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PROCESS FOR TREATING MATERIALS AND PRODUCTS PRODUCED

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8 Claims. (Cl. 8—62)

This invention relates to the coloring of sheet materials. In particular it relates to a method for printing and dyeing textile fabrics and the articles so produced, and to correlated improvements designed to enhance the properties and to increase the utility of such products.

Heretofore, textile fabrics have been printed with pastes comprising a dyestuff thickened with aqueous dispersions of starches, gums, resins, water-soluble cellulose ethers and the like. These thickening agents have been found not to be entirely satisfactory because they are soluble in water in the final product and wash out of the fabric upon laundering and so permit substantial amounts of the dyestuff to become dissipated. Moreover, such agents do not prevent the diffusion of a soluble coloring matter beyond the printed areas.

It is an object of the invention to provide a method for coloring sheet materials to improve their decorative appearance, and in particular to provide a method for the printing of textiles so that the coloring matter is permanently anchored to the textile.

It is a specific object of the invention to produce novel and descriptive color and surface effects on sheet materials such as textiles and the like, and to produce color and surface effects which are resistant to bleeding and crocking and which are fast to laundering, and which are substantially permanent in character.

It is a further object of the invention to provide textiles having dye-printed areas of sharp definition, greater depth and permanency.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

According to the present invention sheet materials such as textiles, papers, foils are colored by applying thereto a composition comprising an undeveloped dyestuff component, a carrier for the dyestuff component comprising a coagulable cellulosic colloid, a dispersion medium for the cellulosic colloid, and treating the sheet material with a developer for the undeveloped dyestuff component and a coagulant for the cellulosic carrier, whereby the water-insoluble carrier permanently binds the developed dyestuff to the sheet material.

The term "undeveloped" used in connection with the dyestuff component includes dyestuffs which may exist in an undeveloped, not fully colored or latent state and which are capable of yielding a colored substance by reaction with a known chemical reagent or by a change in conditions of the medium such as hydrogen-ion concentration and/or temperature.

The term "developer" designates not only such dyestuff components as coupling agents, diazo compounds, amines, bases and the like which will react with an undeveloped dyestuff to yield a colored substance, but also agents which will change the conditions and cause a development of color in the undeveloped dyestuff, as for example acids, bases, oxidants, heat and combinations thereof which will cause, permit or facilitate a stabilized dyestuff component or an undeveloped or latent dyestuff component to yield a colored substance.

The invention accordingly comprises novel products possessing the characteristics, properties, elements and the relation of elements, and a process having the steps and relation of steps, all as exemplified in the following detailed disclosure and the scope of the application of which will be indicated in the claims.

In its broad aspects the invention comprises three embodiments. In one embodiment a sheet material, such as a fabric, is treated in predetermined areas with an undeveloped dyestuff component dispersed in a carrier comprising a coagulable cellulosic colloid and a dispersion medium for the colloid, and the fabric treated with a coagulant for the carrier and a developer for the undeveloped dyestuff component thus insolubilizing the cellulosic colloid and developing the dye in situ on the fabric.

The second embodiment constitutes substantially a reversal of the steps employed in the first embodiment. Instead of the undeveloped dyestuff component being dispersed in the cellulosic carrier, a developer for the dyestuff is dispersed in such carrier. A fabric printed with such composition is then treated with a coagulant for the cellulosic carrier and with an undeveloped dyestuff component which reacts with the developer to form a colored dye in situ.

In a third embodiment, a sheet material is treated, as by printing, with a composition comprising a stabilized dyestuff in an undeveloped and/or colorless form (which stabilized dyestuff comprises two or more separate dyestuff components), a carrier for the stabilized dyestuff comprising a coagulable cellulosic colloid initially soluble in water and a dispersion medium for the cellulosic carrier. The treated material is next treated with a coagulant for the carrier and with an agent which unstabilizes the dyestuff thus permitting or causing a colored dye to be formed. In this embodiment, the coagulant

and the dyestuff-unstabilizing agent may be the same substance or different substances.

