

UNITED STATES PATENT OFFICE

2,628,151

PROCESS FOR SIMULTANEOUSLY STABILIZING AND APPLYING A VAT DYE TO TEXTILE MATERIAL COMPRISING REGENERATED CELLULOSE

Leslie L. Walmsley, Ridley Park, and Raymond E. Smith, Chester, Pa., assignors to American Viscose Corporation, Wilmington, Del., a corporation of Delaware

No Drawing. Application November 25, 1949,
Serial No. 129,498

8 Claims. (Cl. 8-18)

1

This invention relates to a method of stabilizing textile material against progressive dimensional shrinkage on repeated laundering and against normal pulling out during final finishing operations, simultaneously with the application of a vat dyestuff to the textile material.

Normally treatment of a textile material, such as a regenerated cellulose fabric, for example, and the application of a vat dyestuff thereto, involves a two-step process in which the fabric is dyed in one operation and then treated for the purpose of stabilizing it. In this conventional two-step process, the fabric is first dyed in an operation comprising the following steps:

1. Preparation of the fabric for dyeing by desizing, scouring, rinsing and drying the fabric;
2. Application of the vat dyestuff to the fabric by padding;

3. Reduction of the pigment to the leuco vat;
4. Oxidation of the leuco vat to the vat pigment;

5. Scouring of the fabric following the oxidation step;
6. Drying;

7. Framing the fabric to the desired width.
After step 7 has been performed, the fabric is subjected to a treatment intended to stabilize it against shrinkage, a synthetic resin being generally used as the stabilizing agent. This treatment involves the following steps.

8. Application of the resin to the fabric by padding;

9. Drying of the resin-treated fabric;
10. Curing the resin on the fabric to an insoluble condition;

11. Scouring of the fabric carrying the cured resin;

12. Drying the fabric; and

13. Framing the fabric to desired width.

The present invention, in accordance with which textile materials are effectively stabilized against both progressive dimensional shrinkage on repeated laundering and pulling out during finishing, simultaneously with the application of a vat dyestuff, comprises the following steps;

1. Preparation of the fabric by desizing, scouring and drying;

2. Simultaneous application of the vat pigment and a special stabilizing medium;

3. Drying;

4. Curing of the stabilizing medium;

5. Reduction of the pigment to the leuco vat;

6. Oxidation of the leuco vat back to the vat pigment;

7. Scouring after the oxidation;

2

8. Drying; and

9. Framing to desired width.

As will be apparent, by the method of this invention, four of the steps which are required in the normal practice of the trade are entirely eliminated, which reduces the handling and time required to prepare the textile material for the market, and considerably lessens the cost of the fabric by substantial reduction in both the labor and operating costs.

Since the present invention is of special importance in the treatment of fabrics formed from or comprising fibers, filaments, or yarns of regenerated cellulose, including yarns predominantly of spun viscose rayon, it will be discussed in detail in connection with the treatment of such fabrics.

The trade has never been successful in effectively stabilizing a regenerated cellulose fabric against both progressive dimensional shrinkage on repeated laundering and the "pulling out" which normally occurs when such fabrics are subjected to final finishing, simultaneously with the application of color to the fabric. The stabilizing agents available to the trade have not been entirely satisfactory. For example, cellulose ethers, which have been proposed as stabilizing agents, impart a measure of stability against progressive dimensional shrinkage on repeated laundering to the fabric, but do not stabilize it against "pulling out" during final finishing. Moreover, most of the treatments which have been depended upon to impart stability to the fabric have involved the use of substances which are not compatible with, or not adapted to use in conjunction with, the known dyestuffs. Urea-formaldehyde resin is one example of a substance which has been considered for application to regenerated cellulose fabrics in the form of a precondensate and cured to the insoluble condition on the fabric. Regenerated cellulose fabrics cannot be dyed successfully with a vat dyestuff, for example, applied to the fabric in a treating medium comprising a urea-formaldehyde resin, because the resin retards the reduction of the dye to its soluble leuco form which must be effected on the fabric after the resin is cured. Other resins of this type have the same or similar disadvantages. The retarding or inhibiting effect of the resins on reduction of the vat dyestuffs on the fabric is one factor responsible for the fact that stabilization of the fabric simultaneously with the application of color thereto by means of a vat dyestuff has remained a desirable objective which, however, has not

