

1

3,165,374

PROCESS OF PARTIALLY METHYLENATING
CELLULOSE TEXTILES

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No Drawing. Original application Sept. 16, 1959, Ser. No. 838,823. Divided and this application Feb. 17, 1961, Ser. No. 94,111

3 Claims. (Cl. 8—116.4)

This invention relates to a catalyst system for the curing of fabric which has been treated with aldehydic type textile finishing agents and also to an improved method for imparting durable finish effects to fabrics using aldehydic type finishing agents.

As used herein the term "aldehydic" type textile finishing agents contemplates the use of any of the following types of materials as finishing agents:

- (a) Free aldehydes per se,
- (b) Materials or compounds, which upon heating, especially in the presence of acid, liberate free aldehydes,
- (c) Thermosetting or thermoreactive aldehyde resins which either crosslink with hydroxylated polymers under acid conditions to form a water insoluble reaction product or which condense or polymerize, in the presence of acid, to form water insoluble polymers.

Hereinafter, type (a) and (b) materials will sometimes be referred to as methylenating agents and type (c) materials will be referred to collectively as aldehyde resins.

Aldehydes and dialdehydes such as formaldehyde, glyoxal, acetaldehyde, chloral, benzaldehyde, furfural and the like are some of the typical aldehydes which, per se, are useful fabric finishing agents.

Some typical compounds which upon heating, either alone or in the presence of acids, will release or liberate aldehydes, and which are useful as finishing agents are: the methylol-ketones, para-formaldehyde, trioxane, and the like.

Some typical thermosetting aldehyde resins which are useful as fabric finishing agents are the methylol ureas, the methylated methylol ureas, the methylol melamines, the methylated methylol melamines, etc.

Some typical reactive aldehyde resins which are useful as fabric finishing agents are the lower alkylene methylol ureas (e.g., dimethylol ethylene urea, tetramethylol diacetylene urea, the methylol triazones, and their methylated derivatives) and the related compounds having one or more hydroxy group substituted for hydrogen atoms in the alkylene chain (e.g., dihydroxy dimethylol ethylene urea).

All such aldehydic materials, and many other related materials, have heretofore been used or proposed for use as fabric finishing agents for imparting many different types of finishing effects to all kinds of textile fabrics and textile products (of animal, vegetable and synthetic origin). All such aldehyde finishing agents are useful in connection with the present invention, provided they are sufficiently stable at room temperature and under acid pH conditions to enable the material to be applied to the fabric co-jointly with the catalyst without precipitating insolubilized resins or the like.

In all processes where aldehydic compounds are employed as finishing agents, the fabric, at some stage after the finishing agent has been applied to it, is cured by heating. The curing is carried out in the presence of a catalyst to accelerate the reaction or polymerization.

Depending on the type of aldehydic finishing agent employed, the curing treatment will either cause the finishing agent itself or aldehyde released from the finishing agent to react with the fabric, or in the case of the thermoset-

2

ting aldehyde resins, the cure will cause the resin to primarily polymerize to a water insoluble stage although some reaction with the fabric may also occur.

Heretofore many different acidic substances have been employed as curing catalysts. However, all such substances can be generally characterized as falling into two distinct categories, (1) acids per se, and (2) "potentially acid" substances; the latter being materials which are almost neutral or in some cases even alkaline in aqueous solution and which, upon heating to temperature above about 125° C., form an acid curing environment by releasing a strongly acidic material. Hereinafter, when I employ the term "conventional" catalysts, it is intended to cover both the aforementioned types of acidic catalytic materials.

With the straight acid catalysts, the pH of the impregnating bath and that of the cured fabric are approximately the same. This however, will depend somewhat on the buffering action of the finishing agent. With the potentially acid catalysts, the pH of the cured fabric will be lower than that of the impregnating bath.

The use of conventional catalysts gives rise to certain objectionable features, not only in the processing operations but also in the properties of the finished fabric.

Productwise, one of the most significant objections attributed to the use of conventional catalysts is the loss of strength due to hydrolysis or acid degradation of the fabric. Strength losses due to hydrolysis to be differentiated from an apparent strength losses due to "embrittlement" or the loading of the fabric with hardened resins. Hydrolysis involves changing the chemical nature of the fabric and can be caused by the action of the catalyst. The extent of hydrolysis is governed by several factors including the type of catalyst, its concentration, and the curing conditions (time and temperature) employed.

