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METHOD OF TREATING RESIN IMPREGNATED FIBROUS WEBS TO PREVENT DISCOLORATION AND RESULTING COLOR STABILIZED WEBS

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This invention relates to methods for treating resin impregnated fibrous webs in order to stabilize the webs against discoloration and to improved fibrous webs obtained by such treating methods. More particularly, it is concerned with (1) processes for treating textile fabrics which have thereon a permanent finish comprising a cured acetone-formaldehyde resin in order to protect the finished fabrics against discoloration when stored or heated subsequent to exposure to light, and with (2) resulting treated fabrics which possess improved color stability.

It is common practice in the textile industry to apply resin forming materials to textiles or other fibrous webs and to polymerize the applied resin materials in situ on the webs in order to create permanent finishes thereon which impart desired permanent effects to the webs. One of the important, known methods of this type for permanent finishing of fabrics involves the formation of a permanent finish comprising an acetone-formaldehyde resin in the fabric. Thus, as disclosed in U.S. Patent 2,711,971, by applying a low molecular weight condensation product of acetone and formaldehyde to textiles and then subjecting the resulting materials to suitable processing conditions to polymerize the condensation product in situ, durable finishes providing improved dimensional stability and improved fastness to washing of mechanical effects, such as glazing, embossing, beetling, schreinering, pleating and the like can be obtained, particularly with textiles which are formed of cellulosic fibers.

One of the disadvantages of textile materials finished with acetone-formaldehyde resins, is the tendency of the fabric to become badly discolored when stored or heated subsequent to exposure to light. The discoloration cannot then be removed by washing in water or a detergent solution such as soap and where it occurs on a printed fabric with a substantial white area, or an unprinted fabric which is white or dyed to a pale shade, it is regarded as a serious fault.

After the textile has been heated to insolubilize the resin, it is customary to wash it to remove all soluble material and no matter how thorough the washing treatment given, the liability to serious discoloration as a result of exposure to light followed by storage or heating, is still present. It thus appears that some substance which is activated by light subsequently produces a highly colored compound after a period of storage at ordinary temperatures or more rapidly at high temperatures and that this substance is insoluble.

The tendency of acetone-formaldehyde resin finished fabrics to discolor as explained above, has seriously limited the extent of use of acetone-formaldehyde resins in the treatment of textiles, particularly those which are white or not highly colored. Accordingly, considerable research and experimentation has been devoted in the past toward discovering means by which this troublesome discoloration can be mitigated or completely eliminated, since the acetone-formaldehyde resin finishes are otherwise highly attractive as textile finishing agents.

A principal object of this invention is the provision of new improvements in the finishing of textiles or other

fibrous webs with acetone-formaldehyde resins which eliminate the tendency of resulting webs to become discolored as a result of exposure to light followed by storage or heating.

Another object is the provision of a method by which textiles which have a permanent finish comprising an acetone-formaldehyde resin thereon may be treated to eliminate discoloration tendencies normally exhibited by such resin finished textiles without otherwise adversely affecting the desired qualities and properties of the textile, and without substantially increasing the ultimate cost of the treated product.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description gievn hereinafter; it should be understood, however, that the detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

These objects are accomplished according to the present invention by subjecting a fibrous web which has previously been treated to form thereon a permanent finish comprising a cured acetone-formaldehyde resin to mild oxidizing action while the web is substantially saturated with an aqueous medium, thereafter freeing the resulting web of all oxidizing materials and drying the web. The aftertreatment with an oxidizing agent of the fibrous webs which have been finished with acetone-formaldehyde resins in known manner operates in some fashion apparently to remove or destroy the color forming bodies responsible for the discoloration normally experienced in the storage or heating of this type of finished web after exposure to light. Consequently, the oxidizing agent aftertreatment produces finished textiles which may be stored or heated subsequent to exposure to light without any appreciable formation of brown discoloration.

After the aqueous solution having mild oxidizing action has been applied to the fabric, the saturated fabric is subjected to time-temperature conditions which are sufficient to obtain the desired action of removal or destruction of the color forming materials in the resin finished fabric. The particular oxidizing agent employed and its concentration in the aqueous medium applied to the fabric will affect the time-temperature conditions required to produce the desired result. Using an alkaline solution containing 0.3% active hydrogen peroxide, time-temperature conditions of at least ten minutes at 80° C. are representative of conditions which can produce the desired results.

After the mild oxidation treatment, the fabric is freed of the oxidizing agent, preferably by rinsing in water, and also, where the oxidation treatment has been carried out in the preferred manner using an alkaline solution of the oxidizing agent, the fabric may be given a rinse in weak acid. Finally, after the fabric is thoroughly cleaned by water washing and rinsing, it is dried to obtain the final color-stable resin-finished article.

