloride reduces yellowing of the burned out areas, improves the coupling rate of the azo components and induces the development of rich tones due to color saturation of the fiber. The presence of zinc chloride is of particular value in printing on cotton cloth of coarse texture, or upon certain regenerated celluloses, and may also be employed in some cases, in printing on cellulose acetate textiles or textiles made from other organic derivatives of cellulose. A large quantity of zinc salt will, in some cases, impart a stiffness or hand to the cloth. However, the hand of the cloth may be improved by washing. In printing on cotton cloth of coarse texture, improved results are obtained by the use of the zinc salts. In addition to improving gradation and density of the print, a desirable brightness of color is imparted thereto. In the dyeing of cotton cloth by the present invention, the addition of zinc chloride in amounts of from about 5% to about 10% exclusive of any required for forming a salt with the diazonium compound is distinctly beneficial and results in finely gradated prints, as distinct from the contrasty prints preferred in the reproduction of mechanical drawings, an improved color saturation of the fibers, and an improved brightness or brilliance of color. In addition, when blue color forming azo components are employed a distinct shift in shade toward the green is produced. In the dyeing of cloth of regenerated cellulose or cellulose acetate, similar beneficial results are obtained, although in some cases a stiffening of the cloth is encountered. This may be improved by afterwashing, or by the use of lesser amounts of zinc chloride employed, although in the latter case, some loss of color saturation and color brilliance may be encountered. The addition of a thiocarbonic acid compound, such as, for example, thiourea, phenylthiourea and the like, which is a part of the present in-

vention, is beneficial as it improves the hand of the cloth and increases the brilliance of the colors.

The development of the light treated textile material preferably is carried out in an atmosphere of moist ammonia vapor at a suitable temperature. In developing bolts of impregnated cloth which have been exposed to light under a pattern to be reproduced, it is preferred to employ an autoclave or similar apparatus to receive the bolt. Such an apparatus preferably is equipped with a valved conduit for exhausting the air and a valved conduit for admitting ammonia vapor, and the development is carried out by placing the bolt of cloth therein, closing the apparatus, exhausting the air and introducing gaseous ammonia containing a suitable proportion of water vapor. The ammonia preferably is introduced under pressure, with concurrent or subsequent heating of the apparatus to a suitable temperature. By employing ammonia under pressure, the ammonia is caused to penetrate into the bolt of fabric and cause proper and complete development of the printed design.

For printing cloth in small pieces the commercially available diazotype machines may be employed. Such machines, employing a transparent rotating cylinder with a central light source also may be employed to print a recurrent pattern, by applying to the transparent cylinder a transparent sheet or pellicle carrying an opaque or gradated design to be reproduced and feeding the cloth to the rotating cylinder at a suitable speed.

The present invention enables the printing of textile materials in a variety of colors with a contrasty or gradated design in white or other colors. It is thus possible to obtain, for example, a design in a colored field, which shows a fineness of gradation not heretofore obtained on fabrics or textiles by the intaglio roll method or by other procedures heretofore employed. Furthermore, in the reproduction of non-gradated designs, the present method obviates the expense of preparing intaglio rollers, silk screens and the like, as drawings or designs to be reproduced can be made on transparent sheet material directly usable as the original. Where a gradated design is desired this can be conveniently be obtained by photographing the subject on a silver halide film which is developed by the reversal process or is rephotographed to produce a transparent positive of the original. For continuous printing the design may be on a transparent belt or cylinder, and especially in the former case practically any spacing desired can be provided between the designs.

Cloth impregnated or prepared with the photoprinting composition of the present invention may be stored for relatively long periods without substantial deterioration, for use as required and may be printed in small or large yardage, as desired, at a faster rate and with less expense than hand or machine printing processes previously employed.

Preferably, the cloth to be printed is not sized and in making up the photoprinting composition for application thereto, it is preferred to avoid thickening agents which would limit penetration of the composition into the fibers. Thus, in the case of some thin fabrics the design will appear obverse upon the reverse side of the cloth. Frequently it is desirable to employ a wetting agent in the composition to effect uniform penetration into the fibers and promote a level color in the field or background.