It will be noted that all three of the embodiments above described have the essential characteristics of the invention, namely, that the composition applied to the sheet material is colorless or not fully colored as desired and contains a cellulosic carrier which is initially soluble (i. e. dispersed in a fluid medium), whereas the final product comprises a deposit of colored material bound to the sheet material by a water-insoluble cellulosic colloid.

In preferred forms of all the above-mentioned embodiments the carrier is coagulated and the color developed in the same bath, whether with the same or with different reagents.

The process is applicable for coloring sheet materials of various kinds, such as the fibrous sheet materials as well as the non-fibrous foils such as Cellophane. In particular, the process is applicable for coloring textiles, felts and papers, all formed from natural fibres such as cotton, flax, ramie, jute, silk, wool and the like.

Textiles, felts, papers and foils formed from artificial materials may likewise be employed in the invention such, for example, as those materials and structures formed from cellulose, which may include regenerated cellulose or cellulose hydrate, the cellulose ethers, such as alkyl cellulose ethers, aralkyl cellulose ethers, hydroxy-alkyl cellulose ethers, carboxy-alkyl cellulose ethers and the like; the cellulose esters, such as nitrocellulose, cellulose acetate, formyl cellulose and the like; ether-esters of cellulose, resins of all kinds, and from mixtures of these classes of substances, also textiles and papers made from mixtures of different kinds of fibres.

The carrier for the dyestuff component may comprise suitable coagulable cellulosic colloids, such, for example, as alkali-soluble cellulose ethers.

The cellulose ethers which may be used as the carrier comprises the alkyl ethers of cellulose, the hydroxy-alkyl cellulose ethers, the carboxy-cellulose ethers, the mixed ethers, and the like, which are initially insoluble in water but soluble in aqueous solutions of alkalies.

The undeveloped dyestuff component of the invention may comprise uncoupled dyestuff bases such, for example, as the naphthol bases, the phenol bases, and the like; the stabilized dyestuffs such, for example, as "active" stabilized diazo compounds and "passive" stabilized compounds; also the reduced dyestuffs such, for example, as the leuco vat dyestuffs. The uncoupled or "passive" dyestuff bases include such bases as are formed from phenol, naphthol and the like which exist in an uncoupled state, and which may be diazotized and coupled with suitable agents, such as a diazo compound, an amine, and the like to form dyes. For example, such reactions with naphthol bases form the family of dyes known as the "naphthols." In place of using a base as the undeveloped dyestuff, an amine may be substituted therefor and then diazotized and coupled with a suitable base in a known manner to form a dye.

The stabilized dyestuff materials which may be used as the undeveloped dyestuff component comprise "active" stabilized diazo compounds which can be stored for certain lengths of time as a dry powder, either alone or mixed in dry form with the cellulosic carrier of the invention. The classes of "active" and "passive" stabilized compounds employed in the invention may comprise any of the compounds described in an article entitled "Chemical Constitution of the Naphthol AS Type Dyes," by Kenneth L. Dorman, American Dyestuff Reporter, February 20, 1939, pages 7, 8 and 9. Suitable compounds are sold under the trade names of Rapidogens, Rapidozols, Diagens, Pharmasols and the like, all of which may be transformed into developed dyes by treatment with an unstabilizing agent, such as steam or acid.

Examples of the reduced dyestuffs which may be used are the vat dyestuffs, the Indigosols and the like which may exist in a reduced state and which may be transformed and brought to full color value by further treatment, such as by oxidation or steaming.

The composition of the invention, comprising a dye component dispersed in a colloidal cellulosic carrier may be applied to the sheet material by suitable methods known to the art as, for example, by printing, dipping, spraying and the like. Among the printing methods which may be used are those known as intaglio printing, letter-press printing, screen-printing, stenciling, block printing and the like. In screen-printing, the composition of the invention is passed through a screen blocked out in predetermined areas to give desired printing effects upon the sheet materials. To provide "all-over" effects on the various materials they may be coated by dipping, back-filling, padding, spraying, by the use of dye-baths, and the like.

