Patented July 1, 1947

2,423,428

UNITED STATES PATENT OFFICE

2,423,428

PRETREATMENT OF CELLULOSIC TEXTILES WITH MELAMINE FORMALDEHYDE RESIN

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No Drawing. Application December 30, 1943, Serial No. 516,249

7 Claims. (Cl. 117—161)

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This invention relates to the bonding of textile filaments, fibers, threads, cords and fabrics composed of or comprising hydroxyl-containing cellulosic material to coatings, and more particularly to the pretreatment of such cellulosic textiles to form an anchorage for coatings that may subsequently be applied. The invention includes the pretreated cellulosic textiles themselves, methods of pretreatment whereby the bonding properties of the cellulose or cellulosic textiles are improved, and coated cellulosic textiles wherein a stronger and more permanent bond is obtained between the cellulosic base material and the applied coating.

An extremely wide variety of coating, laminating or impregnating materials have heretofore been applied to cellulosic threads, fibers, fabrics and the like. Thus, for example, a wide variety of waterproofing materials have been coated upon cotton, rayon and similar fabrics in the production of raincoats, water-proof bags and the like, including such materials as natural or synthetic rubber, cyclized rubber, chlorinated rubber, polyvinyl butyral coatings including mixtures of polyvinyl butyral with alkyd resins, as well as synthetic resin compositions and the like. Similarly linoxyn coatings, with or without the addition of ground cork, zinc oxide and other fillers have been applied to cellulosic backings in the preparation of oilcloth, certain types of linoleum and the like. The present invention in its broader aspects is not limited to coated compositions containing any one or more coating materials, but is directed primarily to a method of pretreating the cellulosic material in such a manner as to improve its bonding characteristics when coating materials are applied thereto.

I have found that the bonding properties of cellulosic textiles such as filaments, threads, fibers, fabrics and the like are improved by the application thereto of an acidified aqueous colloidal solution of partially polymerized melamine-formaldehyde resin. Although my invention is not limited by any theory of operation. I believe that this remarkable improvement is due to a modification of the surface characteristics of the cellulosic textile fibers by the colloidal melamine-formaldehyde resin. This opinion is supported by the fact that even minute quantities of colloidal, water-insoluble resin on the order of 0.01% of the

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dry weight of the cellulosic textiles will produce a great increase in the bonding properties thereof, whereas a similar improvement is not obtained by impregnating the textiles with small or even moderately large amounts of the same resin in an unpolymerized and water-soluble condition. My invention in its broader aspects therefore comprises the step of impregnating cellulosic textiles with acidified aqueous colloidal melamine-formaldehyde resin solution under conditions such that the treated textile fibers contain small quantities on the order of 0.01–2% of the resin in a water-insoluble condition; i. e., in such a form that the colloidal resin is not removed by washing the fibers with water immediately after impregnation.

The aqueous colloidal solutions of partially polymerized melamine-formaldehyde resin which are used in practicing my invention may be prepared by any one of several different procedures. A melamine-formaldehyde condensation product may be dissolved in acidified water which preferably contains sufficient acid to produce a glass electrode pH value within the range of about 0.5–4.0 when measured at 12% resin solids content and the solution may then be aged at room temperature or at elevated temperatures until a hydrophilic colloid is formed. If desired, the aqueous solvent in which the resin is aged may contain substantial quantities of a polyhydric alcohol such as glycerol, ethylene glycol and the like, but in this case it is not necessary to use such large quantities of acid and the desired hydrophilic colloid can be obtained at pH values as high as 6.8, which means that the quantity of free acid in the solution is almost vanishingly small. However, the resin solution must always contain some water (usually at least 20% for best results) and it must always be acidified with at least a minute quantity of acid, as otherwise the desired hydrophilic colloid is not obtained.

