

March 3, 1959

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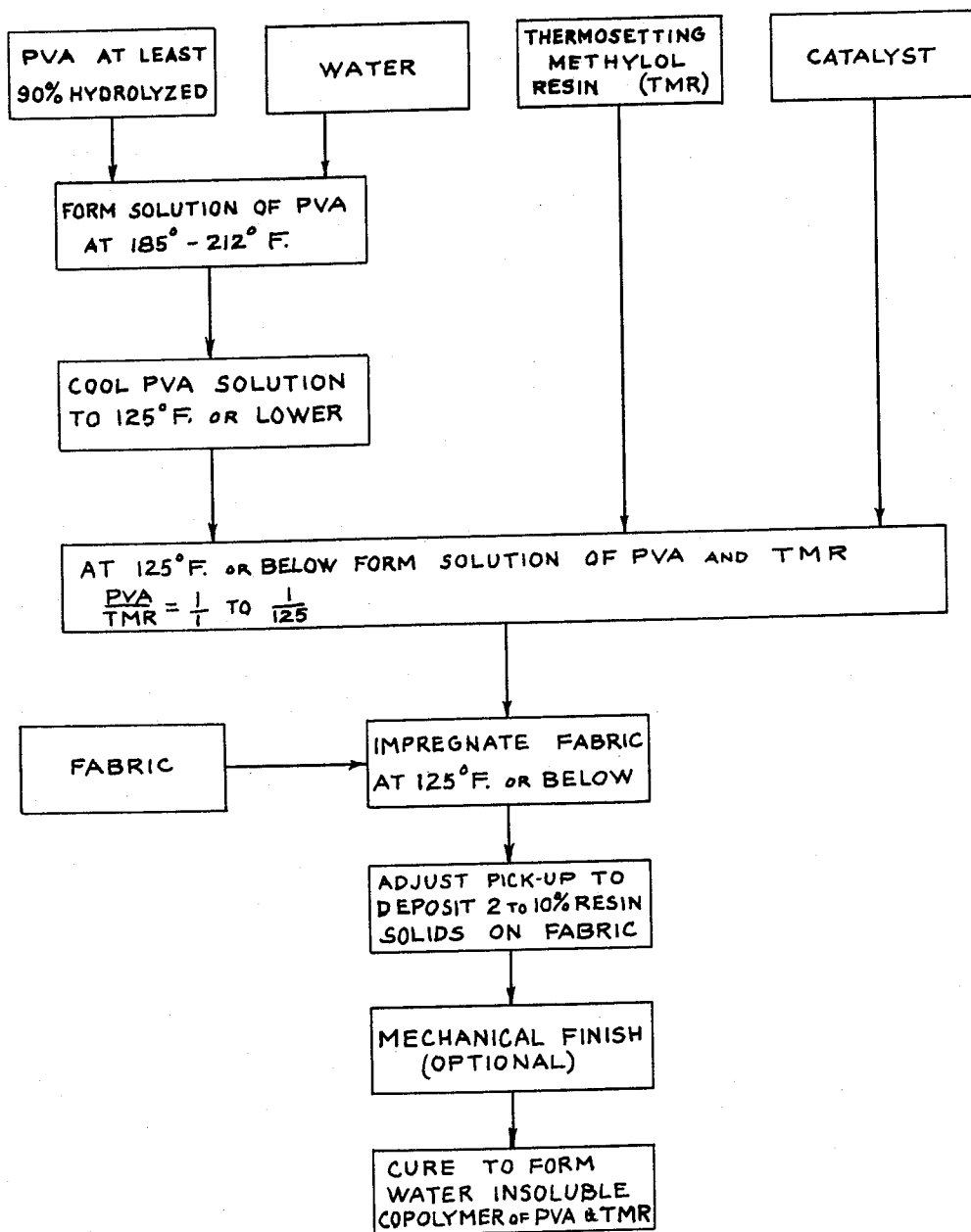
2,876,136

METHOD OF PRODUCING RESINOUS COPOLYMERS IN SITU ON FABRICS

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3 Sheets-Sheet 1

Fig. 1.