The coagulant for the cellulosic carrier is selected having regard for the nature of the particular cellulosic colloid employed. For the alkali-soluble carriers, the coagulant may comprise an aqueous solution of sulphuric acid, acetic acid, hydrochloric acid, and the like. In particular, for alkali-soluble cellulose ethers, the coagulant may be an aqueous solution of a salt, such, for example, as sodium chloride, potassium sulphate, sodium bisulphite, and the like. When the cellulosic carrier is a viscose solution, the coagulant may be heat, an acid, a salt, or a mixture of acids and salts, as known to the art. The carboxy-alkyl cellulose ethers may be insolubilized by coagulating them in aqueous solutions of salts of aluminum, lead, tin, zinc, barium, calcium and the like, the metal salt reacting with the cellulose ether to produce a water-insoluble metal salt thereof. The cellulose ethers may be coagulated by heat, or by the use of water or aqueous solutions. A single agent, such as steam, may be employed simultaneously to coagulate the cellulosic carrier and develop the undeveloped dye component, as, for example, where a paste comprises an undeveloped leuco vat dyestuff dispersed in a heat-coagulable cellulosic carrier, such as a cellulose ether. The same steam treatment may also be employed when using the "passive" stabilized compounds which have been dispersed in a heat-coagulable carrier and applied to a fabric, in order to develop the undeveloped dyestuff component and at the same time coagulate the cellulosic carrier.

By way of illustration, but not by way of limiting the invention, the following examples are given:

Example I

Two solutions were prepared as follows:

Solution A.—A solution comprising 2.5 grs. hydroxy-ethyl cellulose (alkali-soluble type) dissolved in 4 grs. sodium hydroxide in 100 cc. of water was prepared and 2.4 grs. beta-naphthol

(2-hydroxy-naphthalene) were dissolved in this solution. This composition was then printed onto a cotton fabric.

Solution B.—6.2 grams para-nitroaniline (1-amino-4-nitrobenzene) were dissolved in a solution comprising 12 grams of water and 14 grams of concentrated hydrochloric acid heated to a slightly elevated temperature. This was added to a beaker containing about 70 cc. cold water and about 30 grs. of ice. A solution containing 3.6 grams sodium nitrite dissolved in 50 cc. of water was then slowly added. To this mixture, 10 grams of sodium acetate dissolved in 50 cc. of water were added, while stirring, and this entire mixture brought to a total volume of 300 cc. by adding cold water.

The cotton fabric printed with Solution A was then passed through Solution B. The cellulose ether carrier thereupon was coagulated and at the same time the dyestuff component was diazotized to form a dye in situ. The fabric was then rinsed, scoured and finally washed and dried. The print showed up as an unusually full, deep red dye coloration.

Example II

Solution A.—2.0 grams of Primuline were dissolved in 100 grams of a solution comprising 2½ per cent alkali-soluble hydroxy-ethyl cellulose dissolved in a 4 per cent solution of sodium hydroxide.

Solution B.—3.6 grams sodium nitrite were dissolved in 250 grams of water at about 50° F. 7.0 grams of hydrochloric acid dissolved in 25 grams of water was then added. To this solution was added sufficient sodium acetate dissolved in water to convert the free hydrochloric acid to free acetic acid, determined as being neutral to Congo red, and also to make a solution of approximately 300 cc.

A cotton fabric was then printed with Solution A and immediately soaked in Solution B for approximately 10 minutes.

Solution C.—30 grams of beta-naphthol were dissolved in 4 grams of a 50 per cent sodium hydroxide solution, and then diluted to 300 cc. The fabric from Solution B was then passed into Solution C and allowed to remain therein about 5 minutes. The fabric was then withdrawn, washed and dried. The printed area of the material developed into a permanent deep red dye. The carrier remained insoluble and permanently fixed to the fabric.

