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PRODUCTION OF DISCHARGE EFFECTS

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This invention relates to the coloration of textile materials, more particularly materials made of or containing cellulose acetate or other cellulose esters or ethers or animal fibres, for example wool and silk.

It is well known that discharge effects may readily be produced upon colored cotton materials by local application thereto of compositions containing sodium formaldehyde sulfoxylate. Fast colored discharges may be produced by this process by incorporating in the discharge composition leuco compounds of vat dyestuffs in the form of alkali metal salts. In the case of cellulose acetate materials however discharge effects are much less readily produced by means of discharging agents comprising sodium or other alkali metal formaldehyde sulfoxylate. With the aid of zinc formaldehyde sulfoxylate it is however possible to produce excellent discharge effects, but when operating by this process the difficulty arises that it is not practicable to produce colored discharges by incorporating alkali metal salts of leuco vat dyestuffs in the discharge compositions. It appears that the zinc formaldehyde sulfoxylate compound is not compatible with the strongly alkaline alkali metal salts of the leuco vat dyestuffs. Reactions occur between the latter and the zinc compound with the result that the discharging power of the composition is impaired.

We have now observed that, as opposed to the water-soluble alkali metal compounds of leuco vat dyestuffs, the insoluble zinc compounds are compatible with zinc formaldehyde sulfoxylate, and at the same time are capable of coloring cellulose acetate materials. They may therefore be employed in admixture with zinc formaldehyde sulfoxylate for the purpose of producing on cellulose acetate materials valuable discharge effects illuminated with vat dyestuffs. We have found in fact that the zinc compounds of leuco vat dyestuffs and also other insoluble metal compounds of vat dyestuffs are generally applicable in the coloration of cellulose acetate materials. Other cellulose esters and also cellulose ethers may be colored in the same manner and likewise animal fibres, for example wool and silk.

Broadly, therefore, the present invention comprises the coloration of materials consisting of or containing cellulose acetate or other organic derivatives of cellulose or animal fibres by the application of vat dyestuffs in the form of insoluble metal derivatives of their leuco compounds. Insoluble metal compounds of leuco vat dyestuffs exhibit the important advantage that

they are not strongly alkaline and may be applied under either neutral or even moderately acid conditions. They may therefore be utilized, as explained above, for the coloration of discharges produced by means of zinc formaldehyde sulfoxylate or by means of other heavy metal aldehyde or ketone sulfoxylates, and further they may be used to color materials, for instance cellulose esters and animal fibres, which are liable to damage by strongly alkaline baths or printing compositions.

The zinc compounds of leuco vat dyestuffs have been found particularly convenient for application in accordance with the present invention, but other insoluble metal compounds may be utilized if desired, for example compounds with cadmium, aluminium, tin, lead or iron. These insoluble metal compounds of leuco vat dyestuffs are conveniently prepared by interaction between the alkali metal salts of the leuco compounds and appropriate metal salts, preferably such as are water-soluble. For instance, the dyestuff in question may be vatted with sodium hydrosulphite or other reducing agent and just sufficient caustic alkali to yield a solution of the leuco compound. The solution thus obtained, if desired after filtration, may be treated with an aqueous solution of the appropriate metal salt, for example a concentrated solution of zinc chloride, whereby the desired metal compound of the leuco vat dyestuff may be precipitated.

A wide range of vat dyestuffs having affinity for the materials to be colored may be applied by the new process. Particular mention may be made, especially for the coloration of cellulose ester and ether materials, of the anthraquinone vat dyes containing one anthraquinone residue described in U. S. application S. No. 583,392 filed 26th December, 1931 and of indigoid dyestuffs, especially the indigoid dyestuffs described in U. S. application S. No. 583,406 filed 26th December, 1931, and derivatives of indigo and thioindigo.

The insoluble metal compounds of leuco vat dyestuffs, are conveniently applied to the materials in the form of aqueous suspensions or dispersions which may be prepared by any convenient means. For example, the metal compounds may be directly converted into aqueous suspensions or dispersions by mechanical treatment or by treatment with dispersing agents and/or protective colloids or by the combination of these treatments. Thus a preparation adapted for application by printing may be made simply by stirring or grinding the metal compound with gum arabic or other thickening agent.

If desired, however, the metal compounds may be formed in the presence of dispersing agents and/or protective colloids and dispersions suitable for dyeing and printing directly obtained.

Thus, a solution of an alkali salt of a leuco compound may be precipitated with zinc chloride or other appropriate metal salt in the presence of a dispersing agent and/or a protective colloid.

Preferably dispersion is effected in neutral or somewhat acid media, and dispersing agents or protective colloids, where employed, should be stable and capable of exerting their dispersing or protective action in such media. As examples of dispersing agents or protective colloids of this character may be mentioned highly sulphonated compounds such as highly sulphonated castor-oil, sulpho aromatic fatty acids for example sulpho-naphthalene ricinoleic acid (see U. S. Patents Nos. 1,840,572 and 1,694,413), basic dispersing agents soluble in acid media for example oleyl diethyl ethylene diamine or other basic derivative of a fatty acid, also starches, gums, glue, gelatin and the like.

If desired the dispersions or suspensions may be prepared in concentrated form adapted to yield by dilution, with or without addition of thickening agents or further dispersing agents or protective colloids, liquids or preparations adapted for dyeing and printing purposes.

