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DISCHARGE PRINTING

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The present invention relates to the discharge printing of colored textile materials of organic acid esters of cellulose of low free hydroxyl content.

Discharge printing is the destructive removal of dye or dye components from selected areas of textiles containing the dye or dye components. In white discharge printing the selected areas are left as white on a colored background while in colored or illuminated discharge printing the selected areas lose their original color and are dyed a different color by a dye incorporated in the discharge composition. The discharging reaction must take place where the dye to be discharged, i.e. destroyed, is located.

It is therefore necessary that the active components of the discharge composition are able to penetrate into the fibers while of course not injuring the fibers themselves. The substances left in the fibers after discharge has been effected must also be capable of being taken out of the fibers. The discharge composition of course must not be too fluid lest it migrate from the selected areas where applied and act on areas not intended to be discharged.

While it would be desirable to discharge print textile materials comprising organic acid esters of cellulose of low free hydroxyl content, conventional discharge pastes and processes are not satisfactory as applied to such materials in that the treated areas are fuzzy and not distinctly set off from the untreated areas and in that not all of the color is discharged even in the treated areas and discharge products are not removed, resulting in discoloration on exposure to light, heat and gas.

It is accordingly an object of the present invention to provide discharge compositions suited for discharge printing of textile materials comprising organic acid esters of cellulose of low free hydroxyl content.

It is a further object of the invention to provide a novel procedure for the discharge printing of colored textile materials comprising organic acid esters of cellulose of low free hydroxyl content.

It is a further object of the invention to provide a novel procedure for simultaneously discharging the color from selected areas of colored textile materials of organic acid esters of cellulose of low free hydroxyl content, and for improving the physical properties of the textile material.

Other objects and advantages will be apparent from the following description and claims. Throughout the following description and claims all parts and percentages refer to weight units unless otherwise specified.

In accordance with one aspect of the present invention, selected areas of textile materials of organic acid esters of cellulose of low free hydroxyl content, and containing dye or dye components, are treated with an aqueous composition containing a metal formaldehyde sulfoxylate, a reversible hydrophilic thickener, and a swelling agent selected from the group consisting of phenyl-methyl-carbinol, tri-lower alkyl phosphates such as triethyl phosphate and ethers and/or esters of aliphatic polyhydroxy compounds, e.g., of glycols, such as β-phenoxyethanol, glycol diacetate, methoxyethyl acetate.

The textile printed with the discharge composition is dried, steamed and thereafter scoured. Advantageously the textile is heat treated to improve its glaze resistance and to increase its crystallinity and safe ironing temperature in the event that it has not been heat treated either before or during the discharge printing.

For each 40 to 80 parts by weight of water in the discharge composition there are present from about 15 to 30 parts by weight of a metal formaldehyde sulfoxylate and preferably 20 to 30 parts by weight. While monovalent metal formaldehyde sulfoxylates such as sodium formaldehyde sulfoxylate can be used, the formaldehyde sulfoxylates of polyvalent metals are preferred because reduction of the dischargeable dyes is best effected on the neutral or slightly acid side and sodium formaldehyde sulfoxylate, for example, is not stable on the slightly acid side. Representative polyvalent metal formaldehyde sulfoxylates include zinc and barium formaldehyde sulfoxylates and best results are achieved with zinc formaldehyde sulfoxylate.

The swelling agent serves to swell the fibers and to permit the metal formaldehyde sulfoxylate to attack the dyestuff within the fibers. Its swelling action, however, must not be so great as to cause the fibers to coalesce or otherwise to be damaged. Satisfactory results are achieved using from about 2 to 10 or preferably 2 to 6 parts by weight of one or a mixture of swelling agents. The preferred swelling agent is β-phenoxyethanol.

About 1 to 7 and preferably 2 to 5 parts by weight of the reversible hydrophilic thickener should be present in the discharge composition; it serves to thicken the composition and thus to prevent migration of the components beyond the areas to which the composition is selectively applied. In addition to its thickening properties, the thickener should not break down even at temperatures in excess of the boiling point of water at atmospheric pressure and must be hydrophilically reversible, i.e. it must be capable of re-wetting even after hard drying to permit the thickener to be washed out following discharge. The thickener, of course, must be compatible with the metal formaldehyde sulfoxylate. While vegetable carbohydrate gums such as apo gum, British gum, and starch ethers such as methylated and carboxylated starch are suitable, oxyethylated locust bean gum (prepared by reacting locust beam gun with ethylene oxide) is preferred because it does not break down even at the temperatures of pressurized steam and because of the quality of the discharge, its sharpness and freedom from discoloration.

