

## UNITED STATES PATENT OFFICE

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## COMPOSITION FOR DISCHARGE PRINTING

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This invention relates to the obtaining of reduction discharge prints on colored cellulose carboxylic ester fabrics including fabrics comprising mixtures of cellulose carboxylic ester rayon with cotton, viscose and cuprammonium rayon.

It is known in the art of textile printing that colored cellulose carboxylic ester fabrics will not discharge with sodium, potassium or normal zinc sulfoxylate alone, to give a clear and sharply defined white, without the addition of a swelling agent and a suitable catalyst. It is also well known that discharge prints on cellulose carboxylic ester fabrics produced by alkaline earth sulfoxylates or neutral metal sulfoxylates will spread out, or "halo," when subjected to a prolonged or pressure steaming, suitable to destroy or permanently decolorize the dyed ground. It is also well known that anthraquinone paste will speed up the action of the above reducing agents, within a suitable commercial time of aging or steaming. However, it is impossible to completely remove the anthraquinone from the cellulose carboxylic ester fabric without injuring the fabric. The residue which remains oxidizes under the action of light and air to a hue ranging from a pale yellow to a tan. Thus the anthraquinone method is of no commercial value where white discharges are required. Hydroquinone also speeds up the action of the sulfoxylates in a manner similar to anthraquinone paste. However, hydroquinone causes a tendering or weakening of the cellulose ester fibers. Therefore, the use of hydroquinone is limited, from a commercial standpoint, to those fabrics in which the inherent strength of the fabrics is of no importance.

We have now found that the above difficulties can be overcome and the discharge printing of textile materials comprising a cellulose carboxylic ester can be generally improved by employing salicylic acid or a salt of salicylic acid to accelerate the discharging action of the sulfoxylates. It is, accordingly, an object of our invention to provide a new method for discharge printing. A further object of our invention is to provide a new composition for discharge printing. Other objects will become apparent hereinafter.

In accordance with our invention, we effect the discharge of dischargeable colors on textile materials comprising cellulose carboxylic esters with aldehyde metal sulfoxylates, in the presence of salicylic acid or a salt of salicylic acid. The discharge is advantageously effected in the presence of a swelling agent, e. g. triethylene glycol, diacetyethanolamine, propylene glycol, diethylene glycol, sodium thiocyanate, calcium thiocyanate,

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zinc thiocyanate, potassium thiocyanate or thiodiglycol. In practicing our invention, it is advantageous to prepare a paste containing salicylic acid or a salt of salicylic acid, the sulfoxylate, a swelling agent and a thickening agent. This paste composition is then printed upon the fabric which is dyed with a dischargeable dye, and the printed fabric subjected to the action of steam, whereupon discharging takes place.

The following examples will serve to illustrate the manner of practicing our invention.

## Example 1

A 100% cellulose acetate satin material was dyed a light brown with 0.5% Eastone Blue BB, 0.5% Eastone Orange 2R, and 0.125% Eastone Red R in the customary single bath method of dyeing.

The above fabric after drying was printed with a paste made as follows:

|                                                                               |      |       |
|-------------------------------------------------------------------------------|------|-------|
| Sodium formaldehyde sulfoxylate.....                                          | lbs. | 3     |
| Water .....                                                                   | qts. | 1 1/4 |
| Thiodiglycol .....                                                            | qts. | 1/4   |
| Supertex T-125 (solubilized gum karaya textile gum; Jacques Wolf and Company) |      |       |
| Salicylic acid.....                                                           | qts. | 2 1/4 |
|                                                                               | oz.  | 8     |

The above paste was applied by a roller printing machine; the fabric was dried, and aged for 3-6 minutes above 212° F. in the usual manner as vat colors are aged, rinsed well in running water, soaped lightly, rinsed, and dried. A clear sharp white discharge was obtained on the light brown material. The above was run without the use of salicylic acid and an orange-brown discharge was obtained.

## Example 2

A fabric constructed of 50% cellulose acetate rayon and 50% viscose rayon was dyed a blue shade using 2% of Eastone Blue BB based on the weight of cellulose acetate and 1.6% of Pontamine Blue RW (C. I. No. 512) based on the weight of the viscose rayon, using the customary single bath method of dyeing. The above blue-dyed sample was printed by the block screen method using the following paste:

|                                         |      |       |
|-----------------------------------------|------|-------|
| Potassium sulfoxylate formaldehyde..... | lbs. | 1 1/2 |
| Thiodiglycol .....                      | oz.  | 8     |
| Water .....                             | qts. | 1 1/4 |
| Supertex T-125 .....                    | qts. | 2 1/4 |
| Salicylic acid.....                     | oz.  | 4     |

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The fabric was printed, dried, and aged for 3-6 minutes in the usual manner that screen printed vat colors are aged, rinsed well in running water, soaped lightly, rinsed, and dried. A clear, sharp white discharge was obtained on the blue material.