A more complete understanding of the color-stabilized resin-finished fibrous webs of this invention and the processes used for obtaining them, may be had by reference to the following examples of actual operations in accordance with the invention. In these examples, all parts and percentages are by weight unless otherwise specified.

Example I

A low molecular weight, water-soluble, resin-forming condensation product is prepared by reacting together one volume of acetone and four volumes of commercial formalin containing 37% by weight of formaldehyde in

the presence of 0.6 gram of sodium hydroxide, per 100 cc. of reaction mixture, at a temperature about 25% C. for about six hours. The mixture has a pH between 10 and 11 and a specific gravity of 1.04 when the reaction starts. The reaction is spontaneous and as it proceeds the mixture increases in specific gravity so that when the reaction is completed, a specific gravity of 1.12 is reached. At this point the reaction stops and the mixture is a syrupy solution only faintly alkaline having a pH between 7 and 8 containing an acetone-formaldehyde condensation product of low molecular weight and having a specific gravity of 1.12.

A textile finishing bath is prepared by mixing together 224 parts of the above prepared acetone-formaldehyde condensate, 40 parts of anhydrous sodium carbonate, 5 parts of paraffin wax emulsion, 2.5 parts of a textile softening agent ("Ceranine FE"), 1.8 parts of a wetting agent ("Lissapol N"), and sufficient water to make 1060 parts.

A bleached and mercerized cotton cambric of gray construction 80 x 80, 30s/30s is impregnated with the aqueous treating solution by immersing the cotton fabric in the solution which is at approximately room temperature. The fabric is then withdrawn from the treating bath and the excess fluid is squeezed therefrom. Next the fabric is dried and heat treated for two minutes at 143° C. and washed in water to remove soluble matter.

The washed, resin-treated fabric is now subjected to a mild oxidizing action by being immersed for ten minutes at a temperature of 80° C. in a solution containing 0.3% by weight of hydrogen peroxide and 1% by weight of sodium silicate. After this mild alkaline oxidation treatment, the fabric is rinsed, soured in weak acid, again thoroughly rinsed in water and finally dried.

The resulting fabric, after exposure to light and storage, shows no tendency to become discolored, whereas similarly treated fabric which has not been subjected to the mild oxidation treatment prior to exposure and storage under similar conditions, becomes markedly brown in color.

The above mentioned material "Ceranine FE" is a textile softening agent marketed by Sandoz Products Limited and "Lissapol N" is a non-ionic wetting agent marketed by Imperial Chemical Industries Limited.

Example II

A textile finishing bath is prepared by mixing together 280 parts of the acetone-formaldehyde condensate as prepared in Example I, 40 parts of anhydrous sodium carbonate, 7.5 parts of paraffin wax emulsion, 2.5 parts of "Ceranine FE" and 1.8 parts of "Lissapol N" and sufficient water to make 1068 parts.

A bleached and mercerised cotton poplin cloth of gray construction 144 x 76, 2/100s x 2/100s is impregnated by immersing in a bath of the foregoing treating solution. The cloth is then withdrawn from the treating bath and excess liquid squeezed therefrom. Following this, the cloth is dried and then heat treated for four minutes at 132° C., after which it is washed in water, rinsed in 2% acetic acid solution, and washed in water until free from acid.

Next, the cloth is subjected to a mild oxidation after-treatment by steeping at 17° C. for one hour in sodium hypochlorite solution containing 4 parts of available chlorine per 1000 parts of solution. Finally, the oxidation treated fabric is rinsed in water, rinsed in 2% acetic acid, again thoroughly rinsed in water and then finally dried.

There is obtained cotton poplin cloth having high dimensional stability because of the acetone-formaldehyde resin formed in the cloth and which at the same time exhibits substantially no discoloration after exposure to light and followed by storage for several weeks. In contrast, the same fabric treated with the resin containing impregnating solution, but not to the mild oxidation after-treatment, is found to acquire a very deep brown coloration after the same exposure to light and storage conditions.

Example III

A textile treating solution is prepared by mixing together at room temperature 224 parts of the acetone-formaldehyde condensation product of Example I, 40 parts of anhydrous sodium carbonate, and 1.8 parts of "Lissapol N" and sufficient water to make 1060 parts.

A bleached and mercerized cotton poplin of gray construction 122 x 72, 36s/32s is impregnated with the solution by immersing the cotton fabric in a bath of the solution, then removing the cloth from the bath and squeezing excess solution therefrom. This solution saturated fabric is then dried at 93° C. and is heat treated for five minutes at 127° C. to cure the acetone-formaldehyde condensation product and permanently set it in the product. After the heat curing, the resin finished fabric is washed in water, rinsed in 2% acetic acid at 70° C. and again washed in water until free from acid.

