United States Patent Office 2,763,578 Patented Sept. 18, 1956

2,763,578

PROCESS OF FINISHING CELLULOSIC FABRIC AND PRODUCT RESULTING THEREFROM

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No Drawing. Application March 24, 1954, Serial No. 418,462

6 Claims. (Cl. 117—145)

This invention relates to the finishing of fabrics in order to obtain special effects. In particular it relates to the application of polymeric products to impart various finishes, such as a taffeta finish, for example, to fabrics made of cellulose acetate and regenerated cellulose, such as cuprammonium and viscose rayon.

Fabrics constructed completely or partly of these fibers made be soft and limp or stiff and firm depending on their construction. In order to obtain fabrics with increased stiffness and crispness from the softer construction, it is necessary to apply some kind of finish. For example, the crispness, stiffness, and scroop associated with taffetas may be imparted to a cellulose acetate fabric lacking these characteristics by the application of a "taffeta finish." Even more stiffness and paperiness are demanded for utilization of the fabric as ribbon; this may be accomplished by applying a "ribbon finish."

A ribbon or taffeta finish to be acceptable must impart to the fabric other properties besides crispness, stiffness, paperiness, or scroop. The finish must have such adhesion to the fiber that it does not show mark-off or dusting. It must undergo calendering, hot or cold, with no undesirable effects on the hand of the fabric. It must not interfere with the cutting of the fabric by means of a hot knife or wire. It must withstand laundering and dry cleaning. It must impart a certain desirable gloss or sheen to the fabric and, obviously, it must not have adverse toxicological or dermatological effects.

Such finishes have in the past been provided by the application of resinous products of the alkyd type made by the condensation reaction of a polybasic acid, such as phthalic acid and polyhydric alcohols, such as glycerol. These resins are supplied and stored in very viscous alkaline solutions. Because of gradual saponification and other detrimental reactions which occur on storage these products deteriorate with aging and, therefore, the effects produced by these resins change with their age. In fact, upon prolonged storage, they lose their water solubility and become useless.

An object of the present invention is to provide a means of finishing cellulose acetate and other cellulosic fabrics with resins having much improved storage stability. These resins are addition polymers which are quite resistant to saponification and cannot undergo a gradual deterioration of the kind which takes place with alkyd type materials. Another object is to provide a means of finishing fabrics with polymers which are easily handled as low viscosity emulsions. A further object is to provide a finish with superior qualities in color, mark off, hand and permanence to atmospheric conditions.

A resinous product should possess certain qualifications to be useful for finishing fabrics. It is preferable to apply such resins from an aqueous solution whose viscosity must be low enough to allow for correct mechanical action of the fabric and the finishing machinery. Very few of the known resins which can be dissolved in aqueous media are suitable.

Interpolymers from various polymerizable monomers and polymerizable or unsaturated acids are well known. Such products as the copolymers of styrene and maleic acid, vinyl methyl ether and maleic acid, methyl methacrylate and methacrylic acid have been described and

many of them have applications in the textile fields. But although these products have sufficient stability toward saponification, they have disadvantages which have prevented their utilization in certain finishing operations; viz., their solutions at concentrations low enough to give workable viscosities in the bath do not give the desired effect on the fabric and, vice versa, when the bath is made up to a concentration which would probably give the desired effects the viscosity is so high that the fabric cannot be run through it satisfactorily. A further disadvantage of using these products is that they are usually provided as granular or powdery solids which dissolve with difficulty in dilute ammonia or alkalies.

It has been found that finishes of exceptionally fine color and clarity, preserving the finest sheen or gloss of an acetate fabric and yielding fabrics with hand characteristics ranging through a heavy fullness to a thin, crisp paperiness may be obtained by the processes of this invention. Such results are produced by employing an emulsion of an interpolymer of acrylic or methacrylic acid and at least two monomers selected from the group consisting of vinyl acetate, methyl methacrylate, methyl acrylate and ethyl acrylate. These interpolymers are composed of at least three components, e. g., vinyl acetate, an acrylic acid of the formula $CH_2=C(R)COOH$ wherein R is H or CH_3, or mixtures thereof, together with an ester of such an acid and a lower aliphatic alcohol containing not more than 4 carbon atoms. The proportions of each may be varied within limits hereinafter described. In order that these resins may be applied from alkaline or ammoniacal aqueous solution a certain minimum amount of acrylic acid is desirable. It has been found that at least five mol percent based on the total monomer is necessary. The maximum amount that is desirable is dependent on the water solubility of the resulting polymer. A maximum percentage which it is undesirable to exceed is 30 mol percent by weight. The amount of acrylic acid ranges between 5 and 20 mol percent by weight for satisfactory results. Values of 7–10 mol percent by weight are preferred.

