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TREATMENT OF TEXTILE MATERIALS

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This invention relates to the colouration of textile materials and more particularly to the production of coloured pattern effects on textile materials.

ing, a material is obtained having a blue ground colour on which appears a green and yellow pattern, the green being discharged in the places where it overlaps the yellow.

5 As is known pattern effects may be produced on textile materials by applying a ground colouration and then printing with a discharge composition containing a discharging agent which will destroy the ground colour in the printed areas.
10 Alternatively, the discharge composition may be applied prior to the application of the ground colour so that fixation of the ground colour is prevented or resisted in the printed areas. Both of these methods may be modified by incorporating in the discharge composition a colouring matter having affinity for or capable of being fixed on the materials, and which is resistant to the discharging agents, and coloured pattern effects thereby obtained on coloured grounds.

20 A very large number of colouring matters are dischargeable by metallic aldehyde or ketone sulfoxylates, which are hereinafter termed simply "sulfoxylates." We have observed that of these colouring matters a considerable proportion are also dischargeable by stannous salts, while many others resist the action of stannous salts sufficiently well to permit their use for colouring stannous salt discharges. We have found that an exceedingly wide range of very valuable pattern effects may be obtained by printing dyed materials, the colour of which is dischargeable both by sulfoxylates and stannous salts, with both a sulfoxylate discharge composition and a stannous salt discharge composition so that one print overlaps the other, at least one of the discharge compositions containing a colouring matter resistant thereto but dischargeable by the other. The term cover printing will hereinafter be used to indicate the operation of printing a pattern overlapping that of a previous printing operation.

Thus for example a cellulose acetate fabric dyed with a blue ground colour which is dischargeable both by zinc formaldehyde sulfoxylate and by stannous chloride may be printed with a discharge composition containing zinc formaldehyde sulfoxylate and a yellow colouring matter resistant to zinc formaldehyde sulfoxylate. It may then be cover-printed with a composition containing stannous chloride and a green dyestuff resistant to stannous chloride but dischargeable by zinc formaldehyde sulfoxylate, so that the pattern produced by the cover-print overlaps the pattern produced by the first printing. On steaming, ageing or otherwise develop-

5 Instead of sulfoxylates on the one hand and on the other stannous compounds, other combinations of discharging agents may be employed in producing pattern effects in accordance with the present invention, providing that one discharging agent is capable of discharging colouring matters which are not discharged by the other. Thus for example not only may reducing discharges be employed in accordance with the present invention, but oxidation discharges may also be employed. If desired, more than two discharging agents may be employed and a still wider range of pattern effects obtained.

Further, in producing the pattern effects, the ground colour may be applied to or produced on the material after the application of the discharge compositions. In such cases the compositions act as "discharge-resists" in that they "resist" the colouration of the materials in the printed areas by the ground colour. Thus for example the materials may be printed with the discharge compositions and then the ground colour applied, so that only the unprinted areas are coloured thereby. The term "discharging" is therefore used as including not only the destruction of an already applied colour but as including preventing the fixation or production of a colour on the materials. It is to be understood that the terms "discharge" and "discharging" are used throughout the description and claims as including "resist" and "resisting" respectively.

Again, instead of printing on the discharge compositions, they may be applied by any other convenient method of local application, for example by stencilling. Wherever reference is made to printing in this application it is to be understood that other methods of local application may be substituted if desired. Furthermore, yarn may be impregnated with one of the discharging or resist agents and then woven with untreated yarn to form a fabric which may then be overprinted with a composition containing another discharging agent before or after the application of the dischargeable ground colour.

The ground colour dischargeable by the discharging agents may be applied in any desired way, for instance by dyeing or by padding, printing or other mode of mechanical impregnation. It may be applied uniformly to the materials, or, if desired, locally by printing, stencilling or other

means, whereby the range of effects obtainable is increased.

The process of the present invention is particularly applicable to materials made of or containing organic derivatives of cellulose, e. g. cellulose acetate, cellulose formate, cellulose propionate, cellulose butyrate, or other organic ester of cellulose, or ethyl cellulose, methyl cellulose, benzyl cellulose, or other cellulose ether. It may also be applied, however, to the production of pattern effects on other kinds of textile materials, e. g. cotton, regenerated cellulose artificial silk, silk, wool, or like materials, or materials containing these fibres in conjunction with cellulose derivative fibres. Further in the case of mixed materials the components may be coloured in solid or contrasting shades or one component may be coloured and another left uncoloured, according to their respective affinities for the dyestuffs used.

