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METHOD OF DYEING AND PRODUCT

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This invention relates to an improved method of treating and dyeing articles, as well as an improved product derived by the practice of such method. This invention particularly relates to an improved method of treating and dyeing articles comprised of cellulose-acetate silk, which is sometimes known as "Celanese" or "Acele".

It is well appreciated that this product, known by those skilled in the art as cellulose-acetate, has many advantages over other synthetic or natural fibers, but one of the greatest difficulties heretofore encountered has been in connection with the dyeing and printing of yarns and fabrics composed thereof.

More particularly, while during recent years it has become practicable to dye yarns of this character, or yarns of this character mixed with other fibers such as cotton or silk, a solid color, attempts to include designs or patterns in the material have been far from satisfactory.

With types of material, other than the cellulose-acetate group, it has been common practice to dye the entire material body and thereupon to employ what has been known as a discharge agent, which destroyed or removed the color at its point of contact with the material. It was also possible, if desired, to simultaneously dye or color the discharged area with a contrasting shade by the incorporation of a dye or color with the discharging agent. This process is commonly known as "color discharge printing" and will be referred to as such.

Thus, it is an object of the present invention to provide a method or process by means of which designs in contrasting colors may be incorporated in cellulose-acetate materials to produce the product of the present invention, such method being capable of practice at relatively small expense and with facility so that a commercially practicable method is taught and an article is produced which may be sold at a relatively nominal figure.

It is a further object of the invention to furnish a method and product in which perfect designs will be achieved readily by operators possessing merely ordinary skill.

The following specification is to be regarded as illustrative and not in a limited sense. The scope of the invention will be apparent from a perusal of the claims.

In endeavoring to properly dye acylated products of cellulose such as cellulose formate, cellulose acetate or cellulose benzylate, penetrating or swelling agents such as formic acid, acetic acid, ethyl alcohol, acetone or diacetone alcohol, phenol, resorcinol, urea, ammonium sulphocyanide, and lactic acid have been employed. The resultant swelling of the fibers (as disclosed in British Patent No. 285,948, to Henry Dreyfus, granted August 10, 1927,) assists materially in penetrating the fibers with mordanting agents. As is well known, these mordanting agents act to give body and weight to the material and may be, for example, inorganic salts such as ferric chloride or tin chloride.

However, while these swelling or penetrating agents are effective in dyeing or assisting in mordanting, they have not been effective in assisting the color discharge printing of acylated cellulose fabrics. The usual method of discharge printing on fabrics containing acylated cellulose is to treat the fiber with the sulfoxylate of sodium formaldehyde (i. e., the formaldehyde reaction product with sodium sulfoxylate) or the sulfoxylate of potassium formaldehyde. This material destroys the color and leaves a white or contrasted shade where it has come in contact with the fabric. However, in the case of acylated cellulose fabrics, the use of the sulfoxylate of sodium formaldehyde, even in the presence of penetrating and swelling agents, has caused unsatisfactory results, particularly if the material was dyed in a dark shade. It has been found that while these penetrating agents do assist in effecting a discharge by themselves this discharge is not sufficient to be of practicable or commercial value.

Further, when a color discharge print is desired, it is obvious to one skilled in the art that unless the ground color can be success-

fully discharged, it is of little value to mix other colors with the discharge agent in an effort to obtain contrasting colors in the discharged area.

It has recently been found that a discharge on dyed cellulose-acetate fabrics may be obtained by use of the sulfoxylate of zinc formaldehyde. However, this product has the limitation that it cannot be used in conjunction with fast colors to produce contrasting color effects, but can only be used to produce a white discharge or a fugitive color discharge on cellulose-acetate fibers. To one skilled in the art it is clear that discharge work where only white contrasting effects and fugitive color effects may be obtained is far more limited in its application than a discharge where both fast color and white effects may be obtained.

However, the use of organic derivatives of the sulfoxylate of sodium formaldehyde have been found to overcome these difficulties and to give entirely satisfactory results. Where organic derivatives of the sulfoxylate of sodium formaldehyde have been prepared, these organic sulfoxylates have been found to penetrate the fiber much more effectively than the sulfoxylate of sodium formaldehyde and give discharge patterns. The results obtained with the organic sulfoxylate alone were not entirely satisfactory, particularly on the dark shades, but experiments made, using as a discharge agent a mixture of these organic derivatives of the sulfoxylate of sodium or potassium formaldehyde, and a penetrating agent such as glycolic acid, gave perfect and complete discharge. These organic sulfoxylates have the advantage that they not only give a satisfactory white, similar to the sulfoxylate of zinc formaldehyde, but they may be mixed with fast colors of all types without any decomposition.