Substantial quantities of acid are extremely undesirable in cellulosic textiles, since they cause tendering and other forms of degradation of the cellulose. It is therefore a very important advantage of my invention that the necessary quantities of the colloidal melamine-formaldehyde resin are retained by the textile fibers in a water-insoluble condition, for the fibers can be washed with water immediately after they have been im-

pregnated with the resin. This washing step not only removes all the acid, but also removes water-soluble resin which would otherwise remain on the textiles and produce an undesirable stiffness in the treated textiles.

In cases where it is not feasible to wash the textiles with water immediately after impregnation the alcoholic solutions of melamine-formaldehyde resin may be used. When these solutions contain about 20–90% of a polyhydric alcohol substance, the remainder being water and acid, the dissolved resin can be aged to the colloidal condition with very weak acids such as acetic acid, and even such weak acids need be used in only very small quantities. The presence of weak acids in the impregnated textiles in small quantities is not objectionable, and therefore it is easy to deposit the requisite small quantities of the colloidal resin on the textiles in a water-insoluble condition without damaging the fibers.

It has previously been proposed to apply melamine-formaldehyde resins to textile fabrics, including cotton and rayon fabrics, in such quantities as to render them creaseproof or to function as adhesives for stiffening agents, filling agents, softening agents, water-repellents and the like. In all such cases, however, the melamine resin has been employed as a physical bonding agent, and therefore amounts on the order of 10% have usually been impregnated into the fabrics. In such processes it is, of course, impossible to wash the fabric immediately after the impregnation, as the adhesive qualities of the resin are developed only after it has been cured, and therefore the acid employed as a solvent or curing agent is retained in the textiles. The present invention is based on the discovery that small quantities of colloidal partially polymerized melamine-formaldehyde resin on the order of 0.01–2% of the weight of the cellulosic textiles will impart greatly increased bonding properties to the fibers thereof and on the further important discovery that these quantities are retained by the fibers in a water-insoluble condition resistant to washing when the textiles are impregnated with the acidified colloidal aqueous solutions. It is apparent, therefore, that the present invention accomplishes objects which could not be attained by the processes of the prior art and is based on entirely different principles.

The invention in its broader aspects is not limited by the type of cellulosic textile materials to which the colloidal melamine-formaldehyde resins are applied, and improved bonding properties are imparted to any such cellulosic textiles. Such materials as regenerated cellulose including particularly viscose rayon, deacetylated cellulose acetate, denitrated cellulose nitrate, partially methylated, ethylated or otherwise etherified cellulose filaments, and threads and fabrics composed of or containing partially esterified cellulose may be pretreated in accordance with the principles of the invention. The resulting pretreated textiles may be coated with any suitable coating, laminating or impregnating materials such as those enumerated above or other similar materials such as cellulosic coatings.

Although the bonding properties of any cellulosic textile can be improved by applying colloidal melamine-formaldehyde resin solutions thereto there is a considerable difference in the retention of the resin by cellulose of various types. This difference appears to result from differences in the degree of orientation or crystallization in the different materials; thus, for example, in highly oriented cellulose filaments such as are found in spun rayon the resin retention is much lower than in comparatively unoriented fibers such as cotton fibers. Other forms of cellulosic textile materials may vary between these two extremes. I have found, as a further important feature of my invention, that these differences in retention due to differences in orientation may be compensated by proper adjustment of the age and particle size of partially polymerized melamine-formaldehyde resin particles in the colloidal treating solutions. These factors may be regulated by adjusting the acidity, solids content, temperature and aging time of the resin solutions prior to their application to the textiles so that the best results can be obtained with each form of cellulose. Further adjustments may be made by varying the type of acid used to acidify the solution; thus, for example, when cellulose of low hydroxyl content is treated, such as cellulose acetate rayon, it is sometimes advantageous to add chloracetic or alpha-chlorpropionic acid to the originally clear melamine-formaldehyde resin solution either as the sole acidifying agent or in admixture with hydrochloric acid or other acids.

