

UNITED STATES PATENT OFFICE

2,336,341

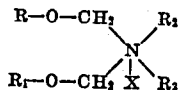
CHANGING THE CAPACITY OF CELLULOSIC FIBERS FOR DYES

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No Drawing. Application December 28, 1940,
Serial No. 372,167

7 Claims. (Cl. 8-15)

This invention relates to a process for producing novel effects in the coloring or dyeing of textile fabrics containing cotton, linen, ramie, or other cellulose fiber or regenerated cellulose fiber. In particular, the invention deals with creating effects in the dyeing of fabrics containing fibers of cellulose or regenerated cellulose by altering the capacity for dyes of at least part of said fibers. This change in capacity of cellulose fibers is obtained by reacting them with a compound of the formula



wherein R is an aliphatic group containing 8 to 12 carbon atoms, R₁ is a member of the class consisting of aliphatic, alicyclic, and aralkyl groups of less than 13 carbon atoms, R₂ and R₃ when taken individually are members of the class consisting of lower alkyl groups and when taken together are a saturated divalent group which jointly with the nitrogen forms a heterocycle, and X is a salt-forming anion.

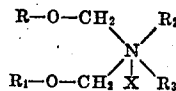
It has previously been proposed to render cellulose fibers indifferent to substantive colors by acetylating fibers or esterifying them with an agent such as toluene sulfonyl chloride or benzoyl chloride. In general, such prior processes have required complicated procedure, excessive times of treatment, and manipulation beyond that found practical in the average textile mill. These processes have often tendered fibers seriously and fibers so treated are also stiff and harsh. Such disadvantages are avoided by the method herein described for altering the susceptibility of cellulosic fibers to dyestuffs.

In accordance with the present invention, decorative and novel effects are obtained in textile fabrics containing cellulosic fibers by treating at least part of the cellulosic materials making up the fabric with a solution of a compound of the formula shown above, heating the treated fibers to cause a reaction between fibers and compound, and subsequently applying a dye to the treated fibers or to the fabric containing the treated fibers. When the dye applied is one which is normally substantive to cotton, the fibers treated as described exhibit a reserve effect and are not more than tinted. Thus, a cotton fabric may be woven in part with normal yarns and in part with yarns which have been treated and heated with a compound of the above formula, and the fabric dyed with a direct dye. The treated yarns form a pattern, differing from the untreated yarn in color, intensity of color or shade. On the other hand, such a fabric may be dyed with an acetate dye whereby the treated fibers or yarns acquire full colors while the rest of the fabric acquires little or no

color. Comparable effects can be produced by printing cellulose fabrics with pastes containing a quaternary ammonium salt of the above type, heating the printed fabric to cause a reaction between the printed portions of the fabric and the compound, and then dyeing the fabric. The difference between treated and untreated fibers, yarns, or areas also gives different colors or shades in cross-dyeing.

As a cellulosic material, there may be used fibers, filaments, yarns, or fabrics of cotton, linen, ramie, jute, wood pulp, regenerated cellulose, and the like.

The quaternary ammonium salts which are suitable for reacting with the cellulosic material, i. e., compounds of the formula