Even with the milder acids such as tartaric acid, the catalyst concentration is an important factor and must be regulated precisely; however, strength losses due to hydrolysis can be controlled by carefully curing the fabric under relatively mild curing conditions and by employing relatively low concentrations of the catalyst (0.25% to 1%). However, with the milder acids, it is usually necessary to employ higher temperature cures in order to obtain a satisfactory degree of resilience and durability in the finish effect. It is, therefore, difficult, if not impossible, to obtain a desired degree of resilience and durability without altering the curing conditions or catalyst concentration to an extent where objectionable strength losses will occur through fabric degradation.

For a given finishing agent, the same factors (catalyst type, catalyst concentration, and curing conditions) will also influence and affect other properties of the finished fabric, especially hand, drapeability, resilience, durability of the finish effect, wash and wear properties, etc. There is no absolute correlation as to how the various properties will be influenced. Generally speaking, however, factors which would tend to increase the resilience or durability and wash and wear properties also tend to adversely affect the strength—both tear and tensile. It is exceedingly difficult to achieve a desirable balance of properties, i.e., a highly durable and resilient fabric with good wash and wear properties, without unduly weakening of the fabric. Conversely, in order to strengthen the fabric by minimizing strength losses, the various factors must be adjusted in such a way that inevitably the resiliency and the wash and wear durability of the finish are reduced.

As previously noted, the hand and drapeability of the fabric can also be influenced and affected by the aforesaid factors. However, the variations in these properties are not of as much significance as strength, resilience, durability, and wash and wear properties, since corrective

modifications can be effected by various after treatments, e.g., the addition of softeners, passing the fabric through button breakers, and the like.

If a relatively strong conventional acid catalyst such as hydrochloric acid is used as the curing agent, the catalyst must be used in very small and critical amounts, e.g., by applying the catalyst in concentrations which will deposit on the fabric less than 0.1% of the catalyst based on the fabric weight. In such cases, only a slight increase in the concentration has a very significant effect, and strength losses due to degradation become very noticeable. Because the maximum permissible catalyst concentration is very low, it is almost impossible, in full scale commercial runs, to uniformly distribute the catalyst in the critical concentration needed for efficient curing and the end results accordingly are quite unpredictable; some portions of the fabric will be highly hydrolyzed and the fabric exceedingly weakened.

With the weaker acids such as succinic acid, in order to fully harden or set the resin or cause the aldehyde to react with the fabric so as to enhance the durability, resilience, wash and wear, etc., it is necessary to employ either very high temperature cures or prolonged heating at somewhat lower temperatures. However, in either case hydrolysis will occur to an objectionable degree when the "harder" cures are employed.

Similarly, with some types of aldehydic finishing agents, especially with methylenating agents such as formaldehyde and ketone-aldehyde precondensates the conventional catalysts were totally unsatisfactory even though extreme efforts were made to regulate the curing conditions. It was practically impossible to obtain uniform properties throughout the fabric; some portions would be objectionably tendered and in other portions the degradation would be less perceptible; the resilience, durability and other properties will also be found to vary quite unpredictably. Hence, despite the known desirability using formaldehyde and other methylenating agents as finishing agents, the difficulty of effectively controlling the process are so great and unpredictable that until the advent of my special catalyst system methylenating agents, per se, were not used in commercial fabric finishing operations.

In order to overcome the foregoing objections, it is one of the objects of this invention to provide a catalyst system and finishing process which is useful in the curing of finishes imparted by all types of aldehydic finishing agents, and which will impart a highly desirable balance of properties by minimizing strength losses in fabrics having high resiliency and high durability.

It is another object of this invention to provide a catalyst system and finishing process which will enable certain aldehydic materials to be used as finishing agents—particularly methylenating agents—which heretofore could not be used effectively.

Still another object of the invention is to provide a catalyst system and finishing process which can be used in such concentrations so that minor variations thereof, as inevitably occur in making up the pad bath and in applying the catalyst to the fabric, will not significantly affect the properties of the finished fabric.