Similar variations in the acidity, solids content, age and particle size of the colloidal melamine-formaldehyde resin solutions may also be employed in pretreating fabrics designed for the application of different coating compositions. Thus, for example, in the application of certain types of polyvinyl acetal to rayon fabrics I have obtained considerable improvements in the strength of the bond by employing chloracetic and hydrochloric acid mixtures as acidifying agents. Other variations within the scope of the appended claims will readily suggest themselves to those skilled in the art, and need not be further detailed.

As is noted above, the presence of free acid in a cellulosic material usually results in an undesirable degradation and loss in strength, and for this reason it is very important to leave as little free acid as possible on the fibers. In practicing the present invention this may be done either by washing the textiles with water after the initial application of the resin solution, or by employing aqueous solutions containing polyhydric alcohols such as glycerine, ethylene glycol and the like containing very small quantities of acid, or both. In the latter case the subsequent washing step is of course not precluded, but the washing does not have to be as thorough as when larger quantities of acid are employed.

In view of the importance of avoiding the presence of substantial quantities of free acid on the textile fibers the resin retention obtained with the colloidal, salt-sensitive melamine-formaldehyde resin solutions is an extremely important feature of the invention. Although the quantity of resin that is retained after thorough washing of the treated fibers with water will vary with the orientation or crystallization of the cellulose, no difficulty is encountered in obtaining retention of the extremely small quantities of the colloidal resin on the order of 0.01–2% of the dry weight of the textiles that are sufficient to produce a stronger bond with coating materials. Larger quantities of applied resin are unnecessary and are usually undesirable since they merely stiffen the textiles without further improving their bonding properties.

Ordinarily the aged colloidal melamine-formaldehyde resin solutions are applied to the cellu-

losic textiles at high dilutions on the order of 0.1–3%, although concentrations up to 6% and higher have been employed with success. The more dilute solutions are usually preferred for several reasons; first, because of greater economy in the use of resin, secondly, because less acid is taken up by the textiles from more dilute solutions, and finally, because of the greater ease of washing the impregnated textiles. The resin solution may also contain plasticizers, softeners, finishing agents or other compatible ingredients for the textiles, such as polyvinyl alcohol, polyethylene oxide having a molecular weight of 1500–4000, and the like.

In some cases even stronger bonding is obtainable by pretreating the cellulosic material prior to the application of the resin colloid thereto. Thus, for example, regenerated cellulose filaments can be pretreated with alcoholic sodium hydroxide and then with alcoholic chloracetic acid or with an alkaline sodium chloracetate solution in alcohol. When samples of finished rayon cloth were pretreated in this manner and then impregnated with a 3% aqueous solution of melamine-formaldehyde resin that had been acidified with 0.8 mol of HCl per mol of melamine and aged 15–18 hours the bonding properties of the fabric to a commercial alkyd-butyral coating composition were greatly increased.

After impregnating the textiles with the colloidal aqueous melamine-formaldehyde resin solution followed by washing if desired and drying, the textiles are usually treated to cure the applied resin. However this curing step is greatly facilitated by the partially polymerized condition in which the resin is applied to the fibers, for only a small amount of additional treatment is necessary to complete the cure of the resin. Thus I have found that the resin will cure spontaneously upon storage of the treated fibers at temperatures as low as 70° F., although ordinarily higher temperatures up to about 240° F. are preferred because of the greater curing speed. It is evident, therefore, that no special curing equipment is necessary in practicing the present invention; ordinary steam or hot air driers may be employed and the curing of the resin may be accomplished at the same temperatures and under the conditions that are usually employed to dry the textile fibers.

The invention will be illustrated in greater detail by the following specific examples. It should be understood, however, that although these examples may describe in detail some of the more specific features of the invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

Example 1

Melamine-formaldehyde resin solutions were prepared from substantially monomeric methylol melamine obtained by the following procedure:

Melamine was added to substantially neutral 37% aqueous formaldehyde solution in the molecular ratio of 1 mol of melamine for each 3.3 mols of formaldehyde and the solution was heated at 60° C. for thirty minutes. The resulting syrup was cooled to separate out crystals of methylol melamine which were centrifuged and dried.