In general, to produce good gradation on cellulosic materials, it is preferred that the coupler employed is at least equimolecularly equivalent to and preferably in excess of that required theoretically to couple with the diazo compound. The degree of excess will depend, among other factors, upon the kind of textile to be printed, the particular kind of coupler, the action of stabilizing or other substances employed upon the fiber, the coarseness of the fiber and other factors. In general, the upper limit of the ratio of coupler to diazo compound employed in carrying out the invention will be determined in most cases by the solubility of the coupler in water. A ratio of 3 to 1 is not excessive in most cases and the ratio in many cases may go even higher. The excess of coupler results in improving the penetration or substantivity of the azo dyestuff for the fiber, and also causes more complete coupling with consequent color saturation of the fibers.

The coupler and diazo compound generally are selected to produce an azo dye having the desired wash fastness. The coupler selected for dyeing of cotton, rayon or cellulose ester fibers preferably is free from functional groups which can form amides, in order to obtain superior wash fastness. However, in dyeing wool, silk, nylon and other animal fibers, or so-called animalized fibers, the presence of sulfonic groups or carboxy groups is desirable in some instances. The coupler also is selected with reference to its speed of coupling and the coupling energy of the diazo compound employed. It is preferred to employ slow couplers with energetic diazo compounds, and more rapid couplers with less energetic diazo compounds, as by a proper selection the stabilizing of the composition against precoupling is facilitated. A diazo component having a low coupling energy preferably is employed, as it is easier to prevent precoupling of such a diazo component, especially where a coupling component having high coupling energy is employed therewith.

I have found, in particular, that good results are obtained by employing as coupling components, the polyhydroxy components of the benzene and naphthalene series which are free from amide forming functional groups, such as sulfonic or carboxy groups, although it will be understood the invention is not limited thereto, as coupling components, containing such groups may be employed where less severe requirements are satisfactory. Other suitable couplers which can be used in accordance with the present invention are those having a reactive methylene group, such as the arylides of acetoacetic acid, and the various pyrazolone or pyrazolone carboxylic acid compounds or mixture of couplers may be employed for producing special colors or effects. Examples of organic compounds coupling in alkaline medium which may be employed in carrying out the present invention are hydroxyaromatic compounds such as 7-hydroxy-1,2-naphthimidazole, 2,3-dihydroxynaphthalene, ethylene-diamine amide of 2,3-hydroxynaphthoic acid, resorcinol, and organic compounds containing a reactive methylene group such as 1-tolyl-3-methyl pyrazolone, acetoacetanilide, acetoacetic acid benzylamide or other pyrazolone compounds or arylides of acetoacetic acid. Or for producing two tone effects, as hereinafter described in detail, a mixture of couplers consisting of 2,3-dihydroxynaphthalene and m-hydroxyphenylurea may be used.

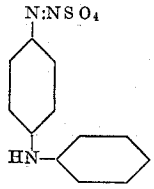
The following tabulation is illustrative of the color effects obtainable in accordance with the present invention by the use of couplers having a reactive methylene group.

Coupler	Diazonium Base	Color
acetoacetanilide	p-diethylamino-m-toluidine (Beilstein: 2-diethylamino-5-amino toluene).	orange.
acetoacetic acid	p-ethylamino-o-toluidine (Beilstein: 3-ethylamino-6-amino toluene).	yellow.
1-tolyl-3-methyl-5-pyrazolone.	p-diethylamino-m-ethoxy aniline	deep red.
Do	p-aminodiphenylamine	orange.

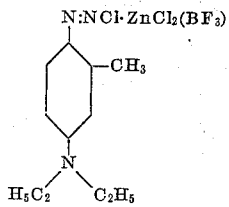
Other examples are given in the recipes below, but it is to be understood the enumeration of examples is illustrative and it is not intended to limit the invention thereto.