contain R and R₁ groups of not over 12 carbon atoms. R may be a straight or branched chain aliphatic group of 8 to 12 carbon atoms, such as an octyl, undecenyl, dodecyl, capryl, 2-ethyl nonyl, butylphenoxyethyl, cresoxyethyl, etc. R₁ may be a similar aliphatic group or a smaller group, such as an ethyl, isopropyl, butyl, amyl, hexyl, or methallyl, an aralkyl group such as benzyl, methylbenzyl, or an alicyclic group such as cyclohexyl. It is significant that one ether group must possess a chain of at least 8 carbon atoms in order to cause the cellulosic material to change in dyeing properties. On the other hand, for satisfactory results, this chain must be limited to not more than 12 carbon atoms. The size of the second ether group should not exceed 12 carbon atoms. The groups represented by R₂ and R₃ when taken individually are lower alkyl groups, represented by methyl, ethyl, propyl, and butyl, or when taken together are a saturated divalent group which jointly with the nitrogen forms a heterocycle as in morpholine, piperidine, pyrrolidine, etc. Typical compounds which are useful in this invention include octyloxymethyl methyloxymethyl piperidinium chloride, dodecyloxymethyl butyloxymethyl pyrrolidinium chloride, dodecyloxymethyl butyloxymethyl diethyl ammonium bromide, didodecyloxymethyl dimethyl ammonium chloride, undecenylloxymethyl amyloxymethyl dimethyl ammonium iodide, octyloxymethyl ethyloxymethyl dibutyl ammonium chloride, dodecyloxymethyl ethyloxymethyl morpholinium bromide, dodecyloxymethyl cyclohexyloxymethyl methyl propyl ammonium bromide, etc. The salt-forming anions in the above compounds may be replaced by known methods with other anions such as sulfate, acetate, formate, etc.

In altering the capacity for dyes of cellulosic materials, it is necessary to use fairly concen-

trated solutions of the reacting compound. A solution containing about 10% or more of the compound is effective, a range of 10% to 25% being preferred. The compound may be dissolved in water, an organic solvent such as ethyl alcohol or acetone, or in a mixture of solvent and water, and may be applied to fiber, yarn, or fabric by spraying, spreading, immersing, printing or other suitable mode of application. Excess solution may be removed by squeezing, centrifuging, vacuum extracting, or equivalent procedure. The material to which the solution has been applied is then dried and baked at a temperature between 100° C. and about 160° C. If desired, drying and baking may be carried out as a single step.

In this way cellulosic fibers are reacted with one of the above quaternary ammonium compounds, and are altered in their dyeing properties. For example, against such dyes as vat dyes, sulfur dyes, and the usual direct dyes for cotton, the treated fibers exhibit a reserve effect, while against such dyes as the direct acetate dyes, they show an increased affinity.

The treatment of cellulosic materials with compounds of the above type and the dyeing of the treated materials are illustrated in the following examples.

Example 1

A skein of cotton yarn was immersed in a 10% aqueous solution of dodecyloxymethyl butyloxymethyl dimethyl ammonium chloride, dried at room temperature and heated in an oven at 130° C. for 30 minutes, rinsed in water, and dyed for 30 minutes at 100° C., in a bath containing 1% Diazine Black OB. The skein so treated was only lightly colored. A second skein of cotton yarn which was not so immersed in the aqueous solution but which was subjected to the same dyeing bath for the same period of time and at the same temperature was dyed a deep black.

Another skein of cotton yarn was immersed in a 20% aqueous solution of the same quaternary ammonium compound and treated as above. This skein showed even greater resistance to dyeing with Diazine Black OB under the same conditions of time, temperature and concentration.

Diazine Black OB is listed in the Yearbook of the American Association of Textile Chemists and Colorists as belonging to Foreign Prototype 147.

Example 2

A piece of cotton sheeting was immersed in a 20% aqueous solution of octyloxymethyl benzylloxymethyl dimethyl ammonium chloride, thereafter dried for ten minutes in an oven at 130° C., and then heated for ten minutes in an oven at 150° C. After the heat treatment, the cloth was washed with a soap solution, rinsed in water several times, and dyed for 30 minutes at 100° C. in a bath containing 1% Diazine Black OB. The resulting cloth was a light, pearl gray.

A piece of cotton sheeting, not treated with the quaternary ammonium salt but dyed in the same bath for the same length of time and at the same temperature, became a rich black in color.

Example 3

Kier-boiled and bleached percale was padded through a 20% aqueous solution of dodecyloxymethyl ethoxyethyl dimethyl ammonium chloride, dried in a frame, and heated in a drier at 130° C. for about 20 minutes, and thereafter washed in soap solution and rinsed. Pieces of

this fabric were then treated in baths of dyes of different types and a piece of the original percale was also entered in each dye bath for purposes of comparison.