Water solutions containing 12% of the methylol melamine were prepared and acidified by the addition of 1.2 mols of concentrated hydrochloric acid for each mol of melamine. In order to determine the effect of aging the solution, samples

of unsized viscose rayon fabrics were impregnated in the unaged solution at 3% solids and after dilution with water to 0.5% resin solids. Other solutions were aged at room temperatures for definite periods of time and then diluted and used to impregnate other samples of the same rayon fabric. All the rayon fabrics were washed thoroughly in warm water to remove the acid and mechanically held resin and were then heated for ten minutes at 200° C.

The pretreated fabrics were then laminated at 70° C. and 120 pounds per square inch pressure to an uncured polyvinyl butyral coated cotton fabric of commercial grade and the laminated fabrics were cured without pressure in an oven for one hour at 250° F. The cured test pieces were then evaluated for adhesion on a Schopper tensile testing machine by the procedure described in Example 3 at a speed of 4 inches per minute. The results are given in the following table:

Soln. No.	Age of 3% soln. before use	Per cent Resin in soln. when applied	Dry tensile strength, lbs./inch width
1	2 minutes	0.5	1.8–2.2
2	2 minutes	3.0	2.4–2.8
3	3 hours	0.5	[1] 5–6
4	3 hours	3.0	[1] 5–6
5	6 hours	0.5	[1] 5–6
6	6 hours	3.0	[1] 5–6
7	24 hours	0.5	[1] 5–6
8	24 hours	3.0	[1] 5–6
9	Control, washed and dried	None	1.8–2.4

[1] The cotton backing was pulled from the sample.

The importance of aging the acidified solutions is clear from the above results. Only a very slight improvement in the bond between the rayon and the coating was obtained when a monomeric resin was used, but when the resin had been partially polymerized to the colloidal condition by aging the acidified solutions the strength of the bond was greatly increased.

Example 2

A partially polymerized melamine-formaldehyde resin was prepared as follows:

To 115 pounds of a commercial 37% aqueous formalin was added 59.5 pounds of melamine and the pH of the resulting slurry was adjusted to 7.0 by the addition of sodium hydroxide solution. The slurry was then heated to 85° C. and maintained at this temperature for 30 minutes, whereupon the batch was cooled to 70° C. and held until it became hydrophobic as shown by the formation of a white cloud when a few drops were added to water at 60° C. The pH was then adjusted to 9.0 and the batch was cooled and sprayed into a current of hot gases (420° F.) in a commercial spray dryer. The finely divided, spray-dried product was obtained as a white, water-insoluble powder.

An acidified 12% solution was prepared by dissolving 0.1 mol of this resin in water containing 0.1 mol of HCl. Portions of this solution were aged for definite periods of time and then diluted. Application tests were made by diluting the solutions to 3% resin solids after aging, padding rayon fabric in the solutions, washing the treated fabric with water, drying and curing ten minutes at 200° F. The cured rayon fabric was then laminated to an uncured polyvinyl butyral coated

cotton fabric and tested for adhesion strength as described in Example 3. The following results were obtained:

Soln. No.	Age of 12% soln. before dilution and use	Per cent Resin in washed fabric	Adhesion, lbs./in. width	
			Dry	Wet
1	1 minute	0.30	[1] 4.5–5.0	0.9–1.1
2	6 hours	0.24	[1] 4.5–5.0	0.7–1.0
3	12 hours	0.19	[1] 4.2–5.0	0.9–1.0
4	48 hours	0.18	[1] 4.2–4.8	0.9–1.1
5	72 hours	0.11	[1] 4.0–4.4	0.7–0.9
6	Control, washed and dried.		3.0–3.5	0.4–0.5

[1] The cotton backing was pulled from the sample.

