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TREATMENT OF TEXTILE AND OTHER MATERIALS

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This invention relates to improvements in the treatment of textile and other materials, and is more particularly concerned with the colouration of such materials. The invention is of greatest importance in its application to the colouration of materials made of or containing organic derivatives of cellulose.

According to the present invention in the production of colourations on textile or other materials by the formation of the actual colour upon the material, one or more components of the final dyestuff are applied to the goods, preferably by mechanical or other impregnation methods, the goods are then subjected to a drying treatment, the drying being preferably partial, and finally the colour is developed upon the material. The new process is most important for the colouration of goods by means of vat dyes or similar dyestuffs applicable to the materials in the form of their leuco compounds or other reduced forms of the dyestuff.

The vat colouring matters find their most extensive application in the colouration of cellulosic materials to which they are applied in the form of the alkali salts of their reduction products, the so-called leuco compounds. When the alkaline vats of leuco compounds are used for the colouration of cellulose ester materials or for the colouration of materials comprising animal fibres, deterioration of the fibre or material is apt to take place. In consequence processes have been developed in which the alkalinity of the vat is reduced, for example by reducing the quantity of caustic alkali present in the vat, this method being only applicable to a limited number of vat dyes, or by replacing the strong caustic alkali wholly or in part by weaker alkali as, for example, the alkali salts of weak organic acids or of phenols, naphthols or the like (see U. S. Patent No. 1,716,720). In U. S. Patent No. 1,900,172, a method is developed in which the leuco compounds are applied to the goods in the free state as opposed to the alkaline solution formerly employed, this method being applicable with great advantage to the colouration of cellulose ester and ether materials and also to the colouration of animal fibres. In all these methods reliance is placed largely upon the substantive affinity of the leuco compounds or of their salts for the materials under treatment. For example the alkali salts of the leuco compounds have a good affinity for cellulosic materials, while the free leuco compounds, and to some extent metal salts of free leuco compounds, have a good affinity for cellulose ester and ether materials and animal fibres. In consequence the goods have in general to be treated for some considerable time in a bath of the vatted or reduced dyestuff to enable the goods to take up the leuco compound or salt thereof. According to the present process the drying operation following the application of the leuco compound or salt thereof to the material enables the material to take up the leuco compound comparatively quickly, so that the whole operation is shortened. In addition the new process enlarges the range of dyestuffs available for the treatment of any particular materials as it is not so essential that the leuco compound should exhibit substantive affinity for the goods under treatment.

In applying the present invention to the colouration of goods by means of vat dyestuffs, the drying operation is carried out in such a way that little or no oxidation of the dyestuff on the material takes place, the development of the colour being carried out in a subsequent operation. In order to avoid or substantially to avoid oxidation of the dyestuff upon the material during the drying operation, said operation may be carried out in an atmosphere of a non-oxidizing gas and/or in vacuo, and with or without the application of heat. Suitable inert atmospheres include nitrogen, hydrogen, carbon monoxide, carbon dioxide, etc.

The leuco compound of the vat or similar dyestuff may be applied to the goods by any suitable method and in any suitable form. While the invention does not exclude the substantive absorption of the leuco compound from a dyebath as previously indicated, it is most advantageous to apply the leuco compound during a relatively short time and to rely on the drying operation to effect absorption by the materials under treatment. The goods may, for example, be passed through a bath or through a padding mangle supplied with a solution or dispersion of leuco compound and may then be carried to the drying apparatus. Other suitable methods for the application of the leuco compounds include spraying, printing and like methods. By means of printing and spraying with the aid of stencils local colourations may be produced. The new process is, however, of particular value for the production of materials coloured all over, or having the whole of at least one component coloured in the case of a mixed material such as a material comprising both cellulose acetate and a cellulosic or animal fibre.

The padding mangle enables the quantity of

liquor taken up by the goods to be determined fairly closely and is therefore advantageous. Passage of the materials through baths containing the leuco compounds is also preferably followed by a squeezing operation or similar operation to determine the amount of liquor retained by the goods.