Especially good results are achieved when from about 2 to 8 and preferably 2 to 6 parts by weight of a water-miscible aliphatic polyhydroxy compound is included in the discharge composition as a humectant. The humectant brings the water within the fiber where it is necessary for the metal formaldehyde sulfoxylate to reduce the dye. Representative water-miscible aliphatic polyhydroxy compounds include glycerol, sorbitol, ethylene glycol, diethylene glycol and higher polyethylene glycols, and preferably thiodiethylene glycol.

About 1 to 6 and preferably 2 to 4 parts by weight of a water-soluble hydroxylated lower aliphatic acid such as tartaric acid and preferably citric or lactic acid increase the discharge effect and are especially useful where a white rather than an illuminated discharge is desired.

Up to about 15 and preferably 5 to 10 parts by weight of an inorganic, insoluble water binding additive may be incorporated into the discharge composition to prevent spreading of the discharge agent upon steaming, thereby improving the sharpness of the discharge prints. Suitable substances include the oxides of one or more metals and/or silicon, such as bentonite, kaolin, fuller's earth, silica, alumina, and especially titanium dioxide.

If desired, up to about 20 and preferably from 1 to 15 parts by weight of a dye or pigment may be incorporated into the discharge compositions so that the discharge printed areas will take on a new color different from their original color.

The composition is prepared by first mixing the thickener and water followed by stirring in the water-solubles, the discharge agent and then the hydrophobic ingredients. Solid substances are added either as solutions or dispersions in water.

The discharge compositions or pastes are applied in conventional manner such as with a screen to colored textile materials made up in whole or in part of organic acid esters of cellulose of low free hydroxyl content, i.e. less than about 0.29 free hydroxyl groups per anhydroglucose unit of the cellulose molecule. Representative esters include cellulose propionate, cellulose butyrate, cellulose acetate-butyrate, and the like, although cellulose acetate is preferred. While cellulose acetate having 0.29 free hydroxyl groups per anhydroglucose unit, i.e. an acetyl value of at least about 59% by weight calculated as combined acetic acid, is suitable, preferably the acetyl value is at least 61%. A particularly suitable fiber is composed of a core of a cellulose acetate of a high acetyl value having an integral thin skin of regenerated cellulose such as is produced by a surface saponification of cellulose acetate having an acetyl value of at least 59%.

Such highly esterified cellulose is capable of developing relatively high crystallinity and of being ironed safely at temperatures in excess of 200° C. upon suitable heat treatment. Preferably, however, the textile material which is printed with the discharge paste contains organic acid esters of cellulose which have not been treated since heat treated materials are considerably more difficult to discharge.

The textile material printed with the discharge composition is dried in air and/or an oven and thereafter steamed to effect discharge, followed by scouring. The steaming generally lasts at least 10 minutes to effect adequate discharge. When steaming is effected at atmospheric pressure with steam at a temperature of about 216° F., it is generally desirable to effect a heat treatment to improve the physical properties of the textile material. To this end, following steaming the textile material is dried and is then heat treated with hot air or the like in the manner described in the copending application of Salvin et al., Ser. No. 472,758, filed December 2, 1954, now U.S. Patent No. 2,982,597.

In a preferred embodiment of the invention, the steaming is effected at a temperature in excess of about 237° F. and preferably from about 239 to 250° F., the steam being under sufficient pressure to permit such temperatures, e.g. about 9 p.s.i.g. or more. The pressure steaming may last from about 45 to 75 minutes, the exact duration depending upon the temperature; at the lower temperatures one hour steaming is adequate. The pressure steaming produces a sharp discharge and also effects heat treatment so that no separate treatment for this purpose is necessary. Heat treatment following normal steaming sometimes yellows the discharge areas slightly, but this yellowing is not evidenced when the steaming is carried out under such conditions as will simultaneously effect heat treatment.