Example III

A dyestuff known as Rapidogen Red GS (ortho-toluidide of beta-oxy-naphthoic acid, and the stabilized nitroso amine of 5-chloro-ortho-toluidine) was wet out with a wetting agent and then mixed with a solution of hydroxy-ethyl cellulose dissolved in a sodium hydroxide solution. Cotton fabric was printed with this paste and allowed to partially dry. The fabric was then passed into a dilute aqueous acetic acid solution which simultaneously coagulated the cellulose ether and developed the color. The fabric was finally washed and dried. It was then scoured in soap and soda ash solution for several minutes at an elevated temperature. It was found that at no time did the color bleed. Furthermore, the fabric showed exceptionally good color value and was fast to laundering.

Example IV

Solution A.—3 grams of beta naphthol were wet out and dissolved in a solution containing 3 grams of sodium hydroxide, 89 grams of water and 5 grams of sulfonated castor oil.

A cotton cloth was padded all over with the above Solution A and then dried at low temperature.

Solution B.—3 grams of para-nitroaniline (1-amino-4-nitrobenzene) was dissolved in 10 grams of water containing 6 grams of concentrated hydrochloric acid. This mixture was then warmed until completely dissolved, and then cooled to 50° F. whereupon the dissolved para-nitroaniline hydrochloride precipitated. Next 1.5 grams of sodium nitrite in 10 grams of water were added to the above preparation, which redissolved the para-nitro-aniline hydrochloride to form an orange solution.

Solution C.—A solution comprising 6 per cent alkali-soluble cellulose ether (viscosity 6) and 4 per cent sodium hydroxide then was prepared.

20 cc. of Solution B was then slowly added to 40 cc. of Solution C while stirring, in such a manner as to prevent local coagulation. No precipitation of the cellulose ether takes place due to the vigorous stirring and low acid concentration. The mixture becomes brown.

The cloth next was printed with this composition, and then exposed to steam containing vapors of acetic acid which developed the dyestuff and coagulated the cellulose ether, yielding sharp red prints with well-defined edges which are resistant to laundering because the insoluble cellulose ether binds the dyestuff to the fabric.

The article of the invention may be varied by adding to the composition, before or after printing, various pigments, metal powder, wetting agents, waterproofing agents, crease-proofing agents and the like.

Unusual effects may be produced by printing with a composition of the invention upon a fabric which has already been given an all-over treatment with a dyestuff and then passing the entire fabric into the developer and coagulant. Alternatively, a sheet material may be given a preliminary treatment with resists, and then printed all over or in predetermined areas according to the invention to provide untreated areas upon removal of the resists.

As a result of the process disclosed in the invention, there is produced an article comprising a sheet material having a deposit of colored material thereon. Since the cellulosic carrier is insoluble in water and binds the dyestuff to the sheet material, the coloration is highly resistant to wear or laundering and the leaching of the dyestuff is substantially prevented.

Since the cellulose ether used in the invention is of a substantially insoluble nature, the fabrics treated according to the invention will bear prints having sharply defined edges. The prints are not subject to bleeding, crocking and similar limitations encountered in the dyeing and printing industry. The dye is developed in the cellulosic deposit with which the fabric is impregnated, as well as in the fabric in situ, and thus becomes fastened to the fibres in the fabric as well as to the cellulosic deposit.

Unusual optical effects are produced in a fabric by the method disclosed in the invention, due to the combined refractive indices of the cellulose ether and the dyestuff.

Another novel characteristic of the product is the fact that the deposit of cellulose ether tends to stiffen and/or improve the hand and feel of the material where applied in contrast to the untreated areas. Thus, the article has a better

hand, surface appearance and a better color value.

