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PRODUCTION OF PATTERN EFFECTS ON
TEXTILE MATERIALSGeorge W. Seymour and Victor Sluyty Salvin,
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6 Claims. (Cl. 8-64)

This invention relates to the treatment of textile and other materials, and relates more particularly to a process for discharging colorations on textile materials for the purpose of producing pattern effects thereon.

An object of this invention is to apply the principle of discharging printing to textile materials to obtain clear white discharges and colored discharges which do not rub.

A further object of this invention is to effect discharge printing on textile materials by means of discharging compositions comprising a derivative of thiourea.

Other objects and advantages of this invention will appear from the following detailed description.

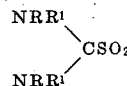
For the production of pattern effects on textile materials, the materials are commonly colored with a ground color, and then printed or otherwise locally treated with a composition which will discharge the ground color in the printed areas. As an alternative, the textile material may first be printed with the discharge composition and then colored with the ground color in which case the printed areas remain uncolored. In both cases colored pattern effects upon a colored background may be obtained by incorporating in the discharge composition a dyestuff having an affinity for the material or capable of being fixed thereon, and which is resistant to the discharging agent. After the application of the discharge composition, the materials are submitted to steaming or ageing or equivalent treatment in order to effect or complete the action of the discharging agent and also to fix properly the coloring matter in the discharge composition and/or the ground color. In general, a short steaming only is necessary to cause the discharging agent to act but a relatively longer steaming is necessary for the fixation of the color on the material.

Examples of substances which have heretofore been employed for the discharge of coloring matters are, among reducing discharges, stannous salts, titanous salts, and aldehyde sulphonylates, and, among substances which discharge by oxidation, chlorates and chromates. Some of these discharging agents are not completely satisfactory since they do not discharge all of the color components thus failing to yield clear white discharges and/or destroy the coloring matter in the discharge composition with the result that poor illumination effects are obtained. It has now been found that highly desirable pattern effects can be produced on textile materials by

means of discharging compositions containing as the discharging agent an oxidation product of thiourea, such as thiourea dioxide, or a derivative of such oxidation product. By the use of these reducing discharging agents improved results are obtained in white discharges and also in colored discharges.

By way of example this invention will be described as applied to textile materials made of or containing cellulose acetate but this process is also applicable to textile materials made of or containing other organic derivatives of cellulose such as cellulose esters and cellulose ethers. Examples of cellulose esters, other than cellulose acetate, are cellulose formate, cellulose propionate and cellulose butyrate, while examples of cellulose ethers are methyl cellulose, ethyl cellulose and benzyl cellulose. This invention is also applicable to textile materials generally whether the same may be made of or contain silk, cotton, wool or artificial silk of the reconstituted cellulose type.

According to the present invention, therefore, clear white discharges and illuminated charge effects are produced on textile materials made of or containing cellulose acetate by means of discharge preparations containing thiourea dioxide, or a derivative thereof in which alkyl, aralkyl and/or aryl groups are substituted on the nitrogen, or a calcium, zinc or sodium salt of thiourea dioxide or alkyl, aralkyl or aryl derivative of thiourea dioxide. Such compositions may be represented by the formula



wherein R or R¹ may be hydrogen, methyl, ethyl or other alkyl group, phenyl, cresyl or other aryl group, or benzyl or other aralkyl group. In the case of a metallic salt of thiourea dioxide R or R¹ may be a metallic radicle such as calcium, zinc or sodium. The discharge preparation may also contain a suitable thickening agent such as gum tragacanth or gum arabic.

It is preferred, however, to employ as the discharging agent thiourea dioxide, which compound is prepared in the following manner:

To 600 cubic centimeters of 14% hydrogen peroxide 76 grams (1 mol) of powdered thiourea are added slowly. Since the reaction is exothermic it is necessary to employ external cooling and to add the thiourea slowly in order to maintain the temperature below 20° C. 50% of the theoretical yield (54 grams) will separate from the solution

on standing. The thiourea dioxide thus prepared is a white crystalline powder containing 24 to 26% nitrogen (theoretical, 25.8%) and has a reduction value of SO_2 against iodine of 117.5-122. The thiourea dioxide is slightly soluble in water and soluble in dilute alkali.