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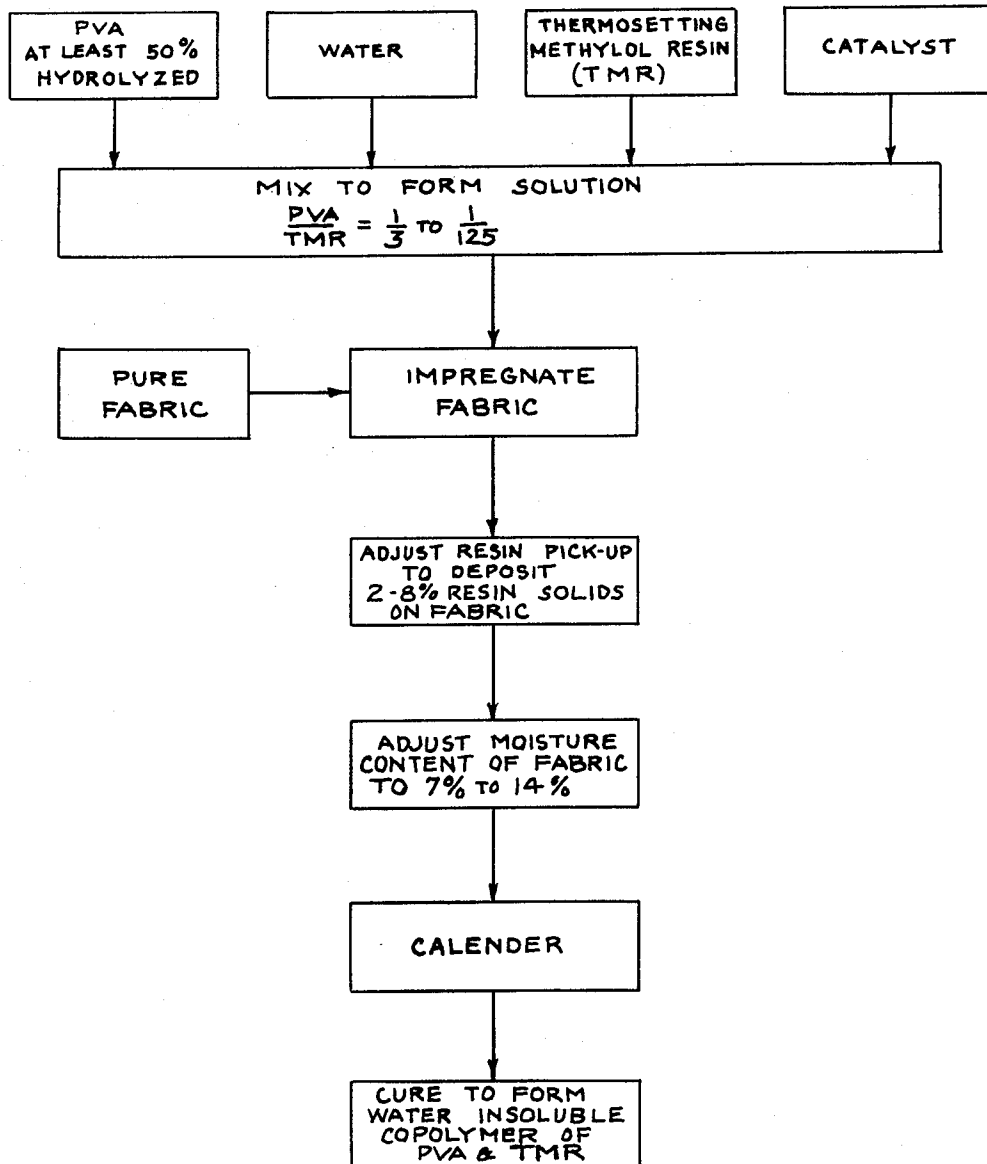
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3 Sheets-Sheet 2

Fig. 2.