In carrying out the new process any suitable discharging agents may be employed. Among the more powerful discharging agents metal aldehyde or ketone sulfoxylates may be mentioned, e. g. the sodium or zinc compounds. The zinc compounds are of especial value in the treatment of cellulose ester or ether materials. As discharging agents exercising a milder discharging action especial mention may be made of stannous salts such for example as stannous chloride, stannous chloracetate, stannous acetate, stannous thiocyanate, or other stannous salts or double salts, which may be acid, neutral, or basic. Again, in the case of an aniline black ground colouration or other colouration produced by oxidation of an aromatic amine on the material, an alkaline substance and/or one of the above or other reducing agents may be used to produce resist effects. Discharging or resist agents may be produced by interaction of suitable compounds in the pastes or other vehicle in which the agents are to be applied to the textile materials, or they may be produced in separate operations as may be desired or convenient.

The discharge or resist compositions may be made up with any desired thickening agents to fit them for application by printing or other means of local application. Again they may contain substances which facilitate the action of the discharging agent, for example anthraquinone in the case of sulfoxylate discharges. Further when colouring materials made of or containing cellulose acetate or other organic derivatives of cellulose, the compositions may with advantage contain swelling agents for the materials, for example thiocyanates, hydroquinone or other phenols, or alcohols.

It will be appreciated that the selection of the discharging agents for use in any particular case will depend upon the nature of the effects it is required to produce and upon the character of the materials to be coloured. In the case of materials made of or containing cellulose acetate or other cellulose esters or ethers particularly satisfactory results may be obtained by the use of zinc formaldehyde sulfoxylate in one discharge preparation and of a stannous salt in another, particularly stannous chlorothiocyanate or stannous chloride or other stannous salt in conjunction with a thiocyanate in the manner described in U. S. application S. No. 479,087 filed August 30, 1930.

The new process admits of many variations both in respect of the types of discharging agents and of the types of colouring matters utilized.

In consequence a very large variety of pattern effects may be obtained.

Still further variations in the effects may be obtained by first printing with a composition, containing or not a dyestuff having affinity for the material, and comprising an oxidizing or other agent which will prevent one or more of the sulfoxylate, stannous or other discharge compositions taking effect in the printed areas.

Again, the fabrics to be treated may comprise undyed yarn and yarn dyed with dyestuffs dischargeable by the discharging agents, or may comprise differently coloured yarns at least one of the colours being dischargeable by the discharging agents. Still other effects may be obtained by making the fabric from yarn made up of filaments some of which are undyed and some of which are dyed with a dyestuff dischargeable by the discharging agents.

According to a modification of the invention the excess discharging agent of one composition may be destroyed, e. g. by steaming and/or ageing, after effecting discharge but before the application of a further discharge composition. Thus for example, if in the previously given specific example of the production of a green and yellow pattern on a blue ground, the material is aged after the application of the zinc formaldehyde sulfoxylate preparation containing the yellow colouring matter but prior to the application of the stannous salt preparation containing the green colouring matter, the green pattern is superimposed on the yellow pattern instead of being discharged thereon. The ageing operation operates by destroying the zinc formaldehyde sulfoxylate and so permits fixation of the green pattern over the yellow pattern.

In the following paragraphs A to F there are indicated in a more detailed manner some of the methods by which pattern effects may be produced in accordance with the invention, which however is not restricted thereto.

A

To a cellulose acetate fabric is applied a ground colouration dischargeable by both zinc formaldehyde sulfoxylate and stannous chloride discharges. It is then printed with a zinc formaldehyde sulfoxylate discharge with or without colouring matters resistant to zinc formaldehyde sulfoxylate, dried, cover printed with a stannous chloride discharge containing dyestuffs resistant to stannous chloride but dischargeable by zinc formaldehyde sulfoxylate, aged, steamed if necessary, and washed off. A white or coloured discharge is obtained on a dyed ground with the coloured pattern produced by the cover printing appearing only on the ground colouration.

