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DIAZOTYPE DYEING AND PRINTING OF WEB OR SHEET MATERIAL

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This invention relates to continuous dyeing and printing of web or sheet materials and more particularly to methods for producing stable dye images or patterns on textile fabrics, paper, and other web or sheet materials.

It is the principal object of the present invention to provide improved processes of applying, by coating or impregnating, in the form of images or fields, one or more colors of azo dyes.

It is a further object of the present invention to provide improved processes of applying, by impregnating or coating, one or more colors in a continuous application.

It is a further object of the present invention to provide improved processes of applying, by impregnating or coating, one or more colors in which standard dyeing materials soluble in or capable of suspension in liquid vehicles other than water, are employed so that restriction to the use of water soluble coupling agents is unnecessary.

In accordance with the present invention a photo-sensitive dye intermediate in a given liquid medium is applied to the material, and subsequent application is made to the material of a coupling compound in another liquid medium. The media are selected so that the dye intermediate is not soluble in the liquid medium of the coupling compound nor is the coupling compound soluble in the liquid medium of the dye intermediate solution.

After exposure to a light source, under a photoplate or its equivalent and subjection of the coated material to a suitable alkaline environment, the coupling compound will unite with the dye intermediate to form insoluble color-compounds on the web or sheet material.

In order to illustrate the invention the following specific examples are given, but it is to be understood that the invention is not limited to the particular products nor materials mentioned therein nor to the specific order of steps as set forth. It is intended however that the sheet or web material be successively and continuously treated to obtain the desired results.

EXAMPLE 1

A photo-sensitive dye intermediate in aqueous solution may be prepared consisting of the following:

Formula No. 1

Zinc chloride double salt of 2-methyl-dithenyl-4:4 diazo-sodium sulphite	grams	10
Boric acid	do	10
Water	cubic centimeters	1000

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A coupling compound in a solution of isopropyl alcohol (which is not a solvent for the dye intermediate of Formula No. 1) may be prepared consisting of the following:

Formula No. 2

Isopropyl alcohol	cubic centimeters	100
Beta-naphthol	grams	5

The sheet or web to be dyed or printed is coated or impregnated with a photo-sensitive dye intermediate in liquid form and in accordance with the formula given in Formula No. 1. The web is then dried, or permitted to dry, under alkaline free conditions, and the sheet or web is next impregnated or coated with a solution of a coupling compound in a solvent or liquid vehicle, such as that of Formula No. 2, in which the dye intermediate is not soluble, and the sheet or web is also dried, or permitted to dry. The sheet or web is then exposed to a strong actinic light source directed through a photo plate or similar light screen and on which there is reproduced the pattern or design to be applied to the sheet or web. The sheet or web, immediately thereafter, is passed into or through a chamber containing water vapor and an alkaline medium, such as ammonium hydroxide, or through an alkaline solution, until the color coupling takes place and an image is produced on the sheet or web. The image thus obtained is an exact reproduction of the photo plate or its equivalent.

If desired the diazo, such as that of Formula No. 1, may be applied to the sheet or web and after drying, the sheet or web may be exposed as before for printing. The coupling compound, as in Formula No. 2 may then be applied. If desired, also, an alkaline component may be added to or applied with the coupling compound and the material thus treated subjected to water vapor or steam for development of the color. If this latter procedure be followed the separate treatment in the chamber in an alkaline environment will not be necessary.

As illustrative of other suitable materials, the following may be employed:

EXAMPLE 2

A photo-sensitive dye intermediate solution is prepared consisting of the following:

Formula No. 3

Copper sulphate double salt of diazotized dianisidine	grams	5
Aluminum sulphate	do	5
Boric acid	do	5
Water	cubic centimeters	1000

A coupling compound in another solvent or vehicle in which the dye intermediate is not soluble is also prepared consisting of the following:

Formula No. 4

2-hydroxy-3-naphtholic acid	grams	5
Ethyl alcohol	cubic centimeters	100

The sheet or web material is treated as before, being impregnated first with the material of Formula No. 3, and, when dry, with the material of Formula No. 4, exposed under a photo plate and passed into an alkaline atmosphere or solution.