These results, when compared with those of Example 1, show that the necessary polymerization of the melamine-formaldehyde resin can be obtained either during the manufacture of the resin, or by aging an acidified solution of the resin, or both. In all cases, however, the resin must be in a partially polymerized condition, as otherwise the strength of the bond is not improved by small amounts of the resin, and in all cases acid must be present to keep the partially polymerized resin in solution and aid in its adsorption by the textile fibers.

Example 3

Colloidal solutions of the resin described in Example 2 were prepared by dissolving 25 gram portions in acidified water heated to 130–140° F. followed by dilution with cold water to a total volume of 208 cc., this being a resin solids content of 12%, and aging at room temperature for 24 hours. Samples of unsized viscose rayon fabrics were padded in these solutions, washed with water, dried in a tentering frame for ten minutes at 200° F. and the dried fabrics were then laminated at 70° C. and 120 pounds per square inch pressure to an uncured polyvinyl butyral coated cotton fabric of a commercial grade and cured without pressure in an oven for one hour at 250° F.

The cured test pieces were evaluated for adhesion on a Schopper tensile testing machine, using 0.5 inch wide test strips and a speed of 4 inches per minute, and the results were expressed as pounds per inch width necessary to pull the pieces apart. In this particular commercial fabric the polyvinyl butyral coating pulled away from its cotton backing at a tension of 5–6 pounds per inch width, and higher values could not be measured. It was apparent, however, that all of the resin-pretreated rayon samples had a much higher degree of coating adhesion since they remained firmly bonded to the resin while the latter was stripped from the cotton.

Wet adhesion values were obtained by soaking the laminated pieces in water at room temperature for 48 hours and then measuring the pull required to separate the strips.

Resin solutions prepared with varying amounts of different acids were applied. In all cases the fabric was washed thoroughly in water at room temperature to remove the acid and excess resin immediately after impregnation with the resin solution and before drying. In the following table the amount of acid is based on 1 mol of melamine; the treating solution contained 3% resin solids and the pH was measured at this dilution. The percent resin is based on the dry weight of the fabric.

No.	Molar quantity of acid	pH	Per cent Resin	Adhesion, lbs./in.	
				Dry	Wet
1	Control, no resin			3.0	0.5–1.0
2	1 Hydrochloric	2.0	0.22	[1] 5–6	2.2–2.8
3	0.8 HCl, 0.2 chloracetic	2.0	0.27	[1] 5–6	2.2–2.8
4	0.8 HCl, 0.2 fumaric	2.1	0.24	[1] 5–6	2.2–2.4
5	0.8 HCl, 0.2 glycollic		0.19	[1] 5–6	2.0–3.0
6	0.8 HCl, 0.2 hydroxy isobutyric.	2.4	0.27	[1] 5–6	1.8–2.6
7	0.6 HCl, 0.4 hydroxy isobutyric.	2.7	0.24	[1] 5–6	1.8–2.4
8	0.4 HCl, 0.6 hydroxy isobutyric.	3.2	0.24	[1] 5–6	2.0–2.6
9	0.8 HCl, 0.2 phthalic	2.1	0.24	[1] 5–6	1.8–2.2

[1] The cotton backing was pulled from the sample.

Example 4

A water solution containing 12% of the resin described in Example 2 and 0.8 mol of HCl per mol of melamine in the resin was aged at room temperature until a blue colloidal haze formed in the solution. Rayon samples were then padded in the colloidal solution at varying concentrations, washed thoroughly, dried and laminated and tested, using the materials and test procedure described in Example 3 except that the wet adhesion was determined after soaking in water for 72 hours. The resin retained by the fiber was determined by Kjeldahl nitrogen analysis. The results obtained were as follows:

Sample No.	Per cent Resin		Adhesion, lbs./in.	
	In soln.	On washed fabric	Dry	Wet
1	12	0.24	[1] 5–6	1.3–1.4
2	6	0.13	[1] 5–6	1.4–1.7
3	3	0.10	[1] 4.5–5	1.1–1.5
4	1	0.05	[1] 4.5–5	1.1–1.5
5	0.5	0.03	[1] 4.4–4.8	1.1–1.5
6	0.1	0.05	[1] 4.4–5	1.0–1.2

[1] The cotton backing was pulled from the sample.