been attained. Treatment of the fabric with a pre-dyed cellulose ether does not accomplish the objectives of this invention because the cellulose ethers do not stabilize the fabric against pulling out during the final finishing operations which must be performed after the ether has been precipitated on the fabric and, additionally, the dyeing is obtained by a mere mechanical fixing of the dye on the surface of the fabric by fixing of the ether thereon. Up to the present, the common practice in the trade has been the old one of dyeing the fabric in one operation and then treating the dyed fabric with a medium intended to impart stability thereto, in a separate, different operation, as outlined in detail above.

The primary object of this invention is to provide a novel process in which textile materials, particularly those predominantly of regenerated cellulose, are stabilized against both progressive dimensional shrinkage on repeated laundering and normal pulling out during final finishing in the stabilized condition and dyed simultaneously, using an aqueous treating liquid containing both the dyestuff and the stabilizing medium. Another object is to dye and stabilize the textile materials comprising or consisting of regenerated cellulose with minimum degradation of the cellulose and loss in tensile strength. A specific object is to dye and stabilize the textile materials, using a treating liquid containing a vat pigment and stabilizing media which do not retard or inhibit reduction of the vat pigment to the soluble leuco vat on the fabric. Other objects and advantages of the invention will be apparent from the following description.

We have now found that textile materials, particularly of regenerated cellulose, can be successfully stabilized against both progressive dimensional shrinkage on repeated laundering and normal pulling out during final finishing subsequent to the stabilization, simultaneously with application of color thereto, provided that the stabilization is effected by means of a water-insoluble, alkali-soluble cellulose ether and formaldehyde applied conjointly to the textile material with the dyestuff under specific controlled conditions as set forth herein.

In accordance with the invention, textile materials, particularly fabrics predominantly of regenerated cellulose, are impregnated or treated with an aqueous treating medium having a pH of from 1.2 to 6.5 and containing the dyestuff, the water-insoluble, alkali-soluble cellulose ether, and formaldehyde, dried in the absence of contact pressure and preferably under tension, heated in the absence of contact pressure to cure the aldehyde, and after-treated, if necessary, to develop the dye on the fabric.

In the presently preferred embodiment of the invention, the dyestuff applied to the fabric in the aqueous treating liquid containing the water-insoluble, alkali-soluble cellulose ether and formaldehyde for stabilizing the fabric, is a vat pigment. Under the conditions of this process, the cellulose ether and aldehyde, which function conjointly to stabilize the fabric, after curing of the aldehyde, do not retard or inhibit reduction of the pigment vat to the soluble leuco vat on the fabric, or regeneration of the dye by oxidation. After the fabric is heated to curing temperature for the formaldehyde and then treated for reduction of the insoluble vat pigment to the soluble leuco vat, followed by oxidation for regenerating the dye on the fabric, the fabric is effectively stabilized and dyed to a level shade of excellent

light and wash fastness. The results of the present process are different from the results which may be obtained by treating textile material with a pre-dyed cellulose ether. In this process, the fabric is stabilized effectively against both progressive dimensional shrinkage on repeated laundering and pulling out during final finishing, and the fibers of the fabric are dyed in cross-section, whereas fabrics treated with a pre-dyed cellulose ether are not effectively stabilized against pulling out during final finishing, and the fibers of the fabric are not dyed in cross-section, the dyeing being obtained by mechanical fixing of the dye on the surface of the fabric.