An additional object of this invention is to provide a catalyst system and finishing process which will enable aldehydic finishing agents to be efficiently and effectively cured under milder curing conditions than can be employed with conventional catalysts and at the same time obtain desirable enhancement of other properties.

Other objects and advantages of the invention will appear from the ensuing description and examples.

According to the invention, the foregoing objectives are achieved by a catalyst system comprising an acid component and an acid salt component, which components, under the heating employed to cure the fabric carrying the finishing agent, are capable of forming in the fabric a residue which imparts to the fabric a lower acidity

(higher pH) than that of the acid-acid salt combination prior to heating.

With respect to the acid component for use in the catalyst system of the present invention, it may be an organic or inorganic acid or acid anhydride such as maleic, tartaric, hydrochloric, phosphoric, citric, itaconic, succinic, and the like. I prefer, however, to employ polybasic acids, and especially non-volatile organic acids having an acidity at least equal to 0.1% citric acid solution since catalyst systems prepared therefrom in accordance with the present invention will develop the desired degree of acidity for efficient finishing and will not, under the finishing conditions for treating the fabric, develop acidity to a degree which will seriously degrade the fabric being treated. Acids which are weakly acidic such as boric acid, are not well suited for purposes of this invention as they do not permit efficient finishing within the time and temperature relationship in equipment used for commercial finishing. Weak acids which are readily volatile under the processing conditions, e.g., formic acid, cannot be effectively used as they will be driven off before a satisfactory cure can be effected. Other highly desirable characteristics of the acid component are that it should be one which with the acid salt component, will not form a water insoluble residue during the heating to cure the fabric. In general, the useful acids are those which will provide a pH in the impregnating bath of from about 1.5 to 5.5.

The preferred acid salts for use in the catalyst system of this invention are the metal salts of either organic or inorganic acids of the Lewis acid type (i.e., an electron acceptor) and especially the polyvalent metal salts of such acids. The Lewis acid salts of monovalent metals with polybasic acids can also be used effectively. Where white goods are to be finished, I prefer to employ those salts of the Lewis acid type which form substantially colorless aqueous solutions. Examples of acid salts which have been found to be especially useful are magnesium nitrate, strontium nitrate, aluminum chloride, zinc chloride, sodium bisulfate, zirconium oxychloride, aluminum acetate, chromium acetate, and the like.

In general, the useful acid-acid salt combinations are those which, when applied to a fabric as a pure aqueous solution of the catalyst components and heated to temperatures of about 250 to 300° F., will form in the fabric a residue (preferably a water soluble residue) which will impart to the fabric a pH that is at least 2, and preferably about 2.3 or more, higher than the pH of the pure aqueous solution of the catalyst components.

Where one or more of these preferred acid salts are used in combination with the preferred acids, the catalyst system will permit efficient finishing of the fabric so as to impart a highly resilient, durable finish with good wash and wear properties and with a minimized loss in strength.

It is preferred to apply to the finishing agent and the catalyst system to the fabric to be treated from the same impregnating bath, as only a single operation is thereby required. It is also possible to apply the finishing agent and the individual catalyst components in separate operations and in any desired sequence—such multistep applications are also well known in the art.

Where the finishing agent and the catalyst system are applied to the fabric at about 60% to 70% pick-up, it is possible to employ impregnating baths in which the finishing agent can be present in quantities as great as 35% of the total weight of the bath, and in quantities as low as a fraction of 1%. Generally, where the finishing agent constitutes about 3–12% of the bath weight and exerts only a mild buffering action, the catalyst system according to the invention should constitute from 0.5 to 3.0% of the bath weight, and where it is desired to increase or decrease the amount of the finishing agent or where the finishing agent is known to exert a strong buffering action (e.g., the ketone-aldehyde precondensates), the total cata-

5

lyst weight should be adjusted accordingly. The bath can if desired also contain buffers and other conventional processing aids or finishing materials such as softeners, wetting agents, tinting agents, and the like.