The choice of other monomers copolymerized with the acrylic acid and the proportions thereof depends upon the quality of the hand desired of the fabric. Vinyl acetate may be used with methyl acrylate or ethyl acrylate, for example, in the proportions by weight of 80 mol percent vinyl acetate, 10 mol percent of methyl or ethyl acrylate and 10 mol percent acrylic acid. The vinyl acetate content in such terpolymers may vary, but should preferably not be less than 50% mol by weight of the total polymer. The proportion of acrylic acid ester which is incorporated into these resins also may be widely varied. Values of 5 to 20 mol percent by weight of the total monomer present have been found satisfactory. Seven to ten mol percent are the preferred values.

Interpolymers from acrylic acid or methacrylic acid and a polymerizable monomer are well known. Certain of these products, e. g., methacrylic acid-methyl methacrylate interpolymers, have been suggested for application to textiles as a size, more particularly as a warp size. These products are not suitable for taffeta or ribbon finish because their solutions, at concentrations low enough to give workable viscosities in the bath do not give the desired effects on the fabric. On the other hand, interpolymers of vinyl acetate with acrylic acid have been found to lack sufficient crispness and stiffness when applied as a taffeta finish. Other polymers of various types which have been found to be unsatisfactory for these reasons are: vinyl acetate-maleic anhydride, methyl vinyl ether-maleic anhydride, styrene maleic anhydride, vinyl acetate-methyl acid maleate and vinyl acetate-crotonic acid.

Many terpolymers are unsatisfactory for the production of taffeta or ribbon finish. For example, resins prepared

from vinyl acetate, acrylic acid and vinyl propionate or vinyl 2-ethyl hexoate were found to yield finishes lacking in crispness and paperiness. Satisfactory terpolymers are obtained using vinyl acetate, acrylic or methacrylic acid and the lower aliphatic esters of acrylic or methacrylic acid. For example, methyl or ethyl acrylate or methyl methacrylate may be incorporated in terpolymers which yield satisfactory finishes. For specific effects the propyl or butyl esters may be used. For taffeta finishes the most desirable third component is either methyl acrylate or ethyl acrylate. For a ribbon finish methyl acrylate is preferred.

The polymers of this invention are prepared by means of the emulsion technique because of the advantages which result from its use, viz., the product is obtained in a finely divided form which readily reacts with ammonia solutions to form clear or slightly hazy solutions. The emulsion itself is of low viscosity and may be handled as a homogeneous liquid.

In carrying out the emulsion polymerization it is possible to charge all of the components at the start, but it has been found that a better product results when a "drip-in" procedure is used. By this procedure a part (e. g. 10%) of the monomer mixture is charged at the start of the polymerization and the balance of the monomer to be charged is added gradually to the polymerizing mixture as the reaction proceeds. In this way polymers which are completely soluble in ammoniacal solutions are obtained.

Other variations common in the emulsion technique of emulsion polymerization are possible. For example, it is possible to use well-known emulsifiers and emulsion stabilizers. Suitable catalysts may be used, for example, peroxides and persulfates. In general, water-soluble catalysts are preferred. Such variations will be obvious to those skilled in the art.

The polymeric products above described are obtained as white emulsions with Brookfield viscosities less than 500 cp. Addition of ammonia or alkali to the undiluted emulsion results in the formation of a thick, very viscous solution. If the emulsion is diluted first, addition of dilute alkalies, e. g. KOH, NH_4OH, produces clear or slightly hazy, colorless solutions of the corresponding salts of the copolymers. The viscosity of the solution of any one polymer salt depends on the concentration and the pH.