The treating medium applied to the fabric in accordance with this embodiment is prepared by mixing the water-insoluble, alkali-soluble cellulose ether with an aqueous alkaline solution, for example, with an aqueous solution of sodium hydroxide, dispersing the insoluble vat pigment through the mixture, and then adding the formaldehyde. The pH of the final mixture is on the alkaline side, usually between 12 and 14, and a pH regulator, for example a strong mineral acid such as sulfuric acid, is added in an amount sufficient to neutralize the alkali and reduce the pH to a value in the range of from 1.2 to 6.5. Generally, sulfuric acid may be added in an amount of from 1.7 to 2.9% by weight, which is in excess of the amount required to neutralize the alkali and convert it to the corresponding alkali metal sulfate, the excess acid serving as a curing or condensing catalyst for the aldehyde when the fabric is heated to curing temperature. The acid may be added to the alkaline medium at room temperature or at temperatures below room temperature.

In practicing the preferred embodiment of the invention, the aqueous treating medium having a pH of from 1.2 to 6.5 and containing the cellulose ether, dispersed vat pigment, and formaldehyde is applied to the fabric to be dyed and stabilized while the fabric is held under tension, for example by padding, and the fabric is dried under tension, for example on the tenter, at a temperature of 240° F. or below, for instance between 200 and 240° F. The dried fabric is then heated at a temperature of 300° F. to 350° F. for a time interval generally inversely related to the temperature, to convert the aldehyde to the insoluble, set condition and to coagulate the cellulose ether. The drying and curing are performed in the absence of pressure. The fabric is heated to cure the aldehyde while it is on a tenter or the like, by blowing hot air on the fabric. Preferably, the curing is performed while the fabric is tensioned, but this is not essential, whereas application of the treating liquid and drying of the treated fabric are performed under tension for optimum results.

The vat pigment may be reduced to the soluble leuco vat on the fabric, after the aldehyde has been cured and the ether coagulated, by the usual methods of reducing vat pigments, for example by treating the fabric with an aqueous solution of sodium hydroxide and sodium hydrosulfite in controlled amounts. Regeneration of the pigment may be effected by treating the fabric carrying the reduced vat with an aqueous solution of a mild oxidizing agent, for example, sodium perborate.

In a preferred embodiment, the treating medium also comprises an agent which exerts a softening or plasticizing action on the cured aldehyde, on the textile material, or on both. The

plasticizer may be added to the medium at either alkaline or acid pH, but is normally added after the dyestuff has been dispersed in the aqueous alkaline medium containing the water-insoluble, alkali-soluble cellulose ether.

The aqueous treating medium having a pH from 1.2 to 6.5 contains from 0.5 to 1.5%, preferably about 1%, of the water-insoluble, alkali-soluble cellulose ether, from 0.01 to 5% of a vat dyestuff, from 1 to 5%, preferably about 3% of formaldehyde, and from 0.5 to 1.5% of the plasticizing agent, the percentages given being by weight based on the weight of the treating medium. The treating liquid also contains sodium sulfate which functions as a buffer to prevent tendering of the fabric by the sulfuric acid catalyst during baking thereof to cure the formaldehyde. Prior to neutralization of the alkali, it is present in the medium in a concentration of from 0.5 to 1.5%.

The term "water-insoluble, alkali-soluble cellulose ether" includes such ethers which are insoluble in water but soluble in aqueous alkali solutions of from 1 to 8% concentration at room temperature or at reduced temperature, including simple alkyl ethers, carboxyalkyl ethers, hydroxyalkyl ethers, mixed alkyl hydroxyalkyl ethers, mixed alkyl carboxyalkyl ethers and the salts of the carboxyalkyl ethers. Hydroxyethyl celluloses having a standard viscosity of from 0.05 to 2, and an average degree of substitution of from 0.10 to 0.40 ethylene oxide group per anhydroglucose unit are satisfactory. The standard viscosity is that of solutions containing 85% water, 6% of the cellulose ether, and 9% sodium hydroxide by weight, measured at 25° C. and expressed as a multiple of the viscosity of glycerol at 25° C.