We have found that it is not essential to prepare the insoluble metal compounds of leuco vat dyestuffs prior to application to the material as, if desired, they may be formed on the material itself. For instance, the unreduced vat dyestuff in admixture with a reducing agent and a metal oxide, carbonate, or other compound may be applied to the material and the latter then steamed, whereby the metal compound of the leuco vat dyestuff is formed in situ. In this process the presence of strong alkalis should of course be avoided, as otherwise the required metal compound may not be formed. This method of carrying out the new process is more particularly applicable when colorations are to be applied locally by printing or otherwise.

The application of the suspensions or dispersions of the insoluble metal compounds of leuco vat dyestuffs to the materials may be effected in any desired manner, for example by dyeing, padding, or printing all over, or locally by printing, stencilling or other method of local application. As explained previously however the invention has been found of greatest value in effecting colorations by printing or other mode of local application, and more particularly when the vat dyestuffs are to be used for the coloration of discharges produced by means of zinc formaldehyde sulphonylate or other metal aldehyde or ketone sulphonylates which are detrimentally effected by caustic alkali. Particular mention may be made of the application of the metal compounds for the illumination of zinc formaldehyde sulphonylate discharges on cellulose ester materials.

After the metal compounds of the leuco vat dyestuffs have been applied to the materials the latter may be subjected to oxidation for the purposes of converting the leuco compound to the dyestuff on the material. The materials may for example be subjected to chroming and may finally be washed, soaped or subjected to any other desired finishing treatment.

Cellulose ester or ether materials colored in

accordance with the present invention may consist, for instance, of cellulose acetate as previously mentioned or of cellulose formate, propionate or butyrate or the products obtainable by esterifying cellulosic materials while retaining their fibrous form, for example the product known as "immunized cotton" obtained by treating alkali cellulose with para-toluene sulphonic chloride, or they may consist of ethyl, methyl or benzyl cellulose or other ether of cellulose. The invention is also applicable, as previously indicated, to the coloration of wool, silk and other animal fibres. Mixed materials comprising two or more types of the foregoing materials, for example cellulose acetate and silk, or comprising one of the foregoing materials and another textile material, for example cotton or the regenerated cellulose type of artificial silk, may likewise be colored by the new processes.

When coloring materials consist of or contain cellulose esters or ethers the insoluble metal compounds of leuco vat dyestuffs may with advantage be applied in conjunction with alcohols, e. g. ethyl alcohol, phenols, e. g. hydroquinone, or other swelling agents for the material under treatment. Again when colored discharge effects are to be produced the discharge composition may contain anthraquinone or other agents facilitating discharge with reducing agents.

The invention is illustrated, but not limited by the following examples:

Example 1

A material consisting of cellulose acetate or a mixture of cellulose acetate and silk is printed with the following printing paste:

	Parts
Ciba yellow G or Ciba scarlet G.....	15
Methylated spirits.....	10
Gum arabic 1:1.....	35
Zinc carbonate.....	5
Water.....	10
Zinc formaldehyde sulphonylate.....	25
	100

After printing the material is dried, aged for 5 minutes and then chromed, washed, soaped, and again washed and dried.

The zinc carbonate is conveniently prepared as a 20% paste by precipitation of zinc sulphate with soda ash in aqueous solution.

Example 2

A cellulose acetate fabric dyed with a dischargeable coloring matter is printed with the following printing paste:

	Parts
Zinc salt of the leuco compound of Ciba yellow G.....	20
Methylated spirits.....	10
Water.....	5
Gum arabic 1:1.....	40
Zinc formaldehyde sulphonylate.....	25
	100

After printing the material is aged for 5 minutes and then chromed, washed, soaped, and finally rinsed and dried. In this manner fast yellow discharge effects may be obtained upon a colored ground.

In place of the zinc salt of the leuco compound of Ciba yellow G, the corresponding zinc compounds prepared from other vat dyestuffs may be

employed, for example, Ciba scarlet G, Durindone red Y, Algol violet BBN, Indigo LL, Indigo LL/2R and Caledon jade green.

5 The zinc compound of the leuco vat dyestuff may be prepared in the following manner:

10 10 parts of dyestuff powder (e. g. Ciba yellow G) 8 parts caustic soda and 400 parts of water are well mixed and heated to 60° C. About 16 parts sodium hydrosulphite are added with good stirring until a clear vat is obtained. This solution is filtered to remove any insoluble matter and whilst still warm a solution of 10 parts of zinc chloride in 30-40 parts of water is added. The zinc salt of the leuco compound separates as a
15 flocculent cream-colored precipitate and is filtered off, washed with a very small quantity of water and retained as an aqueous paste.

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

20 1. Process for the production of discharge effects on materials comprising organic derivatives of cellulose which comprises applying locally thereto a discharge composition containing zinc

formaldehyde sulphonylate and a water-insoluble metal compound of a leuco vat dyestuff.

2. Process for the production of discharge effects on materials comprising cellulose acetate which comprises applying locally thereto a discharge composition containing zinc formaldehyde sulphonylate and a zinc compound of a leuco vat dyestuff. 5

3. Process for the production of discharge effects on materials comprising cellulose acetate which comprises applying locally thereto a discharge composition containing zinc formaldehyde sulphonylate and a zinc compound of a leuco vat dyestuff of the indigoid series. 10

4. Process for the production of discharge effects on materials comprising cellulose acetate which comprises applying locally thereto a discharge composition containing zinc formaldehyde sulphonylate and a zinc compound of a leuco compound of an anthraquinone dyestuff containing a single anthraquinone nucleus. 15

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