The leuco compounds of the vat or similar dyestuffs may be applied in the free state as described in U. S. Patent No. 1,900,172 or in the form of soluble alkali metal salts, particularly where the goods under treatment are cellulosic in character, for example cotton or viscose or other cellulosic artificial silk, or they may be in the form of substantially water-insoluble metal salts, for example zinc compounds of the leuco bodies (see U. S. application S. No. 605,115 filed 20th March 1935). The invention further includes the application of the leuco compounds in the form of their esters, for example their sulphuric esters. Where alkaline vats are used upon cellulose ester or ether materials or upon animal fibres, it is desirable to reduce the alkalinity of the vat, for example by replacing the strong caustic alkali wholly or in part by alkaline salts of weak organic acids or of phenols, naphthols or the like, or by replacing the caustic alkali wholly or in part by a weaker base such as ammonia or an organic base. Alkaline solutions of the leuco compounds may be used upon cellulose ester materials where saponification is desired simultaneously with colouration.

Free leuco compounds or salts or esters thereof soluble in organic solvents may be applied to the materials in solution in organic solvents. To facilitate the subsequent drying operation such organic solvents are preferably relatively volatile. Most conveniently, however, the leuco compounds or derivatives thereof are applied from an aqueous medium, in solution in the case of water-soluble alkaline salts or in aqueous dispersions or suspensions in the case of the free leuco compounds or water-insoluble salts or derivatives thereof. If desired mixed aqueous-organic media may be employed for the application of the leuco compounds. Any organic solvent constituting or contained in the medium from which the leuco compound is applied may have, and preferably has a swelling action upon the materials under treatment, so as to facilitate the absorption of the compound by the material, particularly during the subsequent drying operation. In particular the organic solvents may be so chosen as to have a swelling action upon the cellulose ester or ether materials. Thus for example the medium in which the leuco compounds are applied may consist of or contain alcohols, esters, ketones, glycols, glycol ethers, glycol esters and the like. Where the organic solvent chosen has too strong an action upon the goods either during the application of the leuco bodies or during the drying, it may be diluted with an inert or relatively inert liquid, as for example hydrocarbons, ethers and certain chlorinated hydrocarbons. In the case of aqueous media, swelling agents for the cellulose ester or ether which are of lower volatility than water are advantageously used, e. g. diethylene glycol.

Vat dyestuffs of any desired kind, including sulphur dyestuffs, may be applied in accordance with the process of the present invention. In addition amino-anthraquinones, whether substituted or unsubstituted in the nucleus or an amino group or both, e. g. substituted in an amino group by alkyl, aryl or substituted alkyl or aryl residues, may likewise be applied in the form of their leuco compounds, particularly to cellulose ester and ether materials.

The following are given as instances of vat dyestuffs or similar dyestuffs or classes of vat or similar dyestuffs which may be applied by the process of the invention:—

1. Indigo and allied colouring matters.

(*a*) Indigo and its derivatives, for example N.N^1-dimethyl indigo and halogenated indigos, e. g. Ciba Blue 2B (Colour Index 1184).

(*b*) Halogenated indirubines, e. g. Ciba Heliotrope B (Colour Index 1205).

(*c*) Thioindigo and its derivatives, for instance halogenated thioindigoid dyes, e. g. Ciba Bordeaux B (Colour Index 1208).

(*d*) Dinaphthindigoid dyes, e. g. Ciba Green G (Colour Index 1198).

(*e*) Indigoid dyes obtainable by condensing isatins or thioisatins with α-oxy-naphthalene or α-oxy-anthracene or derivatives thereof and if desired subsequently halogenating, e. g. Alizarin Indigo 3R (Colour Index 1200) and Helindone Blue 3GN (Colour Index 1203).

2. Anthraquinone colouring matters.

(*a*) Simple amino derivatives, e. g. 1-hydroxy-4-amino-anthraquinone, 1:5-diamino-4:8-dihydroxy-anthraquinone, 1-methylamino-anthraquinone, 1:4-dianilido-anthraquinone.

(*b*) Anthraquinone-quinolines, e. g. 1:2-dihydroxy-anthraquinone quinoline (Colour Index 1066).