B

A cellulose acetate fabric coloured with a ground colouration as in A above is printed with a stannous chloride discharge containing dyestuffs resistant to stannous chloride but dischargeable by zinc formaldehyde sulfoxylate. It is then dried, aged, and if desired washed off. It is then cover printed with a zinc formaldehyde sulfoxylate discharge containing dyestuffs resistant to zinc formaldehyde sulfoxylate, aged, steamed if necessary, and washed off. A coloured discharge is obtained on a dyed ground with the pattern produced by the cover print both on the ground colour and on the pattern produced by the stannous chloride discharge.

C

A cellulose acetate fabric is printed with a resist composition containing zinc formaldehyde sulfoxylate, with or without dyestuffs which are resistant to zinc formaldehyde sulfoxylate. It is then dried, coverprinted with a second composition containing an aniline black resist agent, e.g. an alkali, together with dyestuffs resistant thereto but not resistant to zinc formaldehyde sulfoxylate, and dried and padded with an aniline black liquor, aged, steamed if necessary, chromed and washed off. White and/or coloured resists on a black ground with a second coloured resist appearing on the ground only are obtained. If desired the aniline black liquor may be padded on to the material prior to printing the resists but before ageing and chroming.

D

A cellulose acetate fabric is printed with an aniline black resist composition containing dyestuffs which are not dischargeable thereby but which are discharged by zinc formaldehyde sulfoxylate and dried. It is then cover printed with an aniline black resist composition containing zinc formaldehyde sulfoxylate with or without dyestuffs resistant to zinc formaldehyde sulfoxylate, dried, padded with an aniline black liquor, aged, steamed if necessary, chromed and washed off. Coloured resists are obtained on a black ground with white or coloured cover resists appearing both on the black ground and on the first mentioned coloured resist. If desired the aniline black liquor may be padded on to the material prior to printing the resists but before ageing and chroming.

E

A cotton fabric is coloured with colouring matters dischargeable both by sulfoxylate discharges and by stannous discharges, and prepared with a suitable mordant, e.g. tannic acid or the substance sold under the trade name Katanol O, the word "Katanol" being a registered trade-mark. It is then printed with a composition containing sodium formaldehyde sulfoxylate with or without dyestuffs resistant thereto, dried, and cover printed with a stannous chloride discharge containing dyestuffs, e.g. basic dyestuffs resistant to stannous chloride but dischargeable with sodium formaldehyde sulfoxylate. The fabric is finally aged, and where a tannic acid mordant has been employed, the latter is fixed with tartar emetic. White or coloured discharges are obtained on a dyed ground with other coloured discharges appearing on the ground only and not on the first mentioned discharges.

F

A cotton fabric is dyed and prepared as in E above, printed with a stannous chloride discharge containing dyestuffs resistant to stannous chloride but discharged by zinc formaldehyde sulfoxylate, dried, and if desired or requisite aged, and cover printed with a zinc formaldehyde sulfoxylate paste with or without dyestuffs resistant to zinc formaldehyde sulfoxylate. It is then aged, fixed with tartar emetic if prepared with tannic acid, and washed off. Coloured discharges are obtained on a dyed ground with white or coloured discharges appearing on both ground and the first mentioned discharges.

In the following paragraphs G and H there is illustrated the modification of the invention wherein one of the discharging agents is de-

stroyed before the application of the second discharge composition.

G

A cellulose acetate fabric coloured with a ground colour as in A above is printed with a discharge composition containing zinc formaldehyde sulfoxylate with or without dyestuffs resistant to zinc formaldehyde sulfoxylate, dried, aged, and washed off if desired. It is then cover printed with a stannous chloride discharge containing dyestuffs resistant to stannous chloride, aged, steamed if necessary, and washed off. White or coloured discharges are obtained on a dyed ground, the pattern produced by the cover print appearing both on the ground and on the zinc formaldehyde sulfoxylate discharge. Since the intermediate drying and ageing destroys the zinc formaldehyde sulfoxylate the colour produced by the cover print is superimposed on that of the first print where the two prints overlap. For example a yellow cover print on a blue discharge print will give a green colour in the overlapping areas.