The preferred light sensitive diazo compounds are the homologous benzenediazonium series having alkylamine or arylamine substituents in the para-position. As examples of such preferred compounds, there may be mentioned:

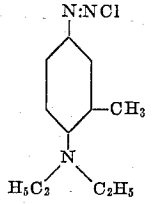
1. p-Phenylaminobenzene diazonium sulfate



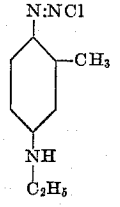
2. Zinc chloride or boron trifluoride double salt of p-diethylamino-o-toluene diazonium chloride



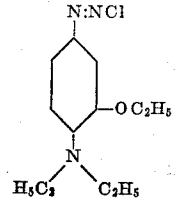
3. p-Diethylamino-m-toluene diazonium chloride



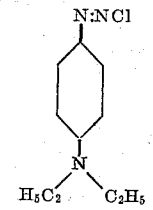
4. p-Ethylamino-o-toluene diazonium chloride



5. p-Diethylamino-m-ethoxy benzene diazonium chloride



6. Zinc chloride double salt of p-diethylamino-benzene diazonium chloride



Aromatic diazonium compounds having hydroxy or carboxy water solubilizing groups also may be employed, although the dyed products obtained therefrom are less fast to washing. Examples of such compounds are zinc chloride double salt of o-carboxy-p-diethylamino-benzene diazonium chloride and N-hydroxy ethyl-N, n-butylaminobenzene diazonium chloride. Other light sensitive salts of the diazonium compounds, such as, for example, the cadmium chloride double salts and the like may be employed.

The present invention is applicable to the dyeing of various cellulosic textile or felted materials such as bleached or unbleached cotton, mercerized cotton, rayon, cellulose ester fibers, nylon, silk, wool, vinyl chloride polymers, casein fibers, leather, and the like.

Where a two color effect is desired the cloth may be preliminarily dyed or grounded with any suitable coloring material, and the photoprinting composition is then applied thereover and the cloth is exposed to actinic light under the desired pattern or matrix and developed. As coloring matters suitable for such preliminary dyeing of the cloth are known to those skilled in the art, specific examples are not here recited. Or, if desired, the composition of the present invention may include any suitable light fast mordant or direct dye of any type whereby the burned out areas are colored the shade of the direct dye, and the areas of lesser exposure are colored a composite color. Where a mordant dye is employed the mordant used will be a metal salt compatible with the light sensitive composition, such as, for example, alum or aluminum sulfate. For example, a blue printed upon a yellow background yields, upon exposure under a negative, a yellow design upon a greenish blue field, and a blue upon a red background yields a red design upon a purple to violet field. If a positive matrix is employed, the color areas are reversed.

In a further modification of the invention, by the use of suitable coupler, as for example, as disclosed in my copending application Serial No. 575,558, filed January 31, 1945, for Photographic Printing Materials, now abandoned, and a matrix or pattern having full and partial densities, two tone or two color prints may be obtained.

Dyeings in natural colors may be produced by treating the cloth first with a composition which upon exposure to actinic light under a suitable matrix or pattern and development will yield a design in one primary color, washing out excess composition, then treating the cloth with a second composition which, upon exposure under a suitable matrix or pattern and development, will yield another primary color, washing out the excess composition and then treating the cloth with a third composition which, upon exposure under a suitable matrix or pattern and development, will yield dyeings of a third primary color, it being understood that suitably prepared patterns

or matrices are employed, and proper registration of the design is secured.

Any suitable precoupling preventative known to the art may be employed in the composition of the present invention to stabilize the composition and prevent coupling or deterioration during storage. Examples of such precoupler preventatives which are suitable for use in accordance with the present invention are citric acid, a mixture of citric, boric and phosphoric acids, tartaric acid, alpha-beta unsaturated aliphatic acids, naphthalene polysulfonic acids and the like. In addition, the composition produced in accordance with this invention may include sensitizers known to the art which increase the light sensitivity of the composition, anti-yellowing compositions, wetting agents and the like.

The addition of metal salts is also desirable in some instances to vary the shade. In general, certain metal salts improve the color saturation or density and in the case of blue dyeings shift the shade toward red. The dyeings, however, are frequently duller than those obtained when zinc chloride is employed, and in some cases the burned out areas are yellowed or greyed.