(*c*) Acylaminoanthraquinones, e. g. 1-acetylamino-anthraquinone, 1:4-dipropionylaminoanthraquinone (obtainable by the action of propionic anhydride on 1:4-diaminoanthraquinone), 1:5-dibenzoylaminoanthraquinone (Colour Index 1132), succinyl-alphaamino anthraquinone (Colour Index 1139), 1:5-dibenzoylamino-4:8-dihydroxy-anthraquinone (Colour Index 1134).

(*d*) Anthrapyridones, e. g. 4-methylamino-anthrapyridone.

(*e*) Anthraquinone-mercaptans including their derivatives substituted in the nucleus and/or the mercapto groups.

(*f*) Benzathrones and dibenzanthrones, e. g. violanthrone (Colour Index 1099), iso-violanthrone (Colour Index 1103), amino-violanthrone (Colour Index 1102), dimethoxy-dibenzanthrone (Colour Index 1101).

(*g*) Pyranthrone and its derivatives.

(*h*) Anthraflavone (Colour Index 1095).

(*i*) Anthraquinone acridones, e. g. anthraquinone 1(NH)-2(CO)-naphthacridone (Colour Index 1162).

(*j*) Dianthraquinonyls and acidylamino derivatives.

(*k*) Dianthraquinonylamines and derivatives, e. g. acidylamino derivatives.

(*l*) Anthraquinone azines and hydroazines, e. g. dianthraquinone-dihydroazines and their halogenated derivatives such as 1:2.1^1:2^1-dianthraquinone azine (Colour Index 1106) and its dichlor derivatives (Colour Index 1113).

(*m*) Anthraquinone oxazines.

(*n*) Anthraquinone dioxides.

(*o*) Anthraquinone thiazines.

(*p*) Anthraquinone disulphides.

(*q*) Anthraquinone xanthones.

(*r*) Anthraquinone thioxanthones.

(*s*) Anthraquinone carbazoles.

(*t*) Anthraquinone thiazoles.

3. Derivatives of benzoquinone and naphthoquinones, e. g. those mentioned in U. S. Patents Nos. 1,991,885 and 1,944,413.

4. Indophenols and their derivatives, e. g. halogen derivatives.

5. Perylene quinones and their amino, halogen and other derivatives.

6. Dyestuffs obtainable by alkali fusion of imides and substituted imides of naphthalene peridicarboxylic acids and the dyestuffs obtainable by condensing naphthalene 1:4:5:8-tetracarboxylic acids with mono- or di-amines.

7. Sulphur dyestuffs including not only those colouring matters commonly applied from sulphide baths but also those sulphur colouring matters commonly applied to cellulosic materials from hydrosulphite or other vats, for example the colouring matters obtained by sulphurizing indophenols derived from carbazol (see Colour Index Nos. 969, 970, 971, etc.).

As previously indicated, subsequent to the application of the leuco compounds of the vat or similar dyestuffs to the goods, the goods are subjected to a drying operation. Preferably such drying is incomplete, since a slight wetness of the material is found to facilitate the subsequent oxidation of the leuco compounds. Further, the drying operation in the case of the vat or similar dyestuffs applied in the form of their leuco compounds is carried out under conditions such that little or no oxidation occurs. In some cases the compounds applied in accordance with the present invention are relatively stable in the presence of air, so that vacuum drying or drying in the presence of air diluted with nitrogen or other inert gas is sufficient to avoid oxidation. This is particularly the case with the free leuco compounds. In other cases, for instance when using alkali metal salts of the leuco compounds, it is desirable to dry the materials in an atmosphere containing little or no oxygen.

The drying operation may be preceded or followed by a steaming treatment which has the advantage that it still further assists the penetration of the leuco compounds into the materials. If desired water vapour may be contained in the drying atmosphere, so as to facilitate absorption and also to limit the extent of the drying to a point short of complete dryness, this as previously indicated being advantageous.

