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PRETREATMENT OF NONCELLULOSIC TEXTILES

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1

This invention relates to the bonding of textile filaments, fibers, threads, cords and fabrics composed of or containing non-cellulosic constituents to coatings, and more particularly to the pretreatment of such textiles to form an anchorage for coatings that may subsequently be applied.

In my copending application, Serial No. 516,249, filed December 30, 1943, I have shown that the bonding properties of cellulose and cellulosic textiles are improved by the application thereto of an acidified aqueous colloidal solution of partially polymerized melamine-formaldehyde resin. The present invention is the result of a continuation of the investigation reported in that application, and is based on my discovery that a similar improvement is obtained when non-cellulosic textiles such as silk, nylon, wool, felted wool, casein fibers and the like are pretreated with the same type of aqueous resin solutions.

I have found that the bonding properties of non-cellulosic textiles in the form of 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 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 dry weight of the textiles will produce a great increase in 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 non-cellulosic textiles of the type exemplified by wool, silk, and linear polymers such as nylon, casein and vinyon with acidified aqueous colloidal melamine-formaldehyde resin solutions 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 resin is then preferably cured on the textiles, as by heating, after which they are in condition for coating by any known or approved coating procedure. Silk and nylon threads and fabrics are most widely used as bases for non-cellulosic coated fabrics, but wool cloth is

2

now being coated for the production of water-repellent and gasproof uniforms for military purposes and may be pretreated by the process of the present invention. The newer synthetic textiles such as casein, polyvinyl chloride, polyvinyl acetate-polyvinyl chloride copolymers and the like can also be pretreated by the same process.

An extremely wide variety of coating, laminating or impregnating materials have heretofore been applied to threads, fibers, fabrics and the like. Thus, for example, a wide variety of waterproofing materials have been coated upon silk, nylon and similar fabrics in the production of raincoats, water-proof bags, light-weight tents, gasproof clothing 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. 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.

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 textiles. It is therefore a very important advantage of my invention that the necessary quantities of the colloidal melamine-form-

aldehyde 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 impregnated 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 quanties 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 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 non-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 presence of free acid in a textile 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. 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, even after thorough washing with water. Larger quantities of applied resin are unnecessary and are usually undesirable since they merely stiffen textiles without further improving their bonding properties.

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

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 textiles 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 drires 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.

Some of the colloidal aqueous solutions of partially polymerized melamine-formaldehyde resin used in practicing the invention are described in U. S. Patent No. 2,345,543, and may be prepared by any of the methods described in that patent. Another method of preparing this type of resin consists in the formation of a hydrophobic melamine-formaldehyde resin syrup, for example by reacting 115 pounds of 37% aqueous fomalin with 59.5 pounds of melamine at a pH of 7.0 at 70–85° C., followed by spray-drying the product in a current of hot gases at 420° F. Upon dissolving the spray dried product in water containing an equimolecular quantity of HCl to a solution containing 12% solids a partially polymerized resin solution is obtained without the necessity of extensive aging.

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, glyceral, 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, spray-dried resin described above 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 nylon 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 improved adhesion obtainable by pretreatment of non-cellulosic textiles with partially polymerized melamine-formaldehyde resin solutions can readily be demonstrated by the following test procedure: A sample of pretreated test fabric, for example silk or nylon fabric, is folded

to 3.5" by 5" size, and between the two faces of fabric is placed a 2" by 4" strip of uncured polyvinyl butyral coating about .008" thick. A thermosetting polyvinyl butyral coating composed of vinyl butyral resin (6–7% hydroxyl) plus curing resin, plasticized with triethylene glycol octacetate and castor oil was used in the tests described below. The test piece is placed between two pieces of canton flannel and pressed for 30 seconds at 60° C. and 190 pounds per square inch. The pressed piece is then cured for one hour at 260° F. without pressure.

In testing for dry coating adhesion, the test samples are conditioned for 24 hours at 73° F., 50% relative humidity and then pulled apart in a Schopper tensile testing machine. Similar tests for wet adhesion are conducted after soaking the laminated pieces in water for 48 hours at room temperature. Adhesion values are recorded as the force in pounds required to separate the two fabrics when pulled apart at a rate of 12" per minute.

The results obtained with various pretreatments of nylon cloth are given in the following table. The test pieces of cloth were immersed in the colloidal resin solution for five minutes, squeezed out, and washed in running water for five minutes. The pieces were then dried in tentering frames for 10 minutes at 200° F. A control sample was immersed in plain water for the same length of time and dried along with the impregnated samples, and a second control sample was laminated without washing.

Resin Solution	Per Cent Resin Solids in Bath	Adhesion, lbs./2" width Dry	Wet
A	1.0	7.5	2.5
A	3.0	6.5	2.0
A	6.0	8.0	2.5
B	0.2	5.5	1.5
B	0.5	6.0	2.0
B	1.0	10.0	3.0
B	3.0	7.5	2.5
B	6.0	5.5	2.5
Control, no resin. Cloth washed and dried		4.0	0.5
Control, no resin		1.5	0.3

A=1 mol trimethylol melamine, 0.8 mol HCl aged 4 hours at 12% resin solids at room temperature, then diluted with water to the concentrations used.

B=25 grams trimethylol melamine, 23.6 grams ethylene glycol, 17.5 grams water and 2.4 grams glacial acetic acid were heated for 1.5 hours at 60° C. The solution was then diluted with ethylene glycol to a total weight of 200 grams, aged 4 hours, and diluted with water to the concentration used.

What I claim is:

1. A method of improving the bonding properties of non-cellulosic organic 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 textiles in a water-insoluble condition.

2. A method of improving the bonding properties of non-cellulosic organic 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 textiles in a water-insoluble condition.

3. A method of improving the bonding properties of non-cellulosic organic 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 textiles in amounts of 0.01–2% of the dry weight thereof.

4. A method of improving the bonding properties of nylon 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 nylon in a water-insoluble condition.

5. A method of improving the bonding properties of non-cellulosic organic 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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REFERENCES CITED

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

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Number	Name	Date
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