H

A cotton fabric is coloured with a ground colour and prepared with mordants as in E above, and is printed with a composition containing sodium formaldehyde sulfoxylate with or without dyestuffs resistant to sodium formaldehyde sulfoxylate. It is then dried, aged, washed if necessary, and cover printed with a stannous chloride discharge containing dyestuffs resistant to stannous chloride but discharged by sodium formaldehyde sulfoxylate. It is then again aged, fixed with tartar emetic if prepared with tannic acid, and washed. White or coloured discharges are obtained on a dyed ground with other discharges appearing both on the ground and on the first mentioned discharges. In this case the colour of the second discharge is superimposed on that of the first discharge, if any, since the intermediate ageing destroys sodium formaldehyde sulfoxylate. For example if the two discharges are respectively yellow and blue, a green is obtained where the two overlap.

A wide range of dyestuffs, dischargeable both by stannous compounds and sulfoxylates, is available for producing the desired dischargeable ground colourations. In the case of cellulose ester and ether materials mention may be made of the insoluble and difficultly soluble colouring matters of the azo and nitro diarylamine series commonly employed in the colouration of cellulose ester materials. Examples of such colouring matters are benzene-azo-1-naphthalene-4-azo-4'-hydroxy benzene, para-nitrobenzene-azo-4-diphenylamine, 4-nitrobenzene-1'-azo-4'-amino-3'6'-dimethylbenzene, 4-nitro-2-methoxybenzene-1-azo-4'-dimethylaminobenzene, 4-nitro-2-methoxybenzene-1-azo-4'-diethylaminobenzene, 2:4-dinitrobenzene-azo-4'-diethylaminobenzene, the azo dyes from dinitro-o-anisidine or para-nitro-o-anisidine and ω -oxyethyl- α -naphthylamine, and o-methoxybenzene-azo- α -naphthylamine diazotized and developed on the material with β -oxynaphthoic acid.

For the colouration of the discharges any suitable colouring matter may be employed. As examples of colouring matters resistant to sulfoxylates particular mention may be made of vat dyestuffs applied in reduced form either as alkali salts or as free leuco compounds as described in U. S. application S. No. 459,828 filed June 7, 1930.

For resisting stannous discharges but not sulphoxylate discharges use may be made of di- or tri-arylmethane dyestuffs or others of the basic dye-stuff series, for example Malachite green crystals, Acronol green BS, Magenta crystals, Rhoduline blue 5B, Rosol scarlet G extra, Setocyanine and Setoglaurine, Brilliant Rhoduline purple R and Turquoise blue BB. Most of these have good direct affinity for cellulose esters and ethers and may be used on cotton with the aid of tannic acid, or the basic dye mordants obtainable by sulphurizing phenols, e. g. the product sold under the registered trade-mark "Katanol".

Dyestuffs having a carboxyl group or a single sulphonic group as substituents, such for example as dyestuffs of the anthraquinone or pyrazolone series having a carboxyl group or a single sulphonic group as substituents, may be employed for colouring both cellulose derivative fibres and animal fibres and are valuable for colouring discharge preparations for the local colouration of such fibres in mixed materials containing cellulose derivative and animal fibres. Thus for example discharge preparations for printing on mixed materials consisting of cellulose acetate and silk may be coloured with Solway Ultra blue B S, Modern yellow powder, or the dyestuff obtained by diazotizing anthranilic acid and coupling with phenyl methyl pyrazolone.

The following examples illustrate the invention without being in any way limitative:—

Example 1

A cellulose acetate fabric is dyed a red shade with 4-nitro-2-methoxybenzene-1-azo-4'-diethylaminobenzene, which is a dyestuff dischargeable both by sulphoxylates and by stannous discharges, and printed in a floral design with the following composition:—

	Grams
20% aqueous paste of the dyestuff para-hydroxy-benzene-azo-1-phenyl-3-methyl-5-pyrazolone	15
Methylated spirits	10
Gum arabic 1:1	55
Water	5
Decrolin sol. conc.	15
	100

After printing, the fabric is dried and immediately cover-printed with a design comprising numerous small spots with a composition of the following constitution:—

	Grams
Malachite green crystals	1.5
Methylated spirits	10.0
Sodium sulphocyanide 50%	5.0
Citric acid	1.0
Water	12.5
Gum arabic 1:1	60.0
Stannous chloride	10.0
	100.0

After cover-printing, the fabric is aged, and, if desired, gassed and steamed further in order to fix colouring matter, and is then washed, dried and finished as desired. A yellow floral design on a red ground is obtained with a green spotted pattern on the ground only.