A section of the fabric as prepared above is dried and is then exposed to the artificial light source of the "Fadeometer" for a period of time sufficient to produce perceptible fading of the American Standard L3. The light exposed cutting is then stored in the dark for a period of six weeks at room temperature. It is found by examination of the fabric after such light exposure and storage that the fabric is very srongly discolored brown. The degree of discoloration will be greater or lesser with increased or decreased periods of storage.

The remaining section of the resin-finished fabric, is after-treated for thirty minutes at 80° C. in an aqueous solution containing 0.3% hydrogen peroxide, 0.5% sodium silicate, and 0.035% magnesium sulphate crystals. After this mild, alkaline, oxidation treatment, the cloth is rinsed in water, rinsed in 2% acetic acid, again rinsed in water until free of acid, and finally dried at room temperature.

This fabric which has been subjected to the mild oxidation treatment, is exposed to light and then stored for six weeks in the same manner as the section of fabric not given the oxidation treatment, after which it is given careful examination for any evidence of discoloration. It is found that there is no evidence of browning or other discoloring of the fabric and it possesses an appearance substantially identical to that which it possessed prior to the light exposure and storage. Even with increased periods of storage no discoloration becomes apparent.

Example IV

A textile treating solution is prepared by mixing together at room temperature 280 parts of the acetone-formaldehyde product of Example I, 40 parts of anhydrous sodium carbonate and 1.8 parts of "Lissapol N" and sufficient water to make 1068 parts.

A bleached furnishing cotton of grey construction 52 x 40, 18s/7s is impregnated with the above solution by the procedure described in Example III.

A mild alkaline oxidation solution is prepared by dissolving 5 parts of sodium percarbonate in 1000 parts of water and heating the solution to 85° C. The resin finished fabric as above obtained is then immersed in the mild oxidation bath and held there for thirty minutes. Then, the cloth is withdrawn from the bath, thoroughly washed in water, rinsed in 2% acetic acid solution, washed until free of acid, and finally dried.

After exposure to light and subsequent storage, the fabric shows no discoloration. In comparison, marked brown discoloration occurs on the same resin finished fabric subjected to similar conditions of light exposure and storage when the fabric is not given the mild oxidation treatment as described.

The formation of a cured acetone-formaldehyde resin finish in a fibrous web obviously constitutes the first stage of the operations contemplated by this invention. Various

forms of low molecular weight acetone-formaldehyde resin forming condensates useful in treatment and finishing of textiles are known. The after-treatment oxidation procedures for improvement of the color as described herein, accordingly, are contemplated for use with all fibrous webs or other textiles which comprise a permanent finish of such acetone-formaldehyde cured resins. Particularly useful in forming such resin treated fabrics are the acetone-formaldehyde precondensates formed in aqueous medium at temperatures below 50° C. and under alkaline conditions to create products having a specific gravity in the range of 1.07 and 1.12 that are stable and neutral in acid condition and contain 1 to 4 methylol groups per mol of acetone. Further detail of the method of producing such resin forming condensates and the procedures used in treating textiles therewith can be had by reference to the aforementioned U.S. Patent 2,711,971.

A wide variety of oxidizing agents may be used in carrying out the after-treatment oxidizing operations of this invention. Broadly the suitable oxidizing agents may be classified as those which are active in neutral or alkaline aqueous solutions. Particularly useful in carrying out the oxidation procedure of the invention are those which possess useful activity within the range pH 9–pH 11. The preferred oxidizing agents of this class include hydrogen peroxide, alkali metal peroxides, alkali metal percarbonates, alkali metal perborates, alkali metal hypochlorites, alkali metal chlorites, and alkali metal persufates, particuarly the sodium compounds. These oxidizing agents are preferred because they do not present any serious safety hazards, and are moreover commonly used in the bleaching of textile materials. Thus they can be safely used upon the resin finished fabrics to produce the color stabilization as described.

In carrying out the mild oxidation step, the fabric being treated is substantially saturated with the aqueous solution comprising the oxidizing agent. This can be accomplished by immersing the fabric in the oxidizing solution and retaining it in the solution at the temperature and time conditions necessary to complete the oxidation action. However, the resin finished fabric can be saturated with the oxidizing agent solution in other ways, including spraying, padding, roller impregnating or the like. The impregnated fabric can be pressed free of excess oxidizing agent solution and steamed or can be stored in the wet state for a time required to allow the necessary action to take place. Similarly, the fabric may be washed in a solution of the oxidizing agent or passed through a plurality of solutions of the oxidizing agent contained in successive tanks.