Suitable organic derivatives of the sulfoxylate of sodium formaldehyde to act as discharge agents are preferably aliphatic or aromatic amine derivatives. Those of particular interest are: the aniline derivative, the alphanaphthylamine derivative, the para-amido-phenol derivative, the diphenylamine derivative, the paraphenylenediamine derivative, the orthotoluidine derivative, the xylidine derivative and the butylamine derivative. The organic derivatives of the sulfoxylate which are particularly effective are the reaction products of primary amines condensed with the sulfoxylate of sodium or potassium formaldehyde, with or without the elimination of water. For example:

$$NaHSO_2.HCOH.2H_2O + C_6H_5NH_2 \rightarrow NaHSO_2.HCHNC_6H_5 + 3H_2O$$

It is understood that I do not wish to be limited to these specific compounds mentioned for it is obvious to one skilled in the art that many other organic compounds could be prepared with similar activity. It is also understood that I do not wish to be limited to the exact formula given in the equation. It should be pointed out that when organic compounds of the type given above are heated with the sulfoxylate of sodium or potassium formaldehyde that a reaction takes place liberating a large amount of heat. The resultant product is what I consider the organic sulfoxylate.

Now, dealing with the application of vat colors, it is known that while acetate cellulose products have been discharged with the aid of sulfoxylate of zinc formaldehyde (the formaldehyde reaction product with zinc sulfoxylate), resulting in a pattern embracing a field of any desired color with a white design, the sulfoxylate of zinc formaldehyde can not be used in conjunction with vat colors. Sulfoxylate of zinc formaldehyde can, however, be used with basic or direct colors. The latter colors have the disadvantage of not being fast to light, rubbing or washing. As a consequence, while it is thus possible to get colored discharges, it is obvious that the resultant product is of limited practical value. The reason that no practical results are obtained when vat colors are mixed with sulfoxylate of zinc formaldehyde is that decomposition, or degradation of the latter compound may take place.

However, when I utilize vat colors in conjunction with the organic sulfoxylate, any desired colored discharge may be obtained which will not be fugitive nor will it be affected by light or rubbing.

By vat colors are meant the broad class of fast colors which are technically known as anthraquinone coloring matters and indigoid coloring matters. These classes of coloring matters have been commonly called vat colors by virtue of the common practice of applying them in a reducing vat.

An example of the present invention is as follows: If I employ a cellulose acetate fabric, and dye this a solid shade by padding through a solution of dianisidine and then developing with nitrite and beta-oxynaphthaic acid, I will have a fabric of deep blue color. This fabric may be properly discharged, for example, by printing with the following paste:

60 parts dextrine
15 parts soda ash
10 parts potassium sulphocyanide
20 parts of the condensation product of aniline and the sulfoxylate of sodium formaldehyde
10 parts Indanthrene Golden orange G Paste (Colour Index #1096)

This mixture is heated to approximately 140 degrees F. until it becomes uniform. The

paste is then printed on the fabric and dried. Subsequently, the fabric is subjected to the action of a vat ager, oxidized and washed in the usual fashion. The resultant product will be found to incorporate contrasting colors having clear lines of demarcation and of the desired values, known as vat discharge prints.

Other examples of the invention may include the substitution of acetone, urea, naphthol or resorcinol in place of potassium sulphocyanide as a penetrant. Further examples may substitute the alpha-naphthylamine derivative, the butylamine derivative, the xylidine derivative, the ortho-toluidine derivative or the para-toluidine derivative in lieu of the aniline derivative of the sulfoxylate of sodium formaldehyde used in the original example. Still further examples of the invention are to be found in substituting Ciba blue B (Colour Index No. 1183), Alizanthene violet R (Colour Index No. 1103), Ponsol blue GD (Colour Index No. 1113) or Algol scarlet G (Colour Index No. 1129) for the Indanthrene Golden orange G paste as afore specified.