(a) A bath was prepared from 2 parts of tetrabromo-indigo (Colour Index No. 1184), 2.5 parts of sodium hydrosulfite, 10 parts of a 20% aqueous sodium hydroxide solution, and 100 parts of water by heating the mixture at 70° C. until reduction was complete, and then diluting with 200 parts of boiled water. Pieces of both treated and original fabric were padded through this solution, thereafter treated in an oxidizing bath, and dried. The original untreated fabric was a full blue, while the treated fabric acquired only a light shade.

(b) Pieces of original percale and treated percale were dyed for one hour in a bath at 70° C., containing 5 parts of SRA Orange III, an acetate dye, 0.5 part of soap, and 200 parts of water. The original fabric held only a trace of dye while the treated fabric acquired a deep, full color.

(c) Other pieces of original and treated fabrics were steeped for one-half hour at 100° C., in a bath composed of 5 parts of Calcogene Dark Brown N, 5 parts of sodium sulfide and 200 parts of water. The treated piece retained very little of the dye while the control was a black-brown.

Example 4

An all-spun rayon fabric was padded through a warm 15% solution of octyloxymethyl butyloxymethyl morpholinium chloride, dried, heated for 20 minutes in an oven at 150° C., and thereafter laundered in hot soap solution, rinsed, and entered in a bath containing 1% of Diazine Black OB, held between 80° and 100° C. The treated fabric took up very little dye, while a piece of the fabric, subjected to the same dye bath under the same conditions but which had not been preliminarily treated, became black.

Example 5

Cotton muslin was padded through a bath containing 15% of dodecyloxymethyl propoxymethyl dimethyl ammonium bromide, dried at a moderate temperature and heated one-half hour in a loop drier at 130° C. It was then washed with soap solution, rinsed, soaked for 15 minutes in a bath at 50° C., containing 5 parts of tannic acid in 200 parts of water, squeezed, immersed in a bath containing two parts of tartar emetic in 200 parts of water, again squeezed, and soaked for 20 minutes in a bath at 50° C., containing 4 parts of Victoria Green 5 Ex. (Colour Index No. 657), 8 parts of acetic acid and 200 parts of water. The treated cloth became pale green whereas a piece of the cloth which was subjected to the dye bath only, at the same temperature and for the same length of time, was dyed a dark green.

In none of the above examples was there any appreciable tendering of the fabric.

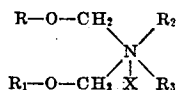
Novel effects in textiles are obtained by altering the capacity of cellulosic fibers and using them along with other fibers in a fabric to give contrast on dyeing. The effect may be obtained by combining the altered fibers with untreated fibers of the same or of a different type of fiber, or by the use of yarns which have been treated and woven into a fabric in patterns, or by altering fibers within certain areas of the fabric by printing or impregnating such area with the treating solution, heating to cause reaction, and subsequently dyeing the fabric. These effects may be described as differential dyeing effects.

There may also be obtained decorative effects as the result of cross-dyeing a fabric containing both treated and untreated fibers.

Fibers or yarns treated as described may be used in the construction of all types of fabrics and may be used in conjunction with untreated cotton; linen, rayon, etc., or with silk, wool, etc., to give designs, patterns, and variegated effects. The process involved in producing these effects is such that it may be practiced with standard textile equipment without damage to fabric or machinery. The results are highly satisfactory and are uniformly obtained.

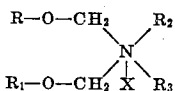
We claim:

1. In the process for producing novel coloring effects in a textile fabric containing fibers selected from the class consisting of cellulose and regenerated cellulose by markedly decreasing the affinity for direct dyes and increasing the affinity for acetate dyes of at least part of said fibers, the steps which comprise treating cellulosic fibers with a solution containing at least 10% of a compound of the formula



wherein R is an aliphatic group containing 8 to 12 carbon atoms, R₁ is a member of the class consisting of aliphatic, alicyclic, and aralkyl groups of less than 13 carbon atoms, R₂ and R₃ when taken individually are members of the class consisting of lower alkyl groups and when taken together are a saturated divalent group which jointly with the nitrogen forms a heterocycle, and X is a salt-forming anion, heating the treated fibers to cause a reaction between such fibers and said compound, and subsequently applying a dye to the reacted fibers.