The relative ratio of the acid component to the acid salt component can vary over a wide range provided that the combination is one which will develop, under the curing conditions involved, an acidity which is sufficient to enable the finish effect to be fixed efficiently, and do this without objectionably degrading the fabric. To prevent objectionable fabric degradation, the combination should be one which alone and under the heating conditions involved, will form a residue in fabric which will impart thereto a pH which is at least 2 points higher than that of the catalyst components impure aqueous solution. Combinations of many different acids with many different types of Lewis acid salts in many widely varying ratios will be found to give this inverse pH relationship and the following illustrations will serve to show particularly useful combinations which have been found to give an optimum balance of properties when used for curing cellulose with different aldehydic finishing agents and fabrics.

Where the catalyst system is intended to be used for the finishing of natural cellulose fabric with formaldehyde or with aldehyde liberating materials which do not exert strong buffering action so as to effect a partial methylation of the cellulose, I prefer to employ those systems which have the acidity characteristics below 200° F. which will not appreciably catalyze the methylenation reaction and which develop an acid methylenating environment at temperatures between 200° and 400° F. Catalysts having acidity characteristics approximating those formed by the combination citric acid (2 pounds), strontium nitrate (3 pounds) and magnesium nitrate hexahydrate (4 pounds) in impregnating baths containing about 3 to 10% of the finishing agent made up to 100 gal. with water (i.e., the total catalyst system is approximately 1% of the weight of the bath and is sometimes hereinafter referred to as the 2-3-4 catalyst), have been found especially useful.

Where the catalyst system is intended to be used for the finishing of natural cellulose fabric or regenerated cellulose fabric with aldehyde resins in bath concentrations of about 3 to 12%, the 2-3-4 catalyst can be effectively used and so too can a catalyst formed by the combination of citric acid (2 pounds) and magnesium nitrate hexahydrate (7 pounds). This is sometimes hereinafter referred to as the 2-7 catalyst.

Where the catalyst system is intended to be used for the finishing of regenerated cellulose fabric with a methylenating type aldehydic finishing agent, I prefer to employ those systems which have the acidity characteristics approximating those formed by the combination citric acid (5 pounds) and magnesium nitrate hexahydrate (12 pounds) in an impregnating bath made up to 100 gal. with water (i.e., the total catalyst system is approximately 2% of the weight of the bath and is sometimes hereinafter referred to as the 5-12 catalyst), have been found especially useful.

Any of the foregoing catalyst systems (i.e., the 2-3-4, the 2-7, and the 5-12 catalysts) exhibit rather similar acidity characteristics at temperatures ranging from room temperature up to where the fabric itself is heated to temperatures as high as 400° F. Curing by infra-red heating, where the fabric is momentarily exposed to very high temperatures, can also be used in conjunction with the process and catalyst system of this invention. In such cases, the fabric itself does not reach the temperature of the heating means.

When the finishing agent is applied from a pad bath to give 60 to 70% pick-up, I prefer to employ the catalyst system of this invention in concentrations which constitute from about ½ to 3% of the bath weight, nevertheless, it is possible by varying other factors such as the solution pick-up or the curing conditions to employ baths

6

in which the catalyst constitutes higher or lower percentages of the bath weight. However, where the total quantity of catalyst applied to the fabric is appreciably in excess of about 10% of the fabric weight there is a strong possibility of objectionably degrading the fabric.

The following examples will serve to illustrate in greater detail some of the various features of the invention. While the following examples are primarily concerned with treating cellulose to impart an all-over non-mechanical finish effect to the fabric, the process and catalyst system should not be deemed to be limited thereby. Both the method and the catalyst system can be effectively utilized in any other type of fabric finishing process where it is necessary to cure one or more aldehydic finishing agents which have been applied to the fabric. Such other processes may involve localized or all-over application of the finishing agent, and if desired, the process may also involve mechanically treating the fabric to alter the shape and relative disposition of the yarns—as for example by calendaring, pleating, ruffling, and the like.

Example 1

A pure cotton (80 x 80, running 4.00 yds./lb.) was padded through an impregnating bath having the following formulation:

	Percent bath weight
37% formaldehyde -----	12.5
Citric acid -----	.25
Strontium nitrate -----	.38
Magnesium nitrate hexahydrate -----	.50
Water -----	Balance

The solution pick-up was adjusted to 60% based on the fabric weight. The fabric was dried and thereafter cured by heating for 3 minutes at 300° F. The resulting wash and wear finish was highly durable and resilient; and the strength losses were considerably lower than losses previously encountered using formaldehyde as a finishing agent, particularly in view of the high durability of the wash and wear properties.