The application to a fabric may be made from an aqueous solution obtained by first diluting the emulsion with water. A thirty percent by weight solids emulsion (1 part) may be diluted with 4 parts of water. Dilute ammonia is added until the pH rises to 8. The amount of ammonia required will depend on the amount of acrylic acid which has been incorporated with the resin. The addition of ammonia converts the milky emulsion to a clear or slightly opaque solution. This solution is padded on the fabric, the excess removed by passage between rolls. The clutch is dried and may or may not be further processed by calendering, etc., depending on the hand which is desired. In general, the amount of the copolymer applied to the fabric is held at as low a quantity as will produce the desired hand. This usually ranges from about 6 to about 20% by weight of the fabric weight.

Alternatively, the resin may be applied to fabrics without forming a solution. The diluted emulsion is applied without adjusting the pH to the alkaline side, using the usual methods of padding, nipping, drying, and calendering.

The following examples are given for illustrative purposes and are not to limit the invention.

Example 1

This example illustrates the use of varying amounts of methyl methacrylate and vinyl acetate with a constant percentage of acrylic acid in the preparation of emulsions of the resins of this invention.

Emulsion No.	1	2	3	4	5
Mol percent composition of monomer mixture:					
Vinyl acetate	80	80	75	70	60
Methyl methacrylate	10	10	15	20	30
Acrylic acid	10	10	10	10	10
Emulsion formula, percent by weight:					
Hydroxyethyl cellulose ("Cellosize" WPHS)	1	1	1	1	1
Sodium dioctyl sulfosuccinate	1		1	1	1
Sodium lauryl sulfate		1			
Potassium persulfate	0.2	0.2	0.2	0.2	0.2
Monomer mixture	28.0	28.0	28.0	28.0	28.0
Water	69.8	69.8	69.8	69.8	69.8

In preparing the emulsions in this example the following procedure was used: The emulsion stabilizer previously dissolved in water, the emulsifier and the persulfate catalyst were dissolved in the necessary amount of water. The mixture was placed in a glass reaction vessel, fitted with a reflux condenser, and stirred mechanically while one tenth of the monomer mixture was added. Heat was applied and when refluxing had been well established the balance of the monomer mixture was added over a period of 2 to 5 hours. When all monomer had been added and no further refluxing occurred at a temperature in the emulsion of 95° C. the polymerization was considered finished.

The products of this example were diluted by the addition of water to a solids content of 7–8% by weight. Dilute ammonia was added until the pH was 8.0. Colorless, clear to hazy solutions were formed in which pieces of cellulose acetate satin were immersed. The wetted cloths were passed between rubber faced rolls to squeeze out excess liquid, leaving about 100% wet pick up. These cloths were dried on frames at 250° F. for five minutes. The resulting materials had stiffness, fullness, scroop, and the fine sheen required of a affeta finish. By calendering by means of hot rolls the stiffness and paperiness were increased.

Example 2

Emulsions were prepared by the general procedure described in Example 1, using by weight 14 mol per cent ethyl acrylate and 76 mol per cent vinyl acetate with 10 mol per cent of acrylic acid in the following formulations. The products of this example illustrate the use of different emulsifiers, emulsion stabilizers and catalysts.

Emulsion No.	6	7	8	9	10	11	12	13
Emulsion Formula, Percent by Weight:								
Polyvinyl alchol ("Elvanol" 50-42)	1							
Polyvinyl alcohol ("Elvanol" 52-22)		1						
Hydroxyethyl cellulose ("Cellosize" WPHS)			0.95	0.95	0.95	0.95	0.95	0.95
Alkyl ether of polyethylene glycol ("Brij" 35)	0.95	0.95	0.95					
Sodium dioctyl sulfosuccinate				2.0	1.0			2.0
Sodium salt of alkylaryl polyether sulfonate ("Triton" X-200 [28% active])						3.4		
Sodium lauryl sulfate							0.95	
Potassium persulfate	0.2	0.2	0.2	0.2	0.2	0.2		
Ammonium persulfate								0.1
Chelating agent (Ethylene diamine tetra acetic acid type)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Monomer mix	28.0	28.0	28.0	28.0	28.0	28.0	28.0	28.0
Water	69.75	69.75	69.8	68.75	69.75	67.45	69.8	68.85

Acetate satin treated with these products had the hand of a taffeta fabric.