Since certain changes may be made in the above process and product produced utilizing the same, and different embodiments of the invention could be made without deterring from the scope thereof, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

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

1. In a process for treating materials, the steps comprising printing a material with a composition comprising an undeveloped dyestuff component and a cellulosic carrier for said undeveloped dyestuff component comprising a coagulable alkali-soluble water-insoluble cellulose ether dispersed in liquid medium, treating the material with a coagulant for the cellulosic carrier and a developer for the undeveloped dyestuff component, the coagulated carrier being water-insoluble and binding the dye-stuff.

2. In a process for treating textile materials, the steps comprising printing a textile in predetermined areas with a composition comprising an undeveloped dyestuff component, a cellulosic carrier for said undeveloped dyestuff component comprising a coagulable alkali-soluble water-insoluble cellulose ether, a dispersion medium for said cellulosic carrier, and thereafter simultaneously treating the material with a coagulant for the cellulosic carrier and a developer for the undeveloped dyestuff component, the coagulated carrier being water-insoluble and binding the dyestuff.

3. In a process for treating textile materials, the steps comprising printing a textile in predetermined areas with a composition comprising an undeveloped dyestuff component, a cellulosic carrier for said undeveloped dyestuff component comprising a coagulable alkali-soluble water-insoluble cellulose ether, a dispersion medium for said carrier, treating the textile in predetermined areas with a substance having the combined function of being able to coagulate the cellulosic carrier and develop the undeveloped dyestuff component, the coagulated carrier being water-insoluble and binding the dyestuff.

4. In a process for treating textile materials, the steps comprising printing a textile in predetermined areas with a composition comprising an undeveloped dyestuff component, a cellulosic carrier for said dyestuff component comprising a coagulable alkali-soluble water-insoluble, cellulose ether, a dispersion medium for said cellulosic carrier, treating the material with steam to coagulate the cellulosic carrier, and a developer to develop the undeveloped dyestuff component, the coagulated carrier being water-insoluble and binding the dyestuff.

5. In a process for treating materials, the steps comprising printing a material in predetermined areas with a composition comprising an undeveloped dyestuff component, a cellulosic carrier for said dyestuff component comprising a coagulable alkali-soluble water-insoluble cellulose ether, a solvent for said cellulosic carrier comprising an aqueous solution of caustic alkali, treating the material with a liquid which will coagulate the cellulose ether and develop the undeveloped dye component, the coagulated carrier being water-insoluble and binding the dyestuff.

6. In a process for treating materials, the steps comprising printing a material in predetermined areas with a composition comprising a passive stabilized diazo undeveloped dyestuff component, a cellulosic carrier for said dyestuff component comprising a coagulable alkali-soluble water-insoluble cellulose ether, a dispersion medium for said cellulosic carrier, treating the material with a coagulant for the cellulosic carrier and a developer for the undeveloped dyestuff component, the coagulated carrier being water-insoluble and binding the dyestuff.

7. In a process for printing textile fabrics, the steps of printing a fabric with a composition comprising an undeveloped dyestuff comprising dye ingredients in a stabilized condition, a cellulosic carrier for the undeveloped dyestuff comprising coagulable alkali-soluble water-insoluble cellulose ether, a dispersion medium for the said carrier, thereafter treating the fabric with a coagulant for the cellulosic carrier and a developer to permit the dye ingredients to react with each other, the coagulated carrier being water-insoluble and binding the dyestuff.

8. In a process for treating textile materials the steps comprising padding a material all over with a composition comprising an undeveloped dyestuff component, printing the material in predetermined areas with a composition comprising a second undeveloped dyestuff component dispersed in a coagulable alkali-soluble water-insoluble cellulosic colloid and a solvent for said colloid, treating the material with a substance having the function of being able to coagulate the cellulosic colloid and develop the dyestuff, the coagulated carrier being water-insoluble and binding the dyestuff.

J. ANDREW CLARK.

CERTIFICATE OF CORRECTION.

Patent No. 2,259,796. October 21, 1941.

JAMES ANDREW CLARK.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 28, claim 1, for "dye-stuff" read --dyestuff--; and second column, line 2, claim 4, after "water-insoluble" strike out the comma; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 2nd day of December, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)