The aqueous medium may be an aqueous solution of a strong inorganic alkali, such as sodium, potassium, or lithium hydroxide. Preferably, the cellulose ether, the vat pigment, and the formaldehyde are mixed with an aqueous solution of sodium hydroxide, in the order named. The ether may be dissolved in the alkaline medium in a concentration higher than that desired finally, and the solution may then be diluted to the desired concentration. The pH regulator which is added to the treating medium may be any acid or salt which adjusts the pH to 1.2 to 6.5. Sulfuric acid is presently preferred. Surprisingly, when sulfuric acid is added to the aqueous medium containing the ether, dyestuff, and formaldehyde in an amount sufficient to adjust the pH to 1.2 to 6.5, the ether is not visibly precipitated, in spite of the fact that sulfuric acid is known to be a precipitant for these ethers.

Any vat dyestuff, whether of the anthracene, indigoid, or sulphide type dyestuffs, may be added to the aqueous alkaline medium containing the water-insoluble, alkali-soluble cellulose ether, and formaldehyde. The insoluble pigment vat is added to the alkaline ether solution or dispersion in the form of a paste and dispersed therein by agitation.

The cellulose ether, pigment vat, and formaldehyde are preferably mixed with the aqueous alkaline solution at room temperature or below and the treating medium is preferably applied to the textile material at room temperature or lower.

The plasticizing or softening agent may be any wax-like material which is self-emulsifiable in the aqueous treating medium and which is compatible with and chemically inert to the remaining in-

gredients of the medium. Examples of suitable plasticizing or softening agents are the ethers and esters of polyhydric alcohols containing one or more free hydroxyl groups, and condensates thereof with ethylene oxide containing for example from 1 to 50 ethylene oxide units per molecule. For instance, the self-emulsifying wax-like material used as plasticizing agent may be a butyl ether of a polyhydric alcohol such as ethylene glycol monobutyl ether, a partial ester of an inner anhydride of a polyhydric alcohol with a fatty acid containing, preferably, at least 8 carbon atoms, or condensates thereof with ethylene oxide; or it may be a partial ester of such alcohols as sorbitol, mannitol, glycerol, glycol, etc. with a fatty acid such as stearic, oleic, myristic, lauric, etc., or condensates of the esters with ethylene oxide. A particularly effective, preferred plasticizing agent comprises a mixture of 50% sorbitan monopalmitate and 50% sorbitan tristearate containing 16 polyethylene oxide units per molecule. In certain instances, the plasticizing agent may be omitted, as for instance when a dyed textile of less pronounced flexibility is desired for any reason, or when a cellulose ether of low viscosity is used.

By the process of this invention, the difficulties encountered previously when it was attempted to stabilize a regenerated cellulose fabric against both progressive dimensional shrinkage on laundering and pulling out during final finishing, simultaneously with the application of color thereto, are overcome. The results obtained by the practice of the invention depend on the conjoint use of the water-insoluble, alkali-soluble cellulose ether and formaldehyde for stabilizing the fabric, and are not obtainable by applying a vat dyestuff to the fabric in conjunction with other agents which have been proposed for imparting stability to a regenerated cellulose textile. An unexpected and unique feature of the present process is that a pigment vat can be reduced to the soluble leuco vat on the fabric in spite of the presence of the cellulose ether and aldehyde on the fabric, and after heating of the fabric to cure the formaldehyde to insoluble condition and coagulate the ether, whereas urea-formaldehyde and similar resins which are condensed on the fabric function as a resist to retard or inhibit reduction of a pigment vat to a soluble leuco vat. The pigment applied to the fabric simultaneously with the water-insoluble, alkali-soluble cellulose ether and formaldehyde in a treating liquid having a pH of 1.2 to 6.5, in accordance with this invention is completely and uniformly reduced to the soluble condition on the fabric, and stabilized fabrics which are dyed to level shades of excellent fastness are obtained.