These results show that a great increase in adhesion is obtained when even a small trace of the cationic resin is retained on the fiber.

Example 5

Rayon test pieces were immersed in solutions prepared by dissolving the resin described in Example 2 to 12% solids in water containing 0.6 mol HCl per mol of melamine, aging two hours at room temperature and diluting to 3% solids. The impregnated pieces were then washed thoroughly in warm water and dried and cured at varying temperatures. Some of the pieces were then boiled for two minutes in a mixture of 65% ethyl acetate, 25% toluene and 10% ethyl alcohol, rinsed in ethyl alcohol and dried for five minutes in an oven at 200° F. All of the pieces were then laminated to polyvinyl butyral-coated cotton and tested as in Example 2. The following results were obtained.

No.	Curing		Per cent Resin retained	Dry Adhesion, lbs./in.	
	Temp., ° F.	Time		Not Extracted	Extracted
1	240	15 min.	0.27	[1] 4–5	[1] 4.5–5
2	200	15 min.	0.27	[1] 5–5.5	[1] 4.5–5
3	140	15 min.	0.22	[1] 4.5–5.5	[1] 4.5–5
4	72	20 hrs.	0.27	[1] 4.5–5.0	[1] 4.5–5
5	200	15 min.	Control, no resin.	1.8–2.0	2.6–2.7

[1] The cotton backing was pulled away from the sample.

These figures show that the bonding qualities imparted by the resin are not dependent on the curing temperatures used, since good results were obtained at room temperatures and at temperatures of 240° F.

Example 6

Samples of unsized 80 x 80 cotton cloth and of wind-resistant cotton poplin were immersed in a colloidal cationic resin solution prepared by dissolving the melamine-formaldehyde resin of Example 2 to 12% solids in water containing 0.8 mol of HCl per mol of melamine, aging 6 hours at room temperature, and diluting to 3% resin solids. After washing in water, drying and curing for ten minutes at 200° F. the samples were laminated to polyvinyl butyral coated cotton fabric and tested for adhesion strength with the following results:

No.	Type Fabric	Per cent Resin in fabric	Dry Adhesion, lbs./in.
1	Cotton poplin	Control, No resin	3.0
2	do	0.16	[1] 5–6
3	80 x 80 cotton	Control, No resin	3.4–3.8
4	do	0.3	[1] 5–6

[1] The original cotton backing was pulled away from the sample.

Example 7

Colloidal cationic water solutions of the resin described in Example 1 were prepared at 12% solids with an aging time of 18 hours and then diluted to 3% resin solids. The following acids were used, the amount shown being mols of acid per mol of melamine.

Solution No. 1—1 mol HCl

Solution No. 2—0.8 mol HCl; 0.2 mol chloracetic acid

Solution No. 3—0.8 mol HCl; 0.2 mol α-chlorpropionic acid

Rayon tire cords were pretreated in these solutions to improve their bonding properties to rubber. "Cordura" cords were impregnated with the resins, washed thoroughly in water, dried and heated 15 minutes at 200° F. They were then heated under pressure with sections of uncured rubber, both natural and synthetic. The finished pieces, consisting of cords embedded in cured rubber, were evaluated by measuring the pull required to strip the cords from the rubber. The test results are shown in the following table:

Adhesion test results

Pretreatment	Per cent Resin retained	Av. of 10 high	Av. of 10 low	Mean lbs. pulled	Per cent Adhesion
NATURAL RUBBER					
No treatment		2.1	1.5	1.80	100
Water washed		2.1	1.4	1.75	97
Soln. No. 1	0.70	3.2	2.4	2.80	155
Soln. No. 2	0.88	3.3	2.5	2.90	161
Soln. No. 3	0.78	3.4	2.5	2.95	164
BUNA S RUBBER					
No treatment		1.3	1.0	1.15	100
Water washed		1.4	1.1	1.25	109
Soln. No. 1	0.70	1.9	1.5	1.70	148
Soln. No. 2	0.88	1.6	1.3	1.45	126
Soln. No. 3	0.78	1.5	1.2	1.35	117

