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ACETYLATED METHYLOL CARBAMATE FINISHING AGENTS WITH REDUCED FORMALDEHYDE ODOR FOR CELLULOSIC CONTAINING TEXTILE MATERIALS

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ABSTRACT OF THE DISCLOSURE

Finishing agents for fabrics of cellulosic fiber are formed by acetylation of methylol carbamates. The acetoxymethyl agents so formed can be used to produce wash-wear and durable-press cellulosic fabric with little release of formaldehyde during treatment of the fabric.

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to the finishing of textiles composed entirely or in part of cellulose, such as cotton or rayon fabrics. It relates in particular to the finishing processes that give wash-wear or durable-press properties to the textile whereby it has a neat, unwrinkled appearance without ironing or pressing after laundering.

The finishing of cellulosic fabric to impart wash-wear and durable-press properties as usually practiced consists in the application and reaction of an agent on the fabric. It is believed that the agent reacts to form chemical bonds or crosslinks between long, linear cellulose molecules. Agents most commonly used for this finishing are methylol amides formed by the addition of formaldehyde to organic compounds of the amide class. Since the formaldehyde forms the methylol group that reacts with cellulose and since the methylol compound must react with more than one group appendant to the cellulose for the treatment to be effective, the average molar ratio of added formaldehyde to amido compound must be greater than one. Quite commonly the agents are dimethylol compounds, such as, dimethylol ethyleneurea, dimethylol ethyl carbamate or dimethylol ethyltriazone. Some agents are compounds with higher functionality such as trimethylol melamine and tetramethylol acetylenediurea. In addition to the methylol agents themselves, ether derivatives of methylol amides are sometimes used as finishing agents and give similar textile products. Other types of compounds have been used as agents in this type finishing, but because of lower reactivity and higher cost than the methylol amides and their derivatives, they have not achieved more than very limited use.

The methylol amide agents, however, do have some undesirable properties. One is the release of formaldehyde as the methylol amide decomposes on the fabric. This occurs slowly when the fabric contains unreacted agent. The unreacted agent is present at intermediate stages of the finishing treatment, that is between application of the agent and the time it reacts with the cellulose, and after the treatment is complete, in unreacted residues that have not been washed from the fabric. Since formaldehyde is irritating at even low concentrations, fumes from fabric containing unreacted agent can be very objectionable.

The release of formaldehyde is a particularly marked disadvantage in deferred-cure finishing processes for making durable-press garments. In these processes the agent is applied to the fabric but final heating to cause reaction between agent and cellulose is postponed until the fabric has been cut and sewn into garments. The deferred-cure process is effective in permanently setting desired creases and folds in the fabric or garment. It does, however, necessitate the storage and handling of fabric on which unreacted agent is deposited. The formaldehyde released from this fabric is enough to make the deferred-cure process unusable with many agents and in many garment manufacturing plants.

This invention consists of new finishing agents for the introduction of wash-wear and durable-press properties into textiles composed in whole or in part of cellulose. These new agents are characterized by noticeably reduced tendency to release formaldehyde fumes which property makes them particularly suitable for deferred-cure durable-press treatments and other treatments that have unreacted agent on the finished fabric.

The new agents of this invention are prepared from the methylol carbamates previously used as finishing agents by treating them with an acetylating agent such as acetic anhydride. This treatment is believed to convert the methylol carbamates to acetoxymethyl carbamates, that is, the acetate ester of the methylol compound. The ester is more stable than the methylol compound and has, therefore, less tendency to decompose and release formaldehyde. As a result fabric containing the unreacted agent, in processing or after processing, will have noticeably less formaldehyde odor, sometimes none at all.