Fabrics dyed and stabilized in accordance with the invention are dimensionally stable on repeated washing and compare very favorably as to shade and fastness with fabrics dyed with the vat dyestuff in one operation and subsequently stabilized by treating them with an aqueous treating liquid having a pH of 1.2 to 6.5 and containing the cellulose ether and formaldehyde.

The following non-limiting examples are given as illustrative of specific embodiments of the invention.

EXAMPLE I

Two pounds of a hydroxyethyl cellulose having a standard viscosity of 2 and an average degree of substitution of 0.36-0.40 ethylene oxide group per glucose unit were wet out in 24 lbs. of water for about 12 hours. A 40% aqueous solution of

sodium hydroxide was added, 2.5 lbs. of the caustic solution being used. 0.5% of the vat dye-stuff Indanthrene Blue BCSN Dbl. Paste (Pr. 115) was pasted in 3 gallons of water and mixed with the alkaline solution containing the cellulose ether. One pound of a mixture consisting of 50% sorbitan monopalmitate and 50% of sorbitan tristearate containing 16 polyoxyethylene units dissolved in 3 gallons of water were added. Twenty pounds of formaldehyde (as 37% commercial formalin) were stirred in, and the mass was diluted with water to 21 gallons. A 20% solution of sulfuric acid was added to adjust the pH to 1.30, and water was added to give 24 gallons of treating medium which was strained into a pad trough to remove any foreign matter.

A plain weave 100% regenerated cellulose challis fabric in the greige, made of 80 warp and 60 filling yarns was desized, boiled off, and dried on a pin tenter. The resulting white fabric had a count of 84 by 64, and weight of 4.0 ounces per yard.

The fabric was padded through the treating solution under tension, pick-up at the pad being about 85%. The fabric was then dried on a clip frame, fed to a tenter without using overfeed, and treated on the tenter to cure the formaldehyde by blowing hot air (330° F.) against the fabric for 2½ minutes. The fabric was then immersed for 15 minutes in a reducing bath having a temperature of 140° F. and containing 15% sodium hydroxide and 0.3% of sodium hydrosulfite, and then immersed for 15 minutes in an oxidizing bath having a temperature of 120° F. and containing 0.12% of sodium perborate. The dyed stabilized fabric was then scoured at 180° F. for 15 minutes, rinsed, and dried relaxed.

The finished fabric, which was dyed to a beautiful level shade of blue, of excellent light and wash-fastness, was subjected to five Standard Cotton Wash Tests for Shrinkage. The extent of shrinkage of the dyed stabilized fabric on repeated laundering, as compared to the shrinkage of an untreated fabric of the same construction, is shown in the table below.

Warplike shrinkage in per cent on washing

(Standard CCC-T-191A Cotton Wash Test)

	First Washing	Second Washing	Third Washing	Fourth Washing	Fifth Washing
Dyed and Stabilized Fabric (Ex. 1).....	Percent -0.6	Percent -0.6	Percent -0.6	Percent -0.3	Percent -0.6
Untreated Fabric.....	Percent -2.5	Percent -2.78	Percent -3.33	Percent -5.28	Percent -5.28

The stability imparted to the fabric by the cellulose ether and formaldehyde conjointly is superior to the stability which can be obtained by treating a regenerated cellulose fabric with either formaldehyde or the cellulose ether alone, although the reasons for this are not readily apparent. It may be that the cellulose ether assists in retarding or hastening conversion of the formaldehyde to the insoluble condition so that the latter is cured when the gel structure of the film or coating on or in the regenerated cellulose fabric or the like is in an optimum condition of swelling. It is possible, also, that during the curing step, the formaldehyde reacts chemically with the free hydroxyl groups of the cellulose ether and/or with the hydroxyls of the regenerated cellulose textile material. Such reactions may, in fact, be initiated during the drying step. In any case, the dried fabric comprises a heat-

convertible composition comprising formaldehyde, which is converted to insoluble, set condition when the fabric is heated to the curing temperature.