Preferably a penetrating agent or a mixture of penetrating agents, such as calcium thiocyanate, sodium thiocyanate, potassium thiocyanate, glycerol monoacetin, glycerol formal, Glycine A, etc., is added to the discharge preparation. Where illuminated discharge effects are desired coloring matter is of course added to the discharge preparation. Buffer compounds may be added to the discharge preparation to control the pH value thereof, salts such as sodium acetate or sodium salts of other fatty acids being employed where a pH of between 7 and 10 is desired, and acids such as acetic acid, citric acid and tartaric acid being employed to discharge at a pH of less than 7.

The proportions in which the ingredients are incorporated in the discharge preparation for use in obtaining clear white discharges vary with textile material and the coloring matter to be discharged. However, a general formula for the application of the discharge compounds of this invention to a dischargeable material is as follows:

	Per cent by weight
Oxidation product of thiourea or derivative thereof.....	10-15
Thickening agent.....	25-50
Penetrating agent.....	5-10
Buffer compound.....	5-10

Where illuminated discharge effects are desired a suitable amount of the desired coloring matter is added to the discharge preparation.

Suitable coloring matters which may be added to the discharge preparation for the production of illuminated effects may be any desired unreduced coloring matters of the anthraquinone series, especially such coloring matters as contain a single anthraquinone nucleus. For instance, there may be used mono-, di-, or polyaminoanthraquinones whether unsubstituted or substituted in the nucleus or in an amino group or both, for example, amino-methyl anthraquinones, acetyl-amino-anthraquinones, alkylamino anthraquinones, and substituted -alkyl-amino anthraquinones, e. g. oxy-alkylamino-anthraquinone. Moreover, hydroxyl- or mercapto anthraquinones or their ethers or other substitution products may be employed. Sulphonated anthraquinone color matters having affinity for cellulose ester or ether materials may likewise be employed for producing illuminated effects on materials containing cellulose esters or ethers. Cotton vat dyes such as the Indanthrene dyes, which are pyranthrones, may also be used as coloring matters in accordance with this invention. Using vat dyestuffs, which have been reduced to their leuco form, it is possible to discharge print and illuminate mixed fabrics such as cellulose acetate and cotton, cellulose acetate and regenerated cellulose, cellulose acetate and silk, etc.

If desired the discharge agents of this invention may be employed in combination with other reducing agents. Thus, for example, thiourea dioxide may be employed to replace a part of other reducing discharging agents such as sodium formaldehyde sulfoxylate or zinc formaldehyde sulfoxylate.

One of the important advantages of the use of the discharging agents of this invention over those heretofore employed is that the former are absorbed in the fibers of the textile material, particularly when the fibers are made of or contain cellulose acetate, where their strong reducing action may be utilized more completely.

The fabric may be previously dyed with a ground color containing any suitable dischargeable dyestuff, examples of which are:

Setacyl Direct Discharge Blue G
Setacyl Direct Yellow 5G
Setacyl Direct Orange GH
Setacyl Direct Red GN
Celliton Discharge Yellow 3GN
Celliton Discharge Blue 5G
Celliton Discharge Yellow RL
Celliton Discharge Red BDL
SRA Red VIII
SRA Navy Base VI + SRA Navy Developer I

Other dyestuffs, which include materials similar to para-nitroaniline coupled with 2-methoxy-5-acetyl-amino-aniline, and meta-dihydroxyethylamino-acetanilide, may also be used. Orthochlor-para-nitroaniline may be employed instead of the para-nitroaniline.

The following are examples of methods of carrying out our invention, which were found to give excellent results, but the invention is not to be considered to be limited to these examples.