Example 3

The formulations in this example were polymerized by the procedure described in Example 1.

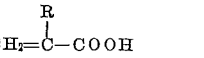
Emulsion No.	14	15	16	17
Mol Percent Composition of Monomer Mixture:				
Vinyl acetate	90	85	80	81.5
Methyl acrylate	3	7.5	10	10
Acrylic acid	7	7.5	10	
Methacrylic acid				8.5
Emulsion Formula, Percent by Weight:				
Hydroxyethyl cellulose ("Cellosize" WPHS)	0.95	0.95	0.95	0.95
Sodium dioctyl sulfosuccinate	2.0		2.0	
Alkyl ether of polyethylene glycol ("Brij" 35)		1.0		0.1
Chelating agent (Ethylene diamine tetra-acetic acid type)	0.1	0.1	0.1	0.3
Potassium persulfate	0.1	0.1	0.1	0.3
Monomer mix	26.2	28.3	28.0	28.0
Water	70.65	69.65	68.85	69.65

These products applied to acetate fabrics produced a stiffer finish than those in Example 2. Application of the ammoniacal solution of emulsion No. 15 to regenerated cellulose taffeta ribbon likewise imparted a stiff finish.

Persons skilled in the art of finishing fabrics will appreciate the usefulness and versatility of this invention. It has already been shown how these polymers may be applied to fabric from an emulsion or from a solution formed by addition of ammonia. Other effects are possible by only partly neutralizing the emulsion, or by application with water-repellent compositions, softeners or fire retardant. The use of ammonia solutions results in the application of a resin finish which probably undergoes important changes on curing due to liberation of ammonia. The use of fixed alkalies or the addition of polyvalent salts or bases will give different results: the finish may be made permanently insoluble in water or it may be given other permanent modifications.

I claim:

1. The process of imparting ribbon and taffeta finishes to a fabric selected from the group consisting of cellulose acetate and regenerated cellulose which comprises impregnating the fabric in a bath containing an interpolymer composed of at least three components consisting by weight of 50–90 mol per cent vinyl acetate, 5–30 mol per cent of an acrylic acid of the formula



wherein R is selected from the group consisting of H and CH_3, and 5–20 mol per cent of an ester of said acrylic acid and a lower aliphatic alcohol containing not more than 4 carbon atoms, removing excess of said bath from the fabric and drying the fabric.

2. The process of imparting ribbon and taffeta finishes to a fabric selected from the group consisting of cellulose acetate and regenerated cellulose which comprises impregnating the fabric in a bath containing an interpolymer composed of at least three components consisting by weight of 80–85 mol per cent vinyl acetate, 7–10 mol per cent of acrylic acid and 7–10 mol per cent of an ester selected from the group consisting of methyl acrylate, ethyl acrylate and methyl methacrylate, removing excess of said bath from the fabric and drying the fabric.

3. The process of imparting ribbon and taffeta finishes to a fabric selected from the group consisting of cellulose acetate and regenerated cellulose which comprises impregnating the fabric in a bath containing an interpolymer composed of at least three components consisting by weight of 80–85 mol per cent vinyl acetate, 7–10 mol per cent of methacrylic acid and 7–10 mol per cent of an ester selected from the group consisting of methyl acrylate, ethyl acrylate, and methyl methacrylate, removing excess of said bath from the fabric and drying the fabric.

4. The process of imparting ribbon and taffeta finishes to a fabric selected from the group consisting of cellulose acetate and regenerated cellulose which comprises impregnating the fabric in a bath containing an interpolymer composed of at least three components consisting by weight of 80–85 mol per cent vinyl acetate, 7–10 mol per cent of acrylic acid and 7–10 mol per cent of methyl acrylate, removing excess of said bath from the fabric and drying the fabric.

5. The process of imparting ribbon and taffeta finishes to a fabric selected from the group consisting of cellulose acetate and regenerated cellulose which comprises impregnating the fabric in a bath containing an interpolymer composed of at least three components consisting by weight of 80–85 mol per cent vinyl acetate, 7–10 mol per cent methacrylic acid and 7–10 mol per cent of methyl acrylate, removing excess of said bath from the fabric and drying the fabric.

6. A cellulosic fabric finished in accordance with the process of claim 1.

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