EXAMPLE II

Example I was repeated, except that the treating medium contained the vat dyestuff Indanthrene Yellow 3 RD Dle. Pst. (C. I. No. 1118).

EXAMPLE III

A regenerated cellulose fabric was stabilized and dyed by the procedure of Example I, except that the treating medium contained, in addition to the ether, Indanthrene Brown BRA. (Pr. No. 118).

EXAMPLE IV

The procedure was the same as in Example I, the treating medium comprising the ether, formaldehyde, and Calcosal Jade Green NP Dle. Paste. (C. I. No. 1101).

Since some variations made in practicing the invention, without departing from the spirit and scope thereof, it will be understood that the invention is not to be limited except as defined by the appended claims.

We claim:

1. A method of stabilizing textile materials predominantly of regenerated cellulose against progressive dimensional shrinkage under repeated washings and against normal pulling out during final finishing operations performed subsequently to the stabilization and simultaneously applying color to the textile which comprises wetting the fibers of the material with a fluid aqueous medium having a pH between 1.2 and 6.5 and containing a water-insoluble alkali-soluble cellulose ether, a dispersed vat pigment and formaldehyde, drying the textile material in the absence of contact pressure, heating the dried textile material in the absence of contact pressure to cure the formaldehyde, treating the textile material, after said heating step, with an aqueous alkaline solution to reduce the vat pigment to the soluble leuco vat on the textile material, and then treating the textile material with an aqueous solution of a mild oxidizing agent to regenerate the pigment on the textile material.

2. A method as in claim 1, wherein the fibers of the textile material are wetted with the treating medium containing the water-insoluble, alkali-soluble cellulose ether, the dispersed pigment vat, and the formaldehyde, while the material is under tension.

3. A method as in claim 1, wherein the textile material is dried under tension.

4. A method as in claim 1, wherein the formaldehyde is cured and the ether is coagulated by blowing hot air against the textile material.

5. A method as in claim 1, wherein the water-insoluble alkali-soluble cellulose ether is a hydroxyethyl cellulose.

6. A method as in claim 1, wherein the aqueous treating medium contains, by weight, from 0.5 to 1.5% of the water-insoluble, alkali-soluble cellulose ether, from 0.01 to 5% of the dispersed pigment vat, and from 1 to 5% of formaldehyde.

7. A method as in claim 1, wherein the regenerated cellulose textile material is a woven fabric.

8. An aqueous treating medium for stabilizing textile materials predominantly of regenerated cellulose against progressive dimensional shrinkage on repeated laundering and against pulling out in response to tension applied subsequently to the stabilization while simultaneously apply-

ing color to the material, said medium having a pH of from 1.2 to 6.5 and containing from 0.5 to 1.5% by weight of a water-insoluble, alkali-soluble hydroxyethyl cellulose, from 0.01 to 5% by weight of a dispersed pigment vat, from 1 to 5% by weight of formaldehyde, from 0.5 to 1.5% by weight of a self-emulsifiable, substance of wax-like consistency as plasticizer, and from 1.7 to 2.9% by weight of sulfuric acid.

LESLIE L. WALMSLEY.

RAYMOND E. SMITH.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,591,922	Karplus	July 6, 1926
1,710,007	Pfeffer	Apr. 23, 1929
1,744,140	Pfeffer	Jan. 21, 1930
1,816,973	Kantorowicz	Aug. 4, 1931
2,107,852	Bolton	Feb. 8, 1938
2,108,520	Wolf	Feb. 15, 1938
2,205,120	Heberlein	June 18, 1940
2,311,080	Pinkney	Feb. 16, 1943
2,441,859	Weisberg	May 18, 1948

OTHER REFERENCES

Rayon Textile Monthly for January 1945, pages 15 79 (25)-82 (28), article by D. M. Martin.