Another example of the present invention is as follows. After the cellulose-acetate fabric has been dyed in a solid shade, it may be properly discharged, by screen or film printing, with the following printing paste:

100 parts water
8 parts gum tragacanth
15 parts glycolic acid
25 parts of the condensation product of xylidine and sulfoxylate of potassium formaldehyde
4 parts Alizanthrene violet R paste (Colour Index No. 1103)

It is understood that this process not only applies to fabrics which consist solely of acylated cellulose fibers, but may be applied with equal effectiveness and value to fabrics which contain mixtures of cellulose-acetate and other synthetic or natural fibers such as real silk, cotton or rayon.

It will thus be seen that a method is provided by means of which vat color discharges may be utilized in conjunction with acetate cellulose fabrics with the aid of penetrating agents and organic sulfoxylates. This latter is to be interpreted sufficiently generically to include the reaction products of an organic amine with sulfoxylate. This process, moreover, permits the simultaneous discharging and printing of an acylated cellulose fabric with vat dyestuff.

From the foregoing, it will be understood that, among others, the objects of the invention as specifically afore stated are achieved. It will, moreover, be appreciated that numerous changes in the steps of the method and the appearance of the finished fabric might be resorted to without in the slightest departing from the spirit of the invention as defined by the claims.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:—

1. A method of dyeing in contrasting colors a fabric of the acylated cellulose group which includes dyeing said fabric and applying thereto an agent embodying a vat dye, and including in said agent an aniline derivative of a formaldehyde sulfoxylate.

2. A method of dyeing in contrasting colors a fabric of the acylated cellulose group which includes dyeing said fabric and applying thereto an agent embodying a vat dye, and including in said agent a reaction product of primary amines condensed with a sulfoxylate.

3. A method of dyeing in contrasting colors a fabric of the acylated cellulose group which includes dyeing said fabric and applying thereto an agent embodying a vat dye, and including in said agent the reaction product of an aromatic amine condensed with a sulfoxylate.

4. A method of dyeing in contrasting colors a fabric of the acylated cellulose group which includes dyeing said fabric and applying thereto an agent embodying a vat dye and including in said agent a reaction product of primary amines condensed with the formaldehyde derivatives of the alkali salts of sulfoxylate.

5. A method of dyeing in contrasting colors a fabric of the acylated cellulose group which includes dyeing said fabric and applying thereto an agent embodying a vat dye, and including in said agent a reaction product of primary amines condensed with sulfoxylate of sodium formaldehyde.

6. A method of dying in contrasting colors a fabric of the acylated cellulose group which includes dyeing said fabric and applying thereto an agent embodying a vat dye, and including in said agent an aniline derivative of the sulfoxylate of sodium formaldehyde.

7. A method of dyeing in contrasting colors a fabric of the acylated cellulose group which includes dyeing said fabric and applying thereto an agent embodying a vat dye, and including in said agent an amine derivative of the sulfoxylate of sodium formaldehyde.

8. A method of dyeing in contrasting colors a fabric of the acylated cellulose group which includes dyeing said fabric and applying thereto an agent embodying a vat dye, and including in said agent an aromatic amine derivative of the sulfoxylate of sodium formaldehyde.

9. A method of dyeing in contrasting colors a fabric of the acylated cellulose group which includes dyeing said fabric and applying thereto an agent embodying a vat dye,

and including in said agent an aniline derivative of the sulfoxylate of sodium formaldehyde.

10. A method of dyeing in contrasting colors fabrics of the acylated cellulose groups which includes initially dyeing said fabric and applying thereto a mixture comprising substantially 60 parts of a thickening agent, 15 parts soda ash, 10 parts of a penetrating agent, 20 parts of the condensation product of aniline and the sulfoxylate of sodium formaldehyde, 10 parts vat color.

11. A method of dyeing in contrasting colors fabrics of the acylated cellulose groups which includes initially dyeing said fabric and applying thereto a mixture comprising substantially 60 parts dextrine, 15 parts soda ash, 10 parts potassium sulphocyanide, 20 parts of the condensation product of aniline and the sulfoxylate of sodium formaldehyde 10 parts vat color.

12. A method of dyeing in contrasting colors a fabric of the acylated cellulose type which includes dyeing said fabric with an initial color, and applying thereto a penetrating agent and an aniline derivative of a formaldehyde sulfoxylate to discharge said fabric, and simultaneously applying to the discharged portions of said fabric anthraquinone and or indigoid vat dyes.

13. A substance to be utilized in connection with the treatment of fibrous materials comprising a hydroxy-ethyl-amine derivative of the sulfoxylate of sodium formaldehyde, combined with a vat dye.

In testimony whereof I affix my signature.

DONALD H. POWERS.