2. A method of producing novel coloring effects in a textile fabric containing fibers selected from the class consisting of cellulose and regenerated cellulose fibers by markedly decreasing the affinity for direct dyes and increasing the affinity for acetate dyes of at least part of said fibers, which comprises impregnating at least part of the fibers with a solution containing about 10% to about 25% of a compound of the formula



wherein R is an aliphatic hydrocarbon group containing 8 to 12 carbon atoms, R₁ is a member of the class consisting of aliphatic, alicyclic, and aralkyl groups of less than 13 carbon atoms, R₂ and R₃ are lower alkyl groups, and X is a halogen, heating the impregnated fibers to cause reaction between fibers and compound, and subsequently subjecting the fabric containing the treated fibers to the action of a dye.

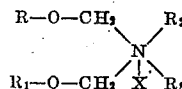
3. A method of producing novel coloring effects in a textile fabric containing fibers selected from the class consisting of cellulose and regenerated cellulose fibers by markedly decreasing the affinity for direct dyes and increasing the affinity for acetate dyes of at least part of said fibers, which comprises impregnating at least part of said fibers with a solution containing about 10% to about 25% of a dodecyloxymethyl butoxymethyl dimethyl ammonium halide, heating the impregnated fibers to cause reaction between fibers and compound, and subsequently subject-

ing the fabric containing the treated fibers to the action of a dye.

4. A method of producing novel coloring effects in a textile fabric containing fibers selected from the class consisting of cellulose and regenerated cellulose fibers by markedly decreasing the affinity for direct dyes and increasing the affinity for acetate dyes of at least part of said fibers, which comprises impregnating at least part of said fibers with a solution containing about 10% to about 25% of a dodecyloxymethyl benzyloxymethyl dimethyl ammonium halide, heating the impregnated fibers to cause reaction between fibers and compound, and subsequently subjecting the fabric containing the treated fibers to the action of a dye.

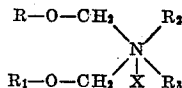
5. A method of producing novel coloring effects in a textile fabric containing fibers selected from the class consisting of cellulose and regenerated cellulose fibers by markedly decreasing the affinity for direct dyes and increasing the affinity for acetate dyes of at least part of said fibers, which comprises impregnating at least part of said fibers with a solution containing about 10% to about 25% of octyloxymethyl butoxymethyl dimethyl ammonium chloride, heating the impregnated fibers to cause reaction between fibers and compound, and subsequently subjecting the fabric containing the treated fibers to the action of a dye.

6. A dyed fabric comprising textile fibers, some of which are unaltered in their affinity for dyes and others of which are cellulosic fibers of decreased affinity for direct dyes and increased affinity for acetate dyes as the result of chemical reaction with a compound of the formula



wherein R is an aliphatic group containing 8 to 12 carbon atoms, R₁ is a member of the class consisting of aliphatic, alicyclic, and aralkyl groups of less than 13 carbon atoms, R₂ and R₃ when taken individually are members of the class consisting of lower alkyl groups and when taken together are a saturated divalent group which jointly with the nitrogen forms a heterocycle, and X is a salt-forming anion.

7. A fabric comprising textile fibers, some of which are unaltered in their affinity for dyes and others of which are cellulosic fibers of decreased affinity for direct dyes and increased affinity for acetate dyes as the result of chemical reaction with a compound of the formula



wherein R is an aliphatic group containing 8 to 12 carbon atoms, R₁ is a member of the class consisting of aliphatic, alicyclic, and aralkyl groups of less than 13 carbon atoms, R₂ and R₃ when taken individually are members of the class consisting of lower alkyl groups and when taken together are a saturated divalent group which jointly with the nitrogen forms a heterocycle, and X is a salt-forming anion, said fabric having an integral design resulting from a difference in dyeing between the altered cellulosic fibers and the unaltered fibers.

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