The advantages of the new agents are obtained with little adverse effects or extra expense. The agents are prepared inexpensively from the methylol compounds by simple methods. Although they are more stable, they react readily. In fact, the reactivity of the acetylated agent appears to be equal to or greater than the reactivity of the methylol compound from which it is derived. The ready reactivity of the acetylated agents is particularly useful in treatments that give highly durable finishes such as those from monocarbamate-formaldehyde adducts. For high durability, the product of reaction between cellulose and the agent must be resistant to hydrolysis. Therefore, ether derivatives of the agent which are chemically similar to the modified cellulose are too inert to react well as finishing agents. Acetylation, however, stabilizes the group with little or no loss in reactivity. Like the methylol compounds, agents of this invention can be designed to give finished fabrics that are not susceptible to damage from hypochlorite bleaching even though this property may require nearly complete reaction of applied agent. Durability of the finish on the fabric is about the same as obtained with the related methylol compound.

In addition to producing lower levels of formaldehyde fumes, the acetylated finishing agents of this invention have the added advantage that they can be applied from organic solvents. Many of the methylol agents are insoluble in solvents other than water. Hence, they usually do not offer a choice of solvents to obtain the durable-press properties.

The finishing agents of this invention are prepared by acetylation of a methylol carbamate compound. The methylol carbamate is prepared from formaldehyde and a carbamate by methods previously known. The carbamate used as starting material must be one that can react with more than one molar equivalent of formaldehyde. This, however, does not mean that the compound must have more than one amido group. Typical amides suitable for the purpose are: monoalkyl carbamates with five or less

carbons, hydroxyalkyl carbamates, alkoxyalkyl carbamates, aminoalkyl carbamates and bis carbamates.

The usual method of preparing methylol carbamates is by allowing the selected carbamate to react with two or more molar equivalents of formaldehyde under alkaline conditions. The reaction is conducted in water or alcohol as solvent, and ordinarily the product is left in solution. For the purpose of this invention, however, the solvent is preferably removed since it can react with the acetylating agent. Removal of solvent is best done by evaporation at only slightly elevated temperatures as excessive heating can cause decomposition or polymerization of the methylol compound.

Acetic anhydride is the preferred reagent for acetylation of the methylol carbamate. Other acetylating agents could be used but would be more expensive or more difficult to handle. It is likely that acylations other than acetylation would be operative in this invention. However, other acylations also seem to offer no advantage but would have disadvantages such as increased costs.

A typical procedure for the preparation of the acetylated agents of this invention follows. A methylol carbamate is prepared by mixing a carbamate with two or more molar equivalents of formaldehyde in an amount of water equal to the weight of reagents and at pH 8–10. The mixture is allowed to stand 16–24 hours for the reaction to proceed. Water is then removed from the solution by heating it to about 40° C. under vacuum. The residue is then mixed with an amount of acetic anhydride slightly greater than one molar equivalent for each methylol group of the methylol carbamate. If the residue from evaporation is too thick a suitable solvent, such as acetic acid, is helpful. Cooling may be required if the acetylation reaction is highly exothermic. In other instances, heating may be required to complete the reaction. After acetylation, excess reagent, byproducts, and solvent are removed by evaporation under vacuum. The residue is now ready for use as a finishing agent.

The new, acetylated finishing agents are applied to fabric by methods quite similar to those commonly used with methylol amide agents. The agent is dissolved in a solvent, usually water, to make a solution of 5–20% concentration. Actual concentration to be used will depend on the particular fabric to be finished and the level of performance desired. An acidic catalyst, preferably an acidic, metallic salt such as zinc nitrate, zinc chloride, or magnesium chloride is employed in the bath. Catalyst concentration will range from 0.4 to 5.0% of hydrated salt in solution with the actual concentration dependent on the particular salt used, the agent concentration, and the treating conditions. The last is a factor since higher concentrations of catalyst are required when treating conditions are limited by the equipment available. In addition to agent and catalyst the solution applied may also contain auxiliary agents, such as softeners, that are commonly used in this type of treatment.