As employed herein, the term "colored" in describing the starting textile material has reference to directly visible color as well as to potentially visible color as when one component of an azo dye is in the fiber and visible color will later be developed by coupling on the fiber. The "color" whether apparent or latent, i.e. whether the starting material is impregnated with a dyestuff or a component thereof, must of course be one which is capable of being discharged; the classes of substances which are dischargeable are well-known.

The following examples are given to illustrate this invention further.

Example I

(*a*) A taffeta fabric, woven from cellulose acetate yarn having an acetyl value of 61% by weight calculated as combined acetic acid and dyed navy blue with Eastone Blue GFD, Eastone Red GLF (2-methylsulfone-4-nitro-4'(N-β,β-difluoroethyl-N-β-hydroxyethyl)aminoazobenzene) and Amacel Yellow G (Color Index No.

11855) in the presence of tripropyl phosphate, is printed with a discharge paste comprising by weight 4.2 parts of oxyethylated locust bean gum, 8 parts of β-phenoxyethanol, 20 parts of zinc formaldehyde sulfoxylate, 2 parts of lactic acid, 2 parts of thiodiethylene glycol, 10 parts of titanium dioxide and 80.8 parts of water. The fabric is dried in air for 30 minutes and then in an oven at 140° F. for 5 minutes.

(*b*) A portion of the dried fabric from (2) is steamed for 10 minutes with steam at atmospheric pressure and 216° F., scoured for 15 minutes at 120° F. in water containing 1 gram per liter of soap and 1 gram per liter of sodium hexametaphosphate, and then dried in an oven at 140° F. There is obtained a full discharge effect with a good sharp edge. The fabric is then heat treated in air for 30 seconds at 446° F. and its safe ironing temperature is raised from 374° F. to 450° F. The discharge area yellows slightly as a result of the heat treatment. If the fabric is heat treated prior to discharge printing, the discharge effect and the sharpness of the edge are not as good as when discharge is effected before heat treatment, but the sharpness of the mark is better.

(*c*) Another portion of the dried fabric from (*a*) is steamed for 1 hour with steam at 10 p.s.i.g. and 239° F. The fabric is scoured for 15 minutes at 150° F. in water containing 1 gram per liter of soap and 1 gram per liter of sodium hexametaphosphate, is dried in air for 30 minutes and is then dried for 10 minutes in an oven at 140° F. The discharge effect and sharpness are as good as in (*b*), the discharge area is white and does not discolor even upon prolonged exposure, and the safe ironing temperature of the fabric is 450° F.

Example II

The process of Example I(*a*) and (*b*) is repeated except that the titanium dioxide is omitted from the discharge paste. The sharpness of the edge is not quite as good as in Example I(*b*) but the discharge effect is slightly better.

Example III

The process of Example I(*a*) and (*b*) is repeated substituting citric acid for lactic acid. A slightly better discharging effect is realized. If the acid is omitted altogether the discharge effect is not quite as complete.

Example IV

The process of Example I(*a*) and (*b*) is repeated, varying the proportions of β-phenoxyethanol and thiodiethylene glycol. Best results are achieved when 4 to 6 parts of each are present.

Example V

A fabric woven of a cellulose acetate yarn having an average acetyl value of 59.5% and composed of filaments having a thin skin of regenerated cellulose integral with a core of cellulose acetate having an acetyl value of 61%, is dyed blue in conventional manner with Eastone Blue GFD to pick up 3% by weight of the dye. The blue fabric is printed with a colored discharge composition comprising 5 parts of oxyethylated locust bean gum, 83 parts of water, 20 parts of zinc formaldehyde sulfoxylate, 2 parts of thiodiethylene glycol, 10 parts of glycol diacetate and 10 parts of Cibanone Brilliant Green BF (Color Index No. 1101). After printing the fabric is dried for 10 minutes at 140° F., is steamed for 1 hour with saturated steam at 239° F. and 10 p.s.i.g., scoured for 20 minutes at 160° F. in water containing 1 gram per liter of soap, and then dried for 10 minutes at 140° F. The printed areas are bright green on a blue background. The lines of demarcation are sharp and the fabric is level, resistant to crocking and resistant to color change in an oxidizing bath. The safe ironing temperature of the fabric is 450° F. as compared with a safe ironing temperature of 374° F. for the fabric prior to printing with the discharge composition.