Example I

A fabric consisting wholly of cellulose acetate yarn and which has been dyed blue with 2,4-dinitro-6-chlorbenzeneazo-2-dihydroxy-ethylamino-4-acetyl-amino-anisole has applied locally thereto by means of engraved rollers a discharge paste of the following formula

	Per cent
Thiourea dioxide.....	15
Monoacetin.....	10
Disodium phosphate.....	10
Gum tragacanth (7 oz. per gal.).....	30
Water.....	35

The fabric, after printing, is passed through an ager where it is exposed for five to twenty minutes to steam at 211-212° F., and is then washed in an open soaper, in which the reduction products of the dyestuff are removed.

A design of white discharge on a blue background is produced.

Example II

The process of Example I is carried out, with the exception that the following discharge paste is employed:

	Per cent
Thiourea dioxide.....	15
Monoacetin.....	10
Vat dyestuff (20% Indanthrene Scarlet B in water).....	20
Disodium phosphate.....	10
Gum tragacanth (7 oz. per gal.).....	30
Water.....	15

This fabric is steamed as in Example I. It is then washed in an open soaper, as follows:

The fabric is subjected to water to remove alkali, then scoured with neutral soap or Gardinol to remove the reduction products of the dyestuff, and then oxidized in the known manner. It is preferable to remove these reduction products prior to oxidation to preclude the pos-

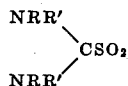
sibility of the formation of dyes of the type of Bismarck Brown and Aniline Black.

A fabric having a design in scarlet red color on a background of blue is produced.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

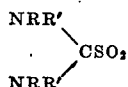
Having described our invention, what we desire to secure by Letters Patent is:

1. Process for the production of discharge effects upon materials having a basis of an organic derivative of cellulose and colored with a dischargeable ground color having an affinity for said organic derivative of cellulose materials, which comprises applying to the materials a discharge composition of a pH less than 7 containing 25 to 50% by weight of a thickening agent, 5 to 10% by weight of a penetrating agent, 5 to 10% by weight of a buffer compound and from 10 to 15% by weight of a reducing agent of the formula



wherein R or R' is hydrogen, alkyl, aryl or aralkyl.

2. Process for the production of discharge effects upon materials having a basis of cellulose acetate and colored with a dischargeable ground color having an affinity for said cellulose acetate materials, which comprises applying to the materials a discharge composition of a pH less than 7 containing 25 to 50% by weight of a thickening agent, 5 to 10% by weight of a penetrating agent, 5 to 10% by weight of a buffer compound and from 10 to 15% by weight of a reducing agent of the formula



wherein R or R' is hydrogen, alkyl, aryl or aralkyl.

3. Process for the production of discharge effects upon materials having a basis of an organic derivative of cellulose and colored with a dischargeable ground color having an affinity for said organic derivative of cellulose materials, which comprises applying to the materials a discharge composition of a pH less than 7 containing from 10 to 15% by weight of thiourea dioxide, 25 to 50% by weight of a thickening agent, 5 to 10% by weight of a penetrating agent and 5 to 10% by weight of a buffer compound.

4. Process for the production of discharge effects upon materials having a basis of cellulose acetate and colored with a dischargeable ground color having an affinity for said cellulose acetate materials, which comprises applying to the materials a discharge composition of a pH less than 7 containing from 10 to 15% by weight of thiourea dioxide, 25 to 50% by weight of a thickening agent, 5 to 10% by weight of a penetrating agent and 5 to 10% by weight of a buffer compound.

5. Process for the production of discharge effects upon materials having a basis of an organic derivative of cellulose and colored with a dischargeable ground color having an affinity for said organic derivative of cellulose materials, which comprises applying to the materials a discharge composition of a pH less than 7 containing 15% by weight of thiourea dioxide, 10% by weight of monoacetin, 10% by weight of disodium phosphate, 30% by weight of gum tragacanth and 35% by weight of water.

6. Process for the production of discharge effects upon materials having a basis of cellulose acetate and colored with a dischargeable ground color having an affinity for said cellulose acetate materials, which comprises applying to the materials a discharge composition of a pH less than 7 containing 15% by weight of thiourea dioxide, 10% by weight of monoacetin, 10% by weight of disodium phosphate, 30% by weight of gum tragacanth and 35% by weight of water.

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