Example 8

In all the preceding examples fairly large quantities of acid were used in water solution to form colloidal aqueous solutions of the melamine-formaldehyde resin and the treated cloth was washed to remove the acid, leaving small but effective quantities of the resin adhering thereto. Numerous solvents other than water may be used as dispersing agents for melamine-formaldehyde resins, and I have found that the resin can be converted to the colloidal condition with the aid of much smaller quantities of aqueous acid when water-soluble di- or polyhydric alcohols or their ethers are present. Typical solvents of this class which may be used are ethylene glycol, glycerol, diglycerol, polyethylene glycols and their monoethers such as the monoethyl ether of ethylene glycol as well as glucose and sucrose. Monohydric alcohols have been tested, but fail to give satisfactory colloidal solutions when reduced quantities of aqueous acid are used.

Several factors govern the optimum proportions of polyhydric alcohols to be used. At a given resin solids content, such as 12%, very concentrated aqueous solutions containing 80–95% of glycerol or ethylene glycol must be used to dissolve the resin when no aqueous acid is present. If, however, an aqueous acid solution is used in conjunction with the polyhydric alcohol solvent the amount of alcohol can be reduced; thus with 0.1 mol of acetic acid per mol of resin only 60% of the alcohol need be used. As the pH is reduced the amount of alcohol necessary is also reduced; for example, if 0.5 mol of acetic acid is used a 40% glycerine or ethylene glycol solution will serve as a solvent.

The aging of acidified solutions containing a high concentration of polyhydric alcohol is very slow; in fact, the colloidal condition is not reached in four months at room temperatures in a 12% resin solution containing 95% glycerol, 1 mol of Hcl per mol of melamine and 5% water. However, if the solution is diluted to contain at least 20% of water the aging period is reduced to 24 hours or less at this high acid concentration, and the same results are obtained with somewhat longer aging times when greatly reduced quantities of acid are used. This is shown by the following experimental results, which were obtained by aging 12% solutions of the partially polymerized resin described in Example 2 at room temperature.

Soln. No.	Solvent used	Mols acid per mol resin	pH	Appearance of 1% dilutions after—			
				1 hr.	1 day	5–6 days	8–10 days
1	Water	0.1 acetic		Not dispersible at 12% solids			
2	60% aq. glycerol	do	5.3	ppt	col	col	gel.
3	60% aq. glycol	do	5.1	ppt	col	col	gel.
4	60% aq. glycol	0.5 acetic	4.5	ppt	col	col	gel.
5	60% aq. glycerol	No acid	7.2	ppt	ppt	ppt	ppt.
6	60% aq. glycerol	0.05 HCl	5.5	ppt	ppt	col	Col.
7	80% aq. glycerol	do	5.4	ppt	col	col	clear.

The colloidal condition is reached in a considerably shorter time when the above solutions are aged at 70°–100° C., even when only small quantities of acid are used. Thus, for example, a 12% resin solution in a solvent composed of 95% glycerol, 5% water and 0.01 mol acetic acid per mol of melamine showed colloidal properties upon dilution with water to 1% resin solids after only six hours aging at 100° C.

The application of a large number of aged melamine-formaldehyde resin solutions containing aqueous glycol, glycerol and other water-soluble polyhydroxy compounds to rayon fabrics has shown that satisfactory retention is obtainable with only slightly polymerized resins, but that in all cases at least a small amount of acid must be present. However, these solvents permit the reduction of the quantity of acid to the point where washing of the fabric is unnecessary. Although this is an advantage in the commercial pretreatment of fabrics it must be emphasized that the impregnating solution should not contain more than a few percent of resin, on the order of 0.5–6% or less, as otherwise the fabric will become stiffened when the resin is cured.