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. The process which comprises applying to selected areas of a colored textile material comprising an organic acid ester of cellulose having less than about 0.29 free hydroxyl groups per anhydroglucose unit a discharge printing composition comprising water, a discharge agent, a swelling agent for the organic acid ester of cellulose and a thickener, drying the textile material, and steaming the textile material with steam at a temperature in excess of about 237° F. and a pressure in excess of about 9 p.s.i.g.

2. The process which comprises applying to selected areas of a colored textile material comprising an organic acid ester of cellulose having less than about 0.29 free hydroxyl groups per anhydroglucose unit a discharge printing composition comprising by weight about 40 to 80 parts of water, about 15 to 30 parts of a discharge agent, about 2 to 10 parts of a swelling agent for the organic acid ester of cellulose, about 1 to 7 parts of a thickener and about 2 to 6 parts of a humectant, drying the textile material and steaming the textile material with steam at a temperature in excess of about 237° F. and a pressure in excess of about 9 p.s.i.g.

3. The process which comprises applying to selected areas of a colored textile material comprising cellulose acetate having an acetyl value of at least about 61% by weight calculated as combined acetic acid a discharge printing composition comprising by weight about 40 to 80 parts of water, about 20 to 30 parts of zinc formaldehyde sulfoxylate as discharge agent, about 2 to 10 parts of β-phenoxyethanol as swelling agent for the cellulose acetate, about 1 to 7 parts of oxyethylated locust bean gum as thickener, about 2 to 6 parts of thiodiethylene glycol as humectant, about 2 to 4 parts of lactic acid and about 5 to 10 parts of titanium dioxide, drying the textile material, and steaming the textile material with steam at a temperature in excess of about 237° F. and a pressure in excess of about 9 p.s.i.g.

4. A discharge printing composition comprising by weight about 40 to 80 parts of water, about 20 to 30 parts of zinc formaldehyde sulfoxylate as discharge agent, about 2 to 10 parts of β-phenoxyethanol as swelling agent for the cellulose acetate, about 1 to 7 parts of oxyethylated locust bean gum as thickener, about 2 to 6 parts of thiodiethylene glycol as humectant, about 2 to 4 parts of lactic acid and about 5 to 10 parts of titanium dioxide.

5. The process which comprises applying to selected areas of a colored textile material comprising an organic acid ester of cellulose having less than about 0.29 free hydroxyl groups per anhydroglucose unit a discharge printing composition comprising by weight about 40 to 80 parts of water, about 15 to 30 parts of a polyvalent metal formaldehyde sulfoxylate as discharge agent, about 2 to 10 parts of a swelling agent for the organic acid ester of cellulose and about 1 to 7 parts of a reversible hydrophilic thickener, drying the textile material and then steaming the textile material until the printed areas are discharged, said swelling agent comprising at least one member selected from the group consisting of phenyl-methyl carbinol, tri-lower alkyl phosphates, ethers of polyhydric alcohols, esters of polyhydric alcohols and ether-esters of polyhydric alcohols.

6. The process which comprises applying to selected areas of a colored textile material comprising an organic acid ester of cellulose having less than about 0.29 free hydroxyl groups per anhydroglucose unit a discharge printing composition comprising by weight about 40 to 80 parts of water, about 15 to 30 parts of a polyvalent metal formaldehyde sulfoxylate as discharge agent, about 2 to 10 parts of a swelling agent for the organic acid ester of cellulose comprising β-phenoxyethanol and about 1 to 7 parts of a reversible hydrophilic thickener, drying the textile material and then steaming the textile material until the printed areas are discharged.

7. A discharge printing composition comprising by weight about 40 to 80 parts of water, about 15 to 30 parts of a discharge agent selected from the group consisting of zinc and barium formaldehyde sulfoxylate, about 2 to 10 parts of a swelling agent comprising β-phenoxyethanol, about 1 to 7 parts of a reversible hydrophilic thickener and about 2 to 6 parts by weight of a water-miscible humectant comprising thiodiethylene glycol.

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