The addition of small amounts of organic solvents, such as isopropyl alcohol or ethyl alcohol frequently is desirable to increase the solubility of the diazonium compound or the coupler in the aqueous solution, and to improve the dyeings. Thus, for example, the dyeings on vinyl chloride polymer are improved by the addition of alcohol, not in excess of about 5%, as greater concentrations tend to matte the threads and produce an increased stiffening of the cloth, which however, is not an important disadvantage for many uses. Excessive amounts of zinc chloride also should be avoided in dyeing "Vinyon" textiles.

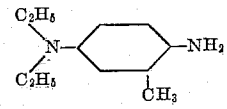
The thickness of the fibers in woven and knitted textiles affects the quality of the dyeings. In general, heavier or thicker threads, especially of the more opaque cellulosic fibers, such as cotton or linen give more contrasty prints lacking in detail, while thinner fibers give better gradation. However, the more transparent fibers, such as rayons and cellulose esters yield dyeings showing better gradation and detail which is less adversely affected by size of thread than in the case of more opaque threads.

The invention will be described in greater detail in connection with the following specific examples, which are given to illustrate preferred embodiments of the invention:

Example 1

An aqueous solution of the following composition was prepared and applied to a cloth of cellulose acetate.

0.5% zinc chloride double salt of diazotized p-diethylamino-o-toluidine (.0019 mol) of the following formula:



0.8% 2,3-dihydroxynaphthalene (.005 mol)
5% citric acid
5% zinc chloride
.01% saponin (approx.)

After drying, the cloth was exposed under a film carrying a photograph and developed in an atmosphere of ammonia at an elevated temperature. The cloth was dyed a bright blue showing excellent gradation in the photograph and of good fastness to washing.

Example 1a

If, in the above example, one per cent of the diazonium compound is employed, the fastness to light of the dyed cloth is improved.

In place of cellulose acetate cloth in the above examples, a cloth of batiste, regenerated cellulose of the xanthate or viscose type, balloon cloth, knitted rayon jersey, or of mixed cotton and rayon may be similarly dyed.

Example 2

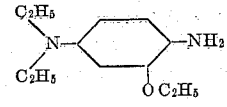
By replacing the dihydroxynaphthalene coupler in Example 1, by 2% of 7-hydroxy-1,2-naphthimidazole (.10 mol) and proceeding as described in Example 1, a red dyeing is obtained on cloth which is of good wash fastness.

Example 3

By replacing the dihydroxynaphthalene coupler in Example 1 by 0.5% of resorcinol (0.55 mol), a sepia dyeing is obtained of good wash fastness. However, on some grades of cellulose acetate, the white areas remain somewhat discolored.

Example 4

By replacing the diazonium compound in Example 1 by .5% of the zinc chloride double salt of diazotized 3-diethylamino-6-amino phenetole of the formula:



and proceeding as in Example 1, a dyeing of a greenish shade with slightly less color saturation is obtained. The wash fastness is good.

Example 5

By replacing the diazonium compound in Example 1, by 0.5% of p-phenylaminobenzene diazonium sulfate, dyes are obtained of a redder shade than in Example 1 and which show less gradation, that is, they are more contrasty.

Example 6

By replacing the diazonium compound in Example 1 by zinc chloride double salt of p-diethylamino-o-carboxylbenzene diazonium chloride, blue dyeings are obtained of fair wash fastness but less brilliant than those obtained in Example 1.

Example 7

By proceeding as described in Example 1, employing as the diazo compound, p-diethylaminobenzene diazonium chloride in the form of the zinc chloride double salt, and as coupler, 7-hydroxy-1,2-naphthimidazole, with the addition of 5 to 10% of thicurea, particularly good red dyeings are obtained. The addition of thiourea is desirable for it increases the brilliance of the colors and improves the hand of the cloth.

Example 8

By employing in Example 1 as the coupler the hydrochloride of the ethylene diamine amide of 2,3-hydoxynaphthoic acid, dull green dyeings of good wash fastness are obtained with the white areas discolored due to the formation of colored products with ammonia, which discoloration can be washed out.