As illustrative of other suitable materials, the following may be employed:

EXAMPLE 3

A photo-sensitive dye intermediate solution is prepared consisting of the following:

Formula No. 5

Zinc chloride double salt of ortho-amino-azo-toluene	grams	5
1% carboxy methyl cellulose	cubic centimeters	500
Lactic acid	do	10
Aluminum sulphate	grams	10

A coupling compound is also prepared consisting of the following:

Formula No. 6

Beta-naphthol	grams	10
Lactic acid	cubic centimeters	1000
Isopropyl alcohol	do	10

The web or sheet material to be treated is impregnated with the material of Formula No. 5 and dried, or permitted to dry, at a temperature in the range of 100° to 140° F. The web or sheet material is then exposed as before to an actinic light source directed through a photo plate having the desired image thereon. The coupling material, such as that of Formula No. 6, is then applied to the web or sheet material and after such application the web or sheet material is dried, or permitted to dry, preferably under a warm air blast. The color may then be developed by subjecting the sheet or web to ammonia vapor, as before.

Coupling, as hereinbefore referred to, can be effected at room temperatures, or if desired elevated temperatures may be employed for increasing the speed of operation, enhancing the penetration into the fibres of the web or sheet material, and enhancing the color fastness. If it is desired to employ elevated temperatures the coated material, during and immediately after coupling, is subjected to live steam or boiling water.

It is not necessary to employ stabilizers, not only because the process is continuous, but also because the printing takes place too rapidly to permit of decomposition of constituents which might be unstable.

The diazo components utilized as dye intermediates in the practice of the present invention must be insoluble in the solvent of the coupling agent and may be any of those generally employed in the diazotype are and having this characteristic, and including diazotized members of strongly basic monoamine groups, such as aniline, phenols, amines, toluidines, xyledines, aminophenols, pyrazolones, carbazoles, sulfones, naphthols, acetoacetic acid esters, acetanilides, monochloroderivatives of the benzenoideamine group where the chlorine atom is meta to the amino group, diamines of the benzidine series,

and alpha and beta-naphthylamine. Other dye intermediates include the sulphonamide and the diphenylamine groups.

The diazos may be utilized as such, or in the form of their stabilized double salts, such as with zinc chloride, cadmium chloride, tin chloride or the like, as the fluoroborates, as the alkyl or aryl sulfonates, such as methyl, ethyl, propyl, phenyl and the like sulfonates, or as the sulfates.

Any suitable diazo coupler which is insoluble in the diazo solvent may be used, the coupling agent being a phenolic or naphthoic coupler, or active methylene compounds, such as beta-naphthol, 2 hydroxy-3 naphthoic acid anilide, diacetoacetictolidide, p-hydroxynaphthoic acid-p-nitroanilide, beta-hydroxynapthoic acid-beta-naphthalide, 1:8 amino-naphthol-2:4 disulphonic acid, 4-hydroxy-6 methyl-2 (1) pyridone, and phloroglucides.

A wide range of colors is available for producing the preferred color or color pattern on the sheet or web.

As examples of color coupling in accordance with the present invention and the colors obtained therewith, the following have been found suitable, it being noted that the liquid medium employed as a solvent for the dye intermediate is not a solvent of the coupling compound and the liquid medium employed with the coupling compound is not a solvent of the dye intermediate:

Beta-naphthol plus diazotised beta-naphthylamine=Vacanceine Red
Beta-naphthol plus diazotised p-nitraniline=Para Red
Beta - naphthol plus diazotised α - naphthylamine=Claret
Beta-naphthol plus diazotised dianisidine=Blue
Beta-naphthol plus diazotised metanitraniline=Orange
Beta-naphthol plus diazotised nitro-o-toluidine=Darker orange
Beta-naphthol plus diazotised p-nitroorthotoluidine=Darker orange
Beta-naphthol plus diazotised metanitro-p-toluidine=Light red
Beta-naphthol plus diazotised o-anisidine=Pink
Beta-naphthol plus diazotised p-nitro-o-anisidine=Pink
Beta-naphthol plus diazotised amidoazotolual=Garnet
Beta-naphthol plus diazotised tolidine=Brown
Beta-naphthol plus diazotised benzidine=Brown
2-hydroxy-3 naphthoic acid anilide plus diazotized dianisidine=Blue
2-hydroxy-3 naphthoic acid anilide plus diazotized p-nitro toluidine=Alizerine Red
Diacetoacetictolidide plus diazotized 2:5 dichloraniline=Yellow
Diacetoacetictolidide plus diazotized o-chloraniline=Yellow
Para-hydroxynaphthoic acid-p-nitroanilide plus diazotized dianisidine=Blue
Beta-hydroxynaphthoic acid - Beta - naphthalide plus o - phenetidine - azo - α - naphthylamine=Black
4-hydroxy-6 methyl-2(1) pyridone plus diazotized p-ethylaminoaniline=Violet
1:8 amino-naphthol-2:4 disulphonic acid plus diazotized p-aminodiphenylamine=Violet
Phloroglucide plus diazotized diethylaminobenzene=Violet