Subsequent to the drying operation the leuco compounds may be oxidized upon the material by any suitable methods. Generally a simple air oxidation is sufficient but more rigorous treatments, for example with bichromate and acid, with bleaching powder, with soap and sodium perborate or a comparatively light oxidation with soap and hydrogen peroxide may be applied. Nitrous acid is usually preferable for the oxidation of leuco esters.

The invention further includes the development upon textile or other materials of azo colouring matters. In this case during the drying operation, before the development of the colour upon the material, it is unnecesary to take precautions to prevent oxidation.

One or more of the azo dye components may be applied to the goods prior to the drying operation characteristic of the invention, and for this purpose the nitrous acid used for the production of a diazo compound is considered as one of the components necessary for the formation of the dyestuff. For example the amino compound or amino-azo compound may be applied alone or the coupling component may be applied alone, or the two may be applied together, or either or both may be applied together with nitrite prior to the drying operation. Where the amino or amino-azo compound is alone applied, the development of colour includes a diazotizing process and development. Where the coupling component is applied alone the development of the colour is effected by the application of a diazo solution. Where both coupling component and amino or amino-azo compound are applied, development of the colour is effected after the drying operation by means of nitrous acid, and finally where amino or amino-azo compound, coupling component, and nitrite are all applied prior to the drying operation, development of the colour is effected by means of acid. Acid may be applied in the form of gas or vapour as an alternative to the usual bath treatment.

The invention includes the application of any desired diazotizable amines or amino-azo compounds and of any desired coupling components. The diazotizable compounds include aniline and the naphthylamines and their homologues and substitution products, including nitro, halogen and alkoxy substitution products, amino-azo benzenes, benzene-azo-naphthylamines, naphthalene azo anilines, amino-azo naphthalenes and similar homologues or substitution products thereof, while the coupling components include aniline, naphthylamines, phenols, naphthols, oxy-naphthoic acid, oxy-naphthoic arylides, pyrazolines, aceto-acetic ester, aceto-acetic arylides and similar ketonic acid esters or arylides and their homologues and substitution products.

Phenols, naphthols, oxy-naphthoic acids and oxy-naphthoic arylides and phenolic coupling components in general may be applied from alkaline solution or from a solution of reduced alkalinity, or may be applied in the free state, and generally the methods applicable to the leuco compounds of the vat dyestuffs described above may be applied in relation thereto.

As indicated in relation to the vat and similar dyestuffs, a steam treatment may precede or follow the drying operation in the production of the azo dyes on the fibres or water vapour may be included in the drying atmosphere.

The new process is, as previously indicated, generally applicable to the colouration of textile or other materials including cotton or other natural or artificial cellulosic materials, for example viscose, cuprammonium and nitrocellulose artificial silks, and to animal fibres, including silk and wool, but is especially valuable in the treatment of materials made of or containing organic derivatives of cellulose, for instance cellulose acetate, cellulose formate, propionate or butyrate, methyl, ethyl or benzyl cellulose, or the products obtained by the esterification or etherification in fibrous form of cellulosic materials, for instance the product known as immunized cotton obtained by treatment of alkalized cotton with paratoluene sulpho-chloride.

Mixed materials containing two or more kinds of textile fibres may be coloured by the process of the invention. To obtain contrasting shades on mixed goods in accordance with the affinity of the particular components applied, it is desirable to have a somewhat extended treatment in a bath prior to the drying operation. For instance the alkali metal salts of leuco vat dyes have a good affinity for cellulosic fibres and lower affinity for cellulose ester materials and animal fibres, and by taking advantage of the differential affinity differential colouration may be produced. Similarly the leuco compounds have a preferential affinity for the cellulose ester and ether materials and for animal fibres as compared with cellu-

losic fibres. Where substantially solid shades on such mixed materials are required irrespective of the particular components applied to the goods, a short padding, spraying or similar treatment followed immediately by drying may be utilized.