The solution of acetylated finishing agent and catalyst is applied by soaking the fabric to be treated and padding to remove excess solution. The fabric is then dried at a relatively low temperature, for instance at 50–100° C. for 2–10 minutes. When dry, the fabric is heated, or cured, at a higher temperature for a brief period, for instance at 150–200° C. for 0.5–5 minutes. It is at this higher temperature that the reaction of the agent with the cellulose occurs. Between drying and curing, any operations necessary for converting the fabric to a usable textile item may be performed. These acetylated agents allow considerable time to elapse in this period without harm to the final properties of the fabric and without making the fabric difficult to use. Fabric cured several months after drying had properties indistinguishable from those of fabric cured immediately after drying.

The following examples illustrate but do not limit the scope of this invention. In these examples all percentages are by weight.

EXAMPLE 1

A 50% solution of dimethylol methyl carbamate was prepared by methods known to the art. Evaporation of 101 g. of this solution under vacuum at room temperature (23° C.) gave 52 g. residue. This residue is mixed with 92 g. glacial acetic acid, 122 g. acetic anhydride, and three drops of sulfuric acid. After heating 30 minutes at 75–85° C., the supernatant liquid was decanted and evaporated under vacuum at 40° C. The residual acetylated, finishing agent was soluble in water, ethanol, and xylene.

An aqueous solution was made containing 16% of the acetylated product and 0.6% zinc nitrate hexahydrate. A sample of cotton printcloth was padded with this solution and dried in a mechanical convection oven at 60° C. for 7 minutes.

A portion of the above sample was compared with a sample similarly treated with dimethylol methyl carbamate. Both portions of fabric samples were placed in mason jars with small amounts of water, and the jars allowed to stand about 20 hours. The jars were then opened, and the odor of the contents noted. Formaldehyde odor developed by the fabric treated with the acetylated agent was noticeably less than developed by the fabric treated with the methylol agent.

Portions of both fabric samples were stored one month, then were heated at 150° C. for 5 minutes and washed. Both fabric samples had high wrinkle resistance, 138–139° warp wrinkle recovery in the American Association of Textile Chemists and Colorists test for wrinkle resistance, and both fabrics had a neat appearance without ironing. Neither sample of fabric lost more than 5% strength in the AATCC test for chlorine resistance.

From the above example, it is clear that finishing with the acetylated agent gave less potential for development of formaldehyde odor before treatment is complete but gives full development of wash-wear properties in the finished fabric.

EXAMPLE 2

A mixture was made of 60 g. paraformaldehyde, 119 g. methoxyethyl carbamate, and 400 ml. methanol. A small amount of sodium hydroxide in 150 ml. methanol was added. The mixture was warmed until essentially all solid material was dissolved. It was then filtered and refluxed 90 minutes. Methanol was then evaporated under vacuum at 45° C. leaving 175 g. of methylol compound. Acetic anhydride, 225 g., was added to the methylol compound with stirring and cooling. After addition was complete the resultant solution was allowed to stand 16 hours and was heated at 75–85° for 30 minutes. Evaporation under vacuum at 40° left 213 g. of acetylated agent.

The acetylated agent was applied to cotton printcloth from a 24% aqueous solution that also contained 6% magnesium chloride hexahydrate. For comparison, another sample of cotton printcloth was treated with a solution of 20% dimethylol methoxyethyl carbamate and 6% magnesium chloride hexahydrate. Both solutions were padded on the fabrics, and the fabrics dried at 60° C. for 10 minutes.

Dried samples of each fabric were stored in mason jars with a small amount of water for about 20 hours. Fabric treated with the acetylated agent developed a hardly noticeable formaldehyde odor while the fabric treated with the methylol agent developed a pronounced formaldehyde odor.