In addition to the diazo compound and coupling agents, the sensitizing solution may contain the usual adjuncts, such as metal salts for intensifica-

tion of the dyestuff image and including for this purpose salts such as aluminum sulphate, titanium ammonium fluoride, nickel sulphate, zinc chloride, and the like; may contain stabilizing agents such as thiourea, thiosinamine, naphthalene trisulfonic acid, and the like; may contain acids for retarding precoupling, such as citric acid, boric acid, tartaric acid, or mixtures thereof, and the like; may contain hydroscopic agents, such as ethylene glycol, glycerine, dextrin and the like; may contain solvents such as isopropyl alcohol, Cellosolve, and the like; may contain wetting agents, such as saponin, sulfonated alcohols and the like, fatty acids such as sulphonated castor oil and the like; and may also contain thickening agents, such as carboxy methyl cellulose, starch and the like.

With the materials heretofore referred to, a single color selected from a wide range of colors may be applied upon a sheet or web. Immediately following the application of one color, if desired, the process may be repeated one or more times to apply one or more different colors successively to the same sheet or web and without objectionable effects on the previously applied color or colors.

In accordance with the present invention, also, two or more colors may be simultaneously printed on the sheet or web in a continuous process.

If it is desired to apply more than one color substantially the same procedure as heretofore referred to may be employed. The material is however coated or impregnated with a solution of a dye intermediate which is not light sensitive or is weakly light sensitive. After the sheet or web has been dried, or permitted to dry, under alkaline free conditions, a solution of a light sensitive dye in a fluid medium other than that used in the first application is applied to the sheet or web.

The first dye intermediate employed is one which is not soluble in the solution of the material employed for the second coating or impregnation, and the light sensitive dye intermediate employed in the second coating or impregnating solution is not soluble in the solution of the first dye intermediate.

The sheet or web, after the application of the second coating or impregnating solution, is dried, or permitted to dry, under alkaline free conditions, and a solution of the coupling compound is applied. The liquid used in the solution of the coupling compound is not miscible with those used with the first dye intermediate and the light sensitive dye intermediate.

The sheet or web, as thus prepared, is exposed under a photo plate, as before, to an actinic light source, and immediately passed through a chamber containing water vapor and an alkaline medium such as ammonium hydroxide, or through an alkaline solution, until color coupling takes place and an image of one color is produced against a background of another color on the web or sheet material.

As a particular illustration of suitable materials to be employed for this purpose, the following may be employed.

EXAMPLE 4

A solution of a dye intermediate which is not light sensitive or which is weakly light sensitive is prepared and may consist of the following:

Formula No. 7—Yellow background color (weakly light sensitive dye intermediate)

Diazotized α-naphthylamine	grams	2
Isopropyl alcohol	cubic centimeters	100

A solution of a light sensitive dye intermediate may be also prepared containing the following:

Formula No. 8—Blue, light-sensitive, dye intermediate

Diazotized dianisole sodium sulphite	grams	10
Copper sulphate	do	5
Boric acid	do	10
Water	cubic centimeters	1000

A coupling solution is also prepared preferably containing the following:

Formula No. 9—Coupling solution

Beta-naphthol	grams	5
Stearic acid	do	5
Benzene	cubic centimeter	100

The materials as thus prepared are applied, as indicated above, and an image of one color will be produced against a background of another color on the sheet or web.

The order of application of the various materials may also be varied as indicated in connection with the preceding example, and with adjunct materials included, and with coupling accompanied by elevated temperature conditions. If desired, also, after completion, the process may be repeated one or more times to apply one or more different and additional colors to the sheet or web.

I claim:

1. The method of applying color to web or sheet material which comprises applying to the material a photosensitive diazo compound in a liquid medium, applying to the material a coupling agent in a liquid vehicle in which the diazo compound is insoluble, and which coupling agent is insoluble in said liquid medium, under the conditions of the process, exposing the material to which the coupling agent and diazo compound have been applied to a light source directed through a color pattern determining screen for determining the pattern of color on the material, and exposing the material to an alkaline environment.