The invention is illustrated but not limited by the following examples, all parts being by weight:—

Example 1

A cellulose acetate fabric is padded on a padding mangle with the following padding liquor, the mangle being adjusted so that the material retains about its own weight of the liquor:—

	Parts
Zinc salt of Ciba Scarlet G (Colour Index No. 1228) (25% aqueous paste)	10
Gum arabic (1:1)	15
Ethyl lactate	7.5
Diethylene glycol	7.5
Water	60
	100

The padded material is then heated at about 60–70° in an atmosphere of carbon dioxide until about three quarters of the water has evaporated, the rate of drying being adjusted so that this requires about 15–30 minutes. The material is then chromed to convert the leuco dyestuff to the dyestuff proper, and finally washed and dried.

Example 2

A padding liquor is prepared as follows:—1 part of Indanthrene Blue 5G (powder) or Indanthrene Turquoise Blue 3GK (powder) is pasted with a little water and 10 parts of diethylene glycol. 1.5 parts of 24% caustic soda solution and 10 parts of gum arabic (1:1) are then added and the whole diluted to 100 parts with water. This is then warmed to 60° C. and 0.75 parts of sodium hydrosulphite sprinkled in and stirred for 15 minutes. After cooling 1 part of Formosul is added and the mixture padded on to a cellulose acetate fabric so that the latter retains its own weight of the mixture. The material is then partially dried at 60–80° C. in an atmosphere of nitrogen, so that about three-quarters of the water is evaporated, the time of drying being 15–30 minutes. The material may then if desired be given a short steaming in air-free steam. Oxidation is then effected in a 0.5 gram per litre solution of sodium perborate and the material washed and dried.

Example 3

A padding liquor is prepared as follows:—

1 part of Caledon Jade Green powder
2 parts of sodium sulphonaphthalene-ricinoleate prepared as described in U. S. Patent No. 1,694,413
1 part caustic soda
1.75 parts sodium hydrosulphite
15 parts gum arabic 1:1
80 parts water

are heated together until the dyestuff is vatted. The liquid is then cooled and formic acid of 40% strength added until it is substantially neutral or only slightly alkaline. A cellulose acetate fabric is then padded with the mixture so that the material retains about its own weight thereof. The fabric is then, at 70–80° in an atmosphere of nitrogen, dried or partially dried so that about three-quarters of the water is removed, the drying operation taking about 30 minutes. The fabric is then hung in the air for a time and finally soaped in a bath containing 1 gram of soap and 0.1 gram of sodium perborate per litre, washed and dried.

With omission of the addition of formic acid the padding liquor is suitable for application to a cellulosic fabric, e. g. one of viscose artificial silk. The padding and other treatment may be conducted as above.

Example 4

A padding bath is prepared as follows:—1 part of 2:3-oxynaphthoic acid anilide is dissolved in 10 parts of water with the aid of 0.5 part of caustic soda. This solution is then added to a solution of 0.5 part of 5-nitro-2-anisidine in 5 parts of alcohol. To the mixture is added 1 part of glucose dissolved in 10 parts of water and 10 parts of diethylene glycol, and the whole is then made up to 100 parts with 15 parts of gum arabic 1:1 and a sufficient quantity of water.

A cellulose acetate fabric is padded with this liquid so that the fabric retains about its own weight thereof. The material is then dried at 50–60° C. until about three-quarters of the water has been evaporated. The time of drying is about 30 minutes. The colour is then developed in a bath containing 2 grams per litre of sodium nitrite and 5 ccs. per litre of glacial acetic acid. Finally the material is washed off, soaped for ½ hour at about 80° C., rinsed and dried.

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

1. Process for the colouration of textile materials, which comprises impregnating the material with a liquid containing a leuco compound of a vat dyestuff, partially drying the material so as to concentrate the impregnating liquid thereon, drying being conducted under such conditions that no substantial oxidation of the leuco compound occurs, and thereafter converting the leuco compound into the parent vat dyestuff.

2. Process for the colouration of artificial silk of an organic derivative of cellulose, which comprises impregnating the material with a liquid containing a leuco compound of a vat dyestuff, partially drying the material so as to concentrate the impregnating liquid thereon, drying being conducted under such conditions that no substantial oxidation of the leuco compound occurs, and thereafter converting the leuco compound into the parent vat dyestuff.