Example 9

By replacing the diazonium compound in Example 1 by 1% of zinc chloride double salt of diazotized p-ethlyamino - m - toluene diazonium chloride, and proceeding as in Example 1, a dyeing of a purplish blue shade of good density and good resistance to fading is obtained.

Example 10

An aqueous solution of the following composition is prepared and applied to a cloth of cellulose acetate. Parts are by weight.

3 parts p-phenylaminobenzene diazonium sulfate
5 parts m-hydroxyphenylurea
0.05 part 2,3-dihydroxynaphthalene
10 parts citric acid
5 parts zinc chloride
0.01 part saponin
7.9 parts isopropyl alcohol
90 parts water

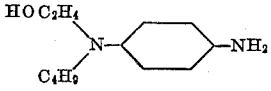
After drying the cloth is exposed to a suitable source of light under a photograph exhibiting portions in full densities and portions in highlights or partial densities, and developed in an atmosphere of ammonia at an elevated temperature. The cloth exhibited a green color in those areas corresponding to full densities of the matrix and grey in the areas corresponding to highlights.

Example 11

Three negative paterns or matrices corresponding to the elemental colors, red, green and blue are first prepared in known manner.

An aqueous solution of the following composition is prepared and applied to a cloth of regenerated cellulose.

1 gram zinc chloride double salt of diazotized p-N-hydroxy ethyl-N,n-butylamino aniline of the following formula:



.3 gram 2,3-dihydroxynaphthalene
5 grams citric acid
5 grams thiourea
5 cc. isopropyl alcohol
.05 gram saponin in 100 cc. of water

Upon drying, the cloth was exposed under a suitable matrix to actinic light and was then developed by exposure to ammonia vapor to yield a blue design. The cloth then was washed and dried and treated with a solution containing 1 gram zinc chloride double salt of diazotized p-diethylamino-o-toluidine, and as a coupler, .3 gram 1-tolyl-3-methyl pyrazolone and citric acid, thiourea, isopropyl alcohol and saponin in the concentration mentioned above. After drying, the cloth was exposed under a suitable matrix to actinic light, developed by ammonia to yield a red design, and then washed. Upon drying, the cloth was then treated with a solution containing .5 gram acetoacetyl-o-anisidine and 1 gram zinc chloride double salt of diazotized p-diethylamino-o-toluidine and the above mentioned auxiliary ingredients, dried and exposed under a suitable matrix to actinic light and developed with ammonia to yield a yellow design. There is thus produced a dyed cloth printed in the three color components which produce natural colors.

It will be understood that various modifications may be made in the invention described in the above examples without departing from the spirit or scope of the invention.

I claim:

The method of reproducing on a textile of regenerated cellulose a multi-colored pattern containing the colors red, green and blue by photoprinting which comprises coating the textile with an aqueous composition containing diazotized N-p-hydroxyethyl-n-butylamino benzene .$ZnCl_2$ double salt, 2,3-dihydroxy naphthalene, and $ZnCl_2$ in a quantity of from about 5% to about 10% exclusive of any required to form a complex salt with the diazonium compound, drying, exposing the thus coated textile to light under a matrix opaque to light in the blue areas of the pattern, developing the image of said blue areas by treatment with ammonia vapors, washing and drying; recoating the textile with an aqueous composition containing diazotized p-diethylamino-o-toluidine .$ZnCl_2$ double salt, 1-tolyl-3-methyl pyrazolone and $ZnCl_2$ in a quantity of from about 5% to about 10% exclusive of any required to form a complex salt with the diazonium compound, drying, exposing the thus recoated textile to light under a matrix opaque to light in the red areas of the pattern, developing the image of said red areas by treatment with ammonia vapors, washing and drying; recoating the textile with an aqueous composition containing diazotized p-diethylamino-o-toluidine .$ZnCl_2$ double salt, acetoacetyl-o-anisidine and $ZnCl_2$ in a quantity of from about 5% to about 10% exclusive of any required to form a complex salt with the diazonium compound, drying, exposing the thus recoated textile to light under a matrix opaque to light in the yellow areas of the pattern and developing the yellow image by treating the thus exposed coated textile with ammonia vapors.

SAM CHARLES SLIFKIN.

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