2. The method applying color to web or sheet material which comprises in a continuous process applying to the dry material a photosensitive diazo compound in a liquid medium, applying to the dry material a coupling agent in a liquid vehicle in which the diazo compound is insoluble and which coupling agent is insoluble in said liquid medium, exposing the material to which the coupling agent and diazo compound have been applied to a light source directed through a color pattern determining screen for determining the pattern of color on the material, and then exposing the material to an alkaline environment.

3. The method as set forth in claim 1 in which the material during coupling is subjected to an elevated temperature.

4. The method of applying a plurality of colors to web or sheet material which comprises applying to the material a diazo compound which is weakly or non light sensitive in a liquid carrier, applying to the material a photosensitive diazo compound which is insoluble in the liquid carrier in a liquid medium in which said first diazo compound is insoluble, applying to the material a coupling agent insoluble in said liquid carrier and said liquid medium in a liquid vehicle in which said diazo compounds are insoluble, then exposing the material to which the diazo compounds and coupling agent have been applied

to a light source directed through a color pattern determining screen for determining the pattern of the color and then exposing the material to an alkaline environment.

5. The method of applying a plurality of colors to web or sheet material which comprises in a continuous process, applying to the material a diazo compound which is weakly or non light sensitive in a liquid carrier, then applying to the material a photosensitive diazo compound which is insoluble in the liquid carrier in a liquid medium in which said first diazo compound is insoluble, then applying to the material a coupling agent insoluble in said liquid carrier and said liquid medium in a liquid vehicle in which said diazo compounds are insoluble, then exposing the material to which the diazo compounds and coupling agent have been applied to a light source directed through a color pattern determining screen for determining the pattern of the color and then exposing the material to an alkaline environment.

6. The method as set forth in claim 4 in which the material during coupling is subjected to an elevated steam temperature.

7. The method of applying a plurality of colors to web or sheet material which comprises in a continuous process, applying to the material a photosensitive diazo compound in a liquid medium, applying to the material a coupling agent insoluble in said liquid medium in a liquid vehicle in which said diazo compound is insoluble, exposing the material to which the diazo compound and coupling agent have been applied to a light source directed through a color pattern determining screen for determining the pattern of the color, exposing the material to an alkaline environment, and repeating the aforesaid steps with a diazo compound and coupling agent which provide a different color, said last diazo and coupling agent each being insoluble in the liquid medium or vehicle of the other.

8. The method of applying color to web or sheet material which comprises applying to the material a photosensitive diazo compound in a liquid medium, applying to the material a coupling agent in a liquid vehicle in which the diazo compound is insoluble and which coupling agent is insoluble in said liquid medium, and developing and fixing the color.

9. The method of applying colors to web or sheet material which comprises in a continuous process, applying to the material a photosensitive diazo compound in a liquid medium, applying to the material a coupling agent insoluble in said liquid medium in a liquid vehicle in which said diazo compound is insoluble, and developing and fixing the colors.

10. The method of applying a plurality of colors to web or sheet material which comprises in a continuous process, applying to the material a photosensitive diazo compound in a liquid medium, applying to the material a coupling agent insoluble in said liquid medium in a liquid vehicle

in which said diazo compound is insoluble, forming an image with a light source and fixing the color, and repeating aforesaid steps with a diazo compound and coupling agent which provide a different color, said last diazo and coupling agent each being insoluble in the liquid medium or vehicle of the other.

11. The method of applying color to web or sheet material which comprises applying to the material a photosensitive diazo compound in a liquid medium, exposing the material to which the diazo compound has been applied to a light source directed through a color pattern determining screen for determining the pattern of color on the material, applying to the material a coupling agent in a liquid in which the diazo compound is insoluble, and developing the color.

12. The method of applying a plurality of colors to web or sheet material which comprises applying to the material a diazo compound which is weakly or non light sensitive in a liquid carrier, applying to the material a photosensitive diazo compound which is insoluble in the liquid carrier in a liquid medium in which said first diazo compound is insoluble, then exposing the material to which the diazo compounds have been applied to a light source directed through a color pattern determining screen for determining the pattern of the color, applying to the material a coupling agent insoluble in said liquid carrier and said liquid medium in a liquid vehicle in which said diazo compounds are insoluble, and developing the color.

13. The method of applying color to web or sheet material which comprises applying to the material a photosensitive diazo compound in a liquid medium, applying to the material a coupling agent in a liquid vehicle in which the diazo compound is insoluble, and which coupling agent is insoluble in said liquid medium, exposing the so treated material to an alkaline environment, and, prior to the alkaline exposure and subsequent to the application of the diazo compound, exposing the material to a light source directed through a color pattern determining screen for determining the pattern of color on the material.

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