#### Example 3

A blue-dyed fabric like that described in Example 2 was printed by the roller printing method using the following formula:

|                                               | Per cent |
|-----------------------------------------------|----------|
| Algol Orange RFA Suprafix (C. I. No. 1217) -- | 20       |
| Vat paste -----                               | 80       |

The vat paste was made up as follows:

|                   |          |
|-------------------|----------|
| British gum-----  | lbs-- 2½ |
| Wheat starch----- | lbs-- ½  |
| Water -----       | qts-- 3½ |

The above ingredients were boiled for ½ hour, the heat turned off, and 1½ lbs. of sodium carbonate, ½ lb. of salicylic acid, and 8 oz. of thiodiglycol were added. Stirring was continued until foaming stopped. (Antifoam agents such as octyl alcohol may be added.) Then 1¼ lbs. of sodium formaldehyde sulfoxylate was added. The fabric was printed, dried, aged 3-6 minutes above 212° F. in the usual manner for printing vat colors on viscose rayon or cotton fabrics. It was rinsed ½ minute in cold water and oxidized for 10 minutes with soap at 140° F., then rinsed well and dried. A bright, well-defined orange print was obtained on the blue ground.

#### Example 4

A 100% acetate knit jersey material was dyed a tomato red shade with 1% Eastone Red R in the customary manner, dried, printed, and processed as in Example 1. A clear, well-defined white was obtained on the red ground.

#### Example 5

A fabric constructed of 50% cotton and 50% spun acetate was dyed a yellow shade with 2% Eastone Yellow 3GM (Tennessee Eastman Corporation) based on the weight of the acetate, and 1.2% of Pontamine Fast Yellow 4GL (Pr. No. 53) and 0.2% Pontamine Fast Yellow RL based on the weight of the cotton. The customary single bath method was employed in carrying out the dyeing operations. The dried fabric was printed by the block screen method using the following printing paste:

|                                            |    |
|--------------------------------------------|----|
| Normal zinc formaldehyde sulfoxylate--oz-- | 12 |
| Sodium formaldehyde sulfoxylate-----oz--   | 8  |
| Thiodiglycol-----oz--                      | 8  |
| Water -----qts--                           | 1½ |
| Supertex T-125-----qts--                   | 2½ |
| Salicylic acid-----oz--                    | 4  |

After printing, the fabric was dried, aged above 212° F. for 6 minutes, washed, and dried. A clear, sharp white discharge was obtained on the yellow material.

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In the above examples, salicylic acid can be replaced by its salts, such as its ammonium salt, its sodium salt, its potassium salt or its calcium salt, for example. In Example 3, the sodium salt of salicylic acid is formed owing to the presence of the alkali.

Our invention is directed especially to fabrics comprising such cellulose carboxylic esters as the hydrolyzed and unhydrolyzed cellulose acetates, cellulose propionates and cellulose butyrates, as well as the mixed cellulose esters, such as the hydrolyzed and unhydrolyzed cellulose acetate-propionates and cellulose acetate-butyrate. All of these cellulose carboxylic esters consist of a cellulose portion or radical and an acid radical which contains from 2 to 4 carbon atoms.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. A composition for discharge printing comprising a formaldehyde metal sulfoxylate and a substance selected from the group consisting of salicylic acid and its salts.

2. A composition for discharge printing comprising formaldehyde sodium sulfoxylate and a substance selected from the group consisting of salicylic acid and its salts.

3. A composition for discharge printing comprising a swelling agent for cellulose carboxylic ester textile materials, a formaldehyde metal sulfoxylate and a substance selected from the group consisting of salicylic acid and its salts.

4. A composition for discharge printing comprising a formaldehyde alkali metal sulfoxylate and salicylic acid.

5. A composition for discharge printing comprising formaldehyde sodium sulfoxylate and salicylic acid.

6. A composition for discharge printing comprising a formaldehyde alkali metal sulfoxylate, normal zinc formaldehyde sulfoxylate and a substance selected from the group consisting of salicylic acid and its salts.

7. A composition for discharge printing comprising formaldehyde sodium sulfoxylate, normal zinc formaldehyde sulfoxylate and a substance selected from the group consisting of salicylic acid and its salts.

8. A process for discharge printing of textile materials comprising a cellulose carboxylic ester comprising printing the textile material colored with a dischargeable dye with a paste comprising a formaldehyde metal sulfoxylate and a substance selected from the group consisting of salicylic acid and its salts, and steaming the printed fabric.

9. A composition for discharge printing comprising normal zinc formaldehyde sulfoxylate and a substance selected from the group consisting of salicylic acid and its salts.

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