Example 2

A cellulose acetate fabric is dyed as in Example

1 and then printed in a floral design with the following composition:—

	Grams
Malachite green crystals	1.5
Methylated spirits	10.0
Sodium sulphocyanide 50%	5.0
Citric acid	1.0
Water	12.5
Gum arabic 1:1	60.0
Stannous chloride	10.0
	100.0

After printing, the fabric is dried and cover-printed with a design comprising numerous small spots with a composition containing:—

	Grams
20% aqueous paste of the dyestuff para-hydroxy-benzene-azo-1-phenyl-3-methyl-5-pyrazolone	15
Methylated spirits	10
Gum arabic 1:1	55
Water	5
Decrolin sol. conc.	15
	100

The fabric is then dried, aged and steamed and washed and finished as requisite. A green floral design is obtained on a red ground with a further spotted design in yellow which appears both on the ground and where the printed and cover-printed designs overlap.

Example 3

An undyed cellulose acetate fabric is printed with a floral design with the following composition:—

	Grams
20% aqueous paste of the dyestuff para-hydroxy-benzene-azo-1-phenyl-3-methyl-5-pyrazolone	15
Methylated spirits	5
Gum arabic	45
Sodium acetate	25
Sodium formaldehyde sulphoxylate	10
	100

After drying, the fabric is immediately cover-printed in an all-over pattern of fine spots with the following composition:—

	Grams
Malachite green crystals	1.5
Methylated spirits	10.0
Water	13.5
Gum arabic 1:1	50.0
Sodium acetate	25.0
	100.0

and is then dried and aged and padded with a liquor containing:—

	Grams
Aniline hydrochloride	120
Acetic acid	24
Methylated spirits	96
Water	350
10% tragacanth thickening	250
Sodium chloride	77
Cupric chloride	3
Water	80
	1000

A cellulose acetate fabric is dyed as in Example

The fabric is finally dried, aged, gassed and steamed if desired, chromed, washed, dried and subjected to any other desired finishing treatment. A yellow floral design is obtained on a black ground with a further spotted green design on the ground only.

The following example illustrates the modification of the invention wherein the first discharging agent is destroyed before the second discharge composition is applied:—

Example 4

A cellulose acetate fabric is dyed and printed as in Example 1 except that after printing but before overprinting it is subjected to an ageing treatment. The effect obtained is a yellow floral design on a red ground with a green spotted pattern both on the ground and where the printed and over-printed designs overlap. In the latter case the shade being an additive one of the green and yellow.

What we claim and desire to secure by Letters Patent is:—

1. Process for the production of colored pattern effects on textile materials by discharge of ground color, comprising applying to selected areas before moist heat treatment, both a composition comprising a discharging agent for the said ground color and a coloring matter resistant to said discharging agent, and a composition comprising an agent which will discharge the ground color and also the coloring matter of the other

composition, so that at least part of the second mentioned discharge composition falls on areas covered by the first, and thereafter subjecting the materials to a moist heat treatment to effect discharge and fix coloring matters.

2. Process for the production of colored pattern effects on textile materials by discharge of ground color, which comprises applying to selected areas a composition comprising a discharging agent for the said ground color and a coloring matter resistant to said discharging agent, and, without removing the said discharge composition, applying a second composition comprising an agent which will discharge the ground color and also the coloring matter of the other composition, so that at least part of the second mentioned discharge composition falls on areas covered by the first.

3. Process for the production of colored pattern effects on textile materials by discharge of ground color which comprises applying to selected areas a composition comprising a discharging agent for the said ground color and a coloring matter resistant to said discharging agent and, without intermediate treatment, applying a second composition comprising an agent which will discharge the ground color and also the coloring matter of the other composition, so that at least part of the second mentioned discharge composition falls on areas covered by the first.

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