The concentration of the aqueous solution of the oxidizing agent may be varied. Since the oxidation should be mild so as to prevent detrimental effects upon the fibrous structure of the web, concentrated solutions are not recommended. The preferred concentration of the oxidizing solution will depend to some extent upon the particular agent employed, but solutions containing between about 0.02% to 2% available oxygen have been found to give most desirable results. Preferably, the oxidizing agent solution should possess a pH on the alkaline side, i.e., above 7, and if the oxidizing agent upon solution in water does not provide an alkaline solution, suitable alkaline agents such as alkali metal hydroxides, carbonates, silicates or the like may be added to the solution in sufficient amount to provide the desired alkalinity.

It is well known that the activity of many oxidizing solutions is dependent upon the pH of the solutions. This can well be illustrated by considering hydrogen peroxide. At a low pH, activity is low and a solution of hydrogen peroxide at pH 7 would be much too slow in reaction rate for the purpose of this invention. On the other hand, at a high pH of 12 or above, activity is so great that decomposition takes place with formation of gaseous oxygen which is thus lost and can play no useful part in treatment of fabrics immersed in such a bath.

It is therefore, necessary to compromise between solutions of low and high activity, and this is done by the addition of alkaline buffers to the treating solution in order to provide conditions where the hydrogen peroxide will react fairly rapidly in bringing about the desired reactions on the cloth without being so rapid that decomposition occurs resulting in loss of much of the total oxidizing power of the solution. The activity of oxidizing solutions is also dependent on temperature, and here again, it is necessary to compromise between low temperatures where activity is very low and very high temperatures where decomposition to gaseous oxygen takes place.

After the saturation of the resin containing fabric with the oxidizing agent solution, sufficient time must be allowed for the required action by the solution to take place upon the fabric. Elevated temperatures increase the speed of the reaction so that shorter times are required with higher treatment temperatures and vice versa. On the other hand, elevated temperatures as stated above may result in some decomposition of the active oxidizing agent. Accordingly, it is recommended that the oxidizing treatment be carried out at a temperature between about 15 and 100° C. depending on the nature of the oxidizing agent. With the preferred oxidizing agents, times between 10 to 60 minutes are usually sufficient to obtain the necessary action in producing the color stabilization. With the mild oxidizing solutions, longer times may be used but usually do not produce any further improvement in results.

After the oxidation treatment, the fabric is freed of any oxidizing agent, preferably by thorough rinsing in water. This may be followed, if desired, by rinsing with a weak acid solution, such as a 2% acetic acid solution, followed by a further water rinsing until the treated fabric is free of acid or other water-soluble materials. Finally, the fabric is dried and may then be employed for all uses for which resin finish textiles are known to be useful.

The operations as above described are particularly useful for webs comprising cellulosic fibers. This includes cotton, viscose rayon, linen and the like. The invention is also effective in treatment of webs composed partly of fibers of cellulosic origin and partly of other natural or synthetic fibers, e.g., polyamide fibers, polyester, polyvinyl alcohol fibers, polyacrylonitrile fibers and the like. The fibrous webs may be in the form of non-woven fabrics, woven fabrics, knitted fabrics or any other similar sheet-like material made up basically of thread-like fibrous structures, whether in the form of a textile or other forms.

No special equipment is required for applying the treating compositions or carrying out the operational steps of the invention. Established padding or impregnation procedures may be used in the various impregnating or saturating steps of the new methods and these may be carried out in standard textile processing equipment. Likewise, the heating and/or drying of the fibrous webs following saturation with the various treatment solutions may be carried out on standard textile handling apparatus. Furthermore, the particular fibrous web treating operations encompassed by the invention, may, if desired, be applied in conjunction with other textile processing procedures, such as water-proofing, calendering, embossing, pressing and the like. Similarly, known finishing agents may be applied at suitable stages in the new methods, and this includes application of such agents as sizing agents, softeners, lubricating materials, water-repellent agents, mothproofing agents, mildew-proofing agents, dyes, pigments and the like.

Having provided a complete description of the invention in such manner as to distinguish it from other inventions and from what is old, and having provided a description of the best mode contemplated of carrying out the invention, the scope of patent protection to be granted the invention is defined by the following claims.

We claim:

1. A process of treating a cotton fabric finished with a cured acetone-formaldehyde resin to protect the web against discoloration during storage following exposure to light which comprises impregnating bleached cotton fabric with an aqueous solution comprising an acetone-formaldehyde resin, drying the impregnated fabric, heating the dried fabric in air at a temperature between about 127° to 143° C. to cure the resin and set it upon the fabric, threafter immersing the fabric in an aqueous alkaline hydrogen peroxide solution containing about 0.02 to 2.0 percent by weight of available oxygen having a temperature between about 15° and 100° C. for between about 10 to 60 minutes, removing the fabric from said hydrogen peroxide solution, washing the fabric free of oxidizing material and drying the treated fabric.

2. A cotton fabric having thereon cured acetone-formaldehyde resin finish, which fabric will not discolor during storage following exposure to light, said fabric having been prepared by the process of claim 1.

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