Example 2

Example 1 was repeated but the strontium nitrate was replaced with 0.38% (additional) magnesium nitrate. The over-all properties of the fabric finished in this way were of a very high order and only slightly inferior to the property balance obtained in Example 1.

Example 3

Example 1 was repeated but the formaldehyde was replaced with approximately 6% dimethylol ethylene urea. Before curing the treated fabric was divided in two sections. One section was cured at 300° F. for 3 minutes, and the other section was cured at 240° F. for 5 minutes. The fabric resilience and wash and wear durability were approximately the same in both sections. The fabric cured at 240° was stronger than the fabric cured at 300°.

Example 4

Example 3 was repeated using the 2-7 catalyst of Example 2 instead of the 2-3-4 catalyst. The results were generally comparable to those obtained in Example 3.

Example 5

Examples 3 and 4 were repeated except that 10% methylated methylol melamine was substituted for the dimethylol ethylene urea and with very similar results. The wash and wear durability and resilience of the fabrics cured at 240° were of about the same order as those cured at 300°; and the fabrics cured at 240° were somewhat stronger.

Example 6

Example 1 was repeated except that 9.5% Rhonite D-12 (a methylol triazone) was substituted for form-

aldehyde. The cured fabric had an excellent balance of properties from the standpoint of strength, resilience and wash and wear durability.

Example 7

Example 1 was repeated using the following formulation for the pad bath and curing at 240° F. for 5 minutes:

	Percent of bath weight
Ketone-aldehyde precondensate	46
Citric acid	1
Strontium nitrate	1.5
Magnesium nitrate hexahydrate	2.0
Water	Balance

(Because of the buffering action and the high concentration of the precondensate, the total catalyst concentration was increased.) The cured fabric had a good over-all balance of properties from the standpoint of strength, resilience and wash and wear durability; and this balance was obtained despite the mild curing conditions employed.

This application is a division of application Serial No. 838,823, filed September 16, 1959, and both cases are continuations in part of earlier filed applications Serial No. 762,934, filed September 24, 1958, now abandoned; Serial No. 804,857, filed April 17, 1959, and Serial No. 804,858, filed April 17, 1959.

I claim:

1. In a process of partially methylenating cellulose textiles involving impregnating the textile with a methylenating agent and thereafter curing the impregnated textile in an acid environment by heating the fabric to temperatures above 250° F. to bring about the reaction of the cellulose and the methylenating agent, the improvement which comprises effecting the cure in the presence of a catalyst that will, upon said heating, form a residue in the textile that will provide the textile with a pH at least two points higher than the pH of a pure aqueous solution of the catalyst.

2. In a process of partially methylenating cotton textile

involving impregnating the cotton with formaldehyde and thereafter curing the impregnated cotton in an acid environment by heating the fabric to temperatures above 250° F. to accelerate the reaction of the cellulose and formaldehyde, the improvement which comprises effecting the cure in the presence of a catalyst that will, upon said heating, form a residue in the textile that will provide the textile with a pH at least two points higher than the pH of a pure aqueous solution of the catalyst, said catalyst being a mixture of 2 parts by weight of citric acid, 3 parts by weight magnesium nitrate hexahydrate and 4 parts by weight strontium nitrate and the total weight of said catalyst comprises from about 0.5 to 3% of the impregnating bath.

3. In a process of partially methylenating regenerated cellulose textile involving impregnating the regenerated cellulose with formaldehyde and thereafter curing the impregnated regenerated cellulose in an acid environment by heating the fabric to temperatures above 250° F. to accelerate the reaction of the cellulose and formaldehyde, the improvement which comprises effecting the cure in the presence of a catalyst that will, upon said heating, form a residue in the textile that will provide the textile with a pH at least two points higher than the pH of a pure aqueous solution of the catalyst, said catalyst being a mixture of 5 parts by weight citric acid and 12 parts by weight magnesium nitrate hexahydrate and the total weight of said catalyst comprises from about 0.5% to 3% of the impregnating bath.

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