The following is typical of results obtainable with water-soluble polyhydroxy compounds and small amounts of acid. In all cases the resin solution was acidified and aged at 12% resin solids, then diluted to 1% and applied to the fabric which was cured ten minutes at 200° F. Duplicate samples were impregnated, the first being dried directly and the second being washed and dried. The quantity of acid in the following table represents mols of acetic acid per mol of melamine.

Soln. No.	Solvent	Mols Acid	Aging		Appearance of 1% soln.	Fabric Washed	Per cent Resin in Dry Fabric
			Temp., ° F.	Days			
1	60% glycerol	0.1	140	8	Colloid	Yes	1.35
1A	do	0.1	140	8	do	No	1.69
2	80% glycerol	0.1	140	8	Clear	Yes	0.07
2A	do	0.1	140	8	do	No	1.59
3	60% glycol	0.1	140	6	Colloid	Yes	1.35
3A	do	0.1	140	6	do	No	1.45
4	100% glycol	0.1	140	6	Clear	Yes	0.08
4A	do	0.1	140	6	do	No	0.73

These retention figures show clearly the importance of colloid formation on the retention of resin when the fabric is washed. When the resin solution has aged to the colloidal, cationic condition it is adsorbed by the textile fibers in a water-insoluble condition, whereas the resin taken up from the clear solutions was easily washed from the fabric.

What I claim is:

1. A method of improving the bonding properties of cellulosic textiles which comprises impregnating said textiles with an acidic aqueous colloidal solution of melamine-formaldehyde resin in a solvent comprising a water-soluble polyhydric alcohol and retaining 0.01–2% of resin on the cellulosic textiles in a water-insoluble condition.

2. A method of improving the bonding properties of cellulosic textiles which comprises impregnating said textiles with an aqueous solution of colloidal melamine-formaldehyde resin in a solvent comprising a water-soluble polyhydric alcohol and sufficient acid to produce a pH below about 6.8 and retaining 0.01–2% of resin on the cellulosic textiles in a water-insoluble condition.

3. A method of improving the bonding properties of cellulosic textiles which comprises the steps of impregnating said textiles in a bath prepared by aging an aqueous solution of a melamine-formaldehyde condensation product in a solvent comprising a polyhydric alcohol and sufficient acid to reduce the pH to about 4.5–6.8 until a colloidal melamine-formaldehyde resin solution is formed, whereby colloidal particles of the resin are deposited on the cellulosic textiles in amounts of 0.01–2% of the dry weight thereof.

4. A method of improving the bonding properties of textiles containing highly oriented cellulose filaments which comprises impregnating said textiles in a bath prepared by aging an aqueous solution of a melamine-formaldehyde condensation product containing chloracetic acid until a colloidal melamine-formaldehyde resin solution is formed, whereby colloidal particles of the resin are deposited on the cellulosic textiles in a water-insoluble condition in amounts of 0.01–0.5% of the dry weight thereof.

5. A method of improving the bonding properties of textiles containing highly oriented cellulose filaments which comprises first impregnating said textiles with alcoholic alkali and organic carboxylic acid and then impregnating the textiles with an acidic aqueous colloidal solution of partially polymerized melamine-formaldehyde resin, whereby 0.01–5% of the resin is retained on the textiles in a water-insoluble condition.

6. A method of improving the bonding properties of rayon textiles which comprises impregnating them with an acidic aqueous colloidal solution of melamine-formaldehyde resin in a solvent comprising a water-soluble polyhydric alcohol and retaining 0.01–2% of resin on the rayon in a water-insoluble condition.

7. A method of improving the bonding properties of cellulosic textiles which comprises impregnating said textiles with an aqueous solution of colloidal melamine-formaldehyde resin in a solvent comprising a water-soluble polyhydric alcohol and a small amount of acid sufficient to reduce the pH to 4.5–6.8 and drying the textiles and curing the water-insoluble resin on the fibers thereof.

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