3. Process for the colouration of artificial silk of an organic derivative of cellulose which comprises impregnating the material with a liquid containing a leuco compound of a vat dyestuff in the form of an alkali salt, partially drying the material so as to concentrate the impregnating liquid thereon, said drying being effected in an atmosphere substantially free from oxygen, and thereafter converting the leuco compound into the parent vat dyestuff by oxidation.

4. Process for the colouration of cellulose acetate artificial silk, which comprises impregnating the material with a liquid containing a leuco compound of a vat dyestuff, drying the material so as to concentrate the impregnating liquid thereon, partially drying being conducted under such conditions that no substantial oxidation of the leuco compound occurs, and thereafter converting the leuco compound into the parent vat dyestuff.

5. Process for the colouration of cellulose acetate artificial silk, which comprises impregnating the material with a liquid containing a leuco compound of a vat dyestuff in the form of an

alkali salt, partially drying the material so as to concentrate the impregnating liquid thereon, said drying being effected in an atmosphere substantially free from oxygen, and thereafter converting the leuco compound into the parent vat dyestuff by oxidation.

6. Process for the colouration of cellulose acetate artificial silk, which comprises impregnating the material with an aqueous liquid containing a leuco compound of a vat dyestuff and a difficultly volatile swelling agent for the cellulose acetate of lower volatility than water, partially drying the material so as to concentrate the impregnating liquid thereon, said drying being effected under such conditions that no substantial oxidation of the leuco compound takes place, and thereafter oxidizing the leuco compound to the parent vat dyestuff.

7. Process for the colouration of cellulose acetate artificial silk, which comprises impregnating the material with an aqueous solution of a leuco compound of a vat dyestuff in the form of an alkali salt, partially drying the material so as to concentrate the impregnating liquid thereon, said drying being effected under such conditions that no substantial oxidation of the leuco compound takes place, and thereafter oxidizing the leuco compound to the parent vat dyestuff.

8. Process for the colouration of cellulose acetate artificial silk, which comprises impregnating the material with an aqueous liquid containing a leuco compound of a vat dyestuff in the free state, partially drying the material so as to concentrate the impregnating liquid thereon, said drying being effected under such conditions that no substantial oxidation of the leuco compound takes place, and thereafter oxidizing the leuco compound to the parent vat dyestuff.

9. Process for the colouration of cellulose acetate artificial silk, which comprises impregnating the material with an aqueous liquid of low alkalinity containing a leuco compound of a vat dyestuff in the form of an alkali salt and a swelling agent for the cellulose acetate of lower volatility than water, partially drying the material so as to concentrate the impregnating liquid thereon, said drying being effected under such conditions that no substantial oxidation of the leuco compound takes place, and thereafter oxidizing the leuco compound to the parent vat dyestuff.

10. Process for the colouration of regenerated cellulose artificial silk, which comprises impregnating the material with an aqueous solution of a leuco compound of a vat dyestuff in the form of an alkali salt, partially drying the material so as to concentrate the impregnating liquid thereon, said drying being effected under such conditions that no substantial oxidation of the leuco compound takes place, and thereafter oxidizing the leuco compound to the parent vat dyestuff.

11. Process for the colouration of cellulose acetate artificial silk, which comprises impregnating the material with an aqueous liquid containing an azo dyestuff coupling component and a swelling agent for the cellulose acetate of less volatility than water, partially drying the material and thereafter converting the coupling component into a dyestuff by coupling with a diazo compound.

12. Process for the colouration of textile materials which comprises impregnating the material with a liquid containing a leuco compound of a vat dyestuff, drying the material so as to concentrate the impregnating liquid thereon until it contains about a quarter of its dry weight of liquid, drying being conducted under such conditions that no substantial oxidation of the leuco compound occurs, and thereafter oxidizing the leuco compound to the parent vat dyestuff.

13. Process for the colouration of cellulose acetate artificial silk which comprises impregnating the material with a liquid containing a leuco compound of a vat dyestuff, drying the material so as to concentrate the impregnating liquid thereon until it contains about a quarter of its dry weight of liquid, drying being conducted under such conditions that no substantial oxidation of the leuco compound occurs, and thereafter oxidizing the leuco compound to the parent vat dyestuff.

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