EXAMPLE 3

A mixture was made of 66 g. paraformaldehyde and 200 ml. methanol. A small amount of potassium hydroxide was dissolved in a few ml. of methanol and 5 drops were added to the paraformaldehyde solution. The mixture was warmed until essentially all solid material was dissolved and then filtered. To this mixture was added 200 ml. methanol containing 75 g. methyl carbamate and then refluxed 60 minutes. Methanol was then evaporated under vacuum at 55–60° C. leaving 118 g. of methylol

compound. Acetic anhydride, 204 g., was added to the methylol compound with stirring and cooling. After addition was complete the resultant solution was heated at 75–85° C. for 30 minutes and then allowed to stand 16 hours. Evaporation under vacuum at 40° C. left 147 g. of acetylated product.

The acetylated agent was applied to cotton printcloth from a 16% aqueous solution that also contained 0.38% zinc nitrate hexahydrate. For comparison, another sample of cotton printcloth was treated with a solution of 10% dimethylol methyl carbamate and 0.38% zinc nitrate hexahydrate. Both solutions were padded on the fabrics, and the fabrics dried at 60° C. for 10 minutes.

Dried samples of each fabric were stored in mason jars with a small amount of water for about 20 hours. Fabric treated with the acetylated agent developed a hardly noticeable formaldehyde odor while the fabric treated with methylol agent developed a pronounced formaldehyde odor.

Portions of both samples were immediately after drying at 60° C. heated at 160° C. for four minutes and washed. Both fabric samples had high wrinkle resistance, 260° warp and filling. Neither sample of fabric lost more than 6% strength in the test for chlorine resistance.

Portions of both fabric samples were stored six weeks and then were heated at 60° C. for four minutes and washed. Both samples had greater than 250° warp and filling wrinkle recovery angles.

Other portions of both fabric samples, after drying were weighed and then stored in sealed mason jars with 10 milliliters of water in a small vial for three weeks. The samples were removed and the mason jars and vials were rinsed collecting all water quantitatively and then the formaldehyde concentration was determined. The fabric treated with the acetylated agent released 30% less formaldehyde than did the methylol agent.

This clearly illustrates that the acetylated finishing agents are as satisfactory for prolonged periods of storage as are the methylolated finishing agents. Yet the acetylated agents have the added advantage of reduced formaldehyde odor.

EXAMPLE 4

A 50% aqueous solution of dimethylol methoxyethyl carbamate was prepared by methods known to the art. Evaporation of 150 g. of this solution under vacuum at room temperature (23° C.) gave 77 g. residue. This residue was mixed with 100 g. acetic anhydride, heated 30 minutes at 75–85° C., then the supernatant liquid was decanted and evaporated under vacuum at 40° C.

An aqueous solution was made containing 23.5% of the acetylated product and 0.4% zinc nitrate hexahydrate. A sample of cotton printcloth was padded with this solution and dried in a mechanical convection oven at 60° C. for 10 minutes.

A portion of the above sample was compared with a sample similarly treated with dimethylol methoxyethyl carbamate. Both portions of fabric samples were placed in mason jars with small amounts of water, and the jars allowed to stand for about 48 hours. The jars were then opened and odor of the contents noted. Formaldehyde odor developed by the fabric treated with the acetylated agent was noticeably less than that developed by the fabric treated with the methylol agent.

Portions of both fabric samples were stored six weeks and then were heated at 160° C. for four minutes and washed. Both fabric samples had high wrinkle resistance 249–258° warp and filling, and both fabrics had a neat appearance without ironing.

We claim:

1. A process of modifying a cellulosic fabric comprising:
   (a) treating the fabric with an aqueous solution comprising an acidic catalyst and an agent prepared by acetylating a methylol alkyl carbamate containing up to five carbons in the alkyl group under anhydrous conditions with acetic anhydride using at least one molar equivalent of anhydride for each methylol group of the carbamate,
   (b) drying the fabric,
   (c) heating the fabric to promote reaction of the acetylated agent with the cellulose.

2. The process of claim 1 where the carbamate acetylated is dimethylol methyl carbamate.

3. The process of claim 1 where the carbamate acetylated is dimethylol methoxyethyl carbamate.

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