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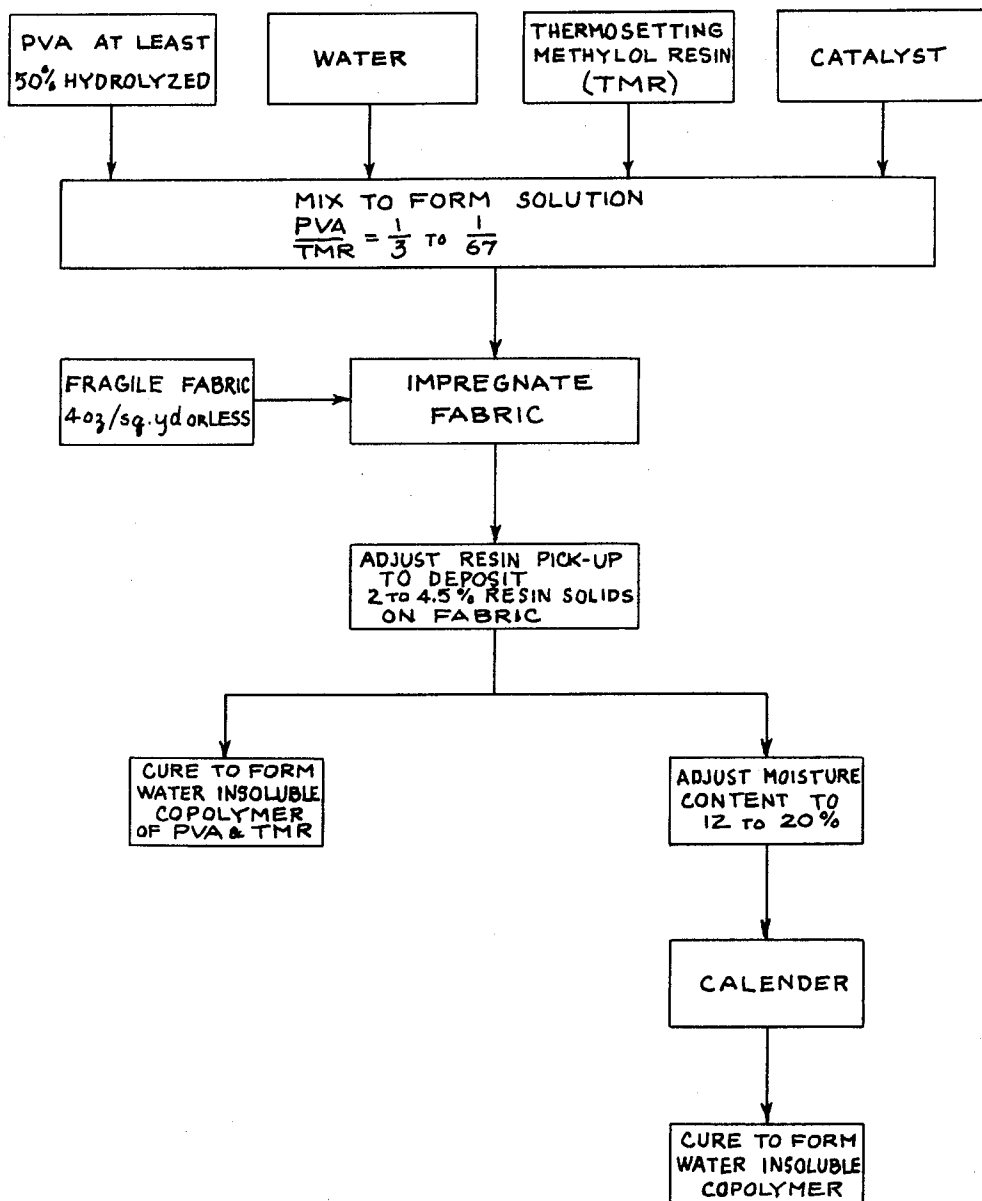
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3 Sheets-Sheet 3

Fig. 3.



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METHOD OF PRODUCING RESINOUS COPOLYMERS IN SITU ON FABRICS

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Application March 20, 1957, Serial No. 647,193

6 Claims. (Cl. 117-65)

This invention relates to the art of applying textile finishing agents to and fixing such agents on textile fabrics, especially cellulosic fabrics in woven or knitted form, made, for example, from cotton, regenerated cellulose, linen or mixtures thereof.

As schematically illustrated in Figure 1, of the accompanying drawing, the invention is particularly applicable to the kind of fabric finishing treatment in which an impregnating solution containing the constituents to be permanently retained by the fabric is preliminarily prepared from a very highly hydrolyzed polyvinyl alcohol, and is then applied to the fabric, as by padding, following which the fabric is treated to cure or set resinous constituents incorporated in the impregnating solution. Other fabric finishing steps may also be involved, such, for example, as calendering, in which event the curing of the resinous constituents on the fabric may serve to render durable not only the hand and other characteristics contributed by the impregnating constituents retained by the fabric, but also the finish imparted by the calendering.

It is contemplated according to the invention to employ certain particular interreactable resinous constituents in the impregnating solution, and the invention has in view, as a general objective, a sequence of steps ensuring copolymerization or interreaction of the interreactable constituents in situ in and on the fibers of the fabric, rather than at an earlier stage of the processing, notwithstanding the fact that the interreactable constituents are preliminarily intermixed in a common aqueous medium prepared as an impregnating solution.

More specifically, the invention contemplates employment, as two interreactable resinous constituents, of polyvinyl alcohol and an aldehyde compound in the water-soluble precondensate state.

The aldehyde precondensate may be a methylol urea, methylol melamine, or ketone aldehyde, specific examples of which are dimethylol urea, dimethylol melamine, methylated dimethylol melamine, dimethylol ethylene urea, urea formaldehyde, sesquimethylol urea, and dimethylol acetone.

It is further contemplated according to the invention that these compounds be employed in the precondensate or partially condensed form, rather than using the constituents merely capable of yielding such precondensates, for the reason that a compound such, for example, as free formaldehyde, if present in the impregnating solution, will preferentially react with the polyvinyl alcohol, thereby precluding or at least impairing the type of reaction product desired to be present on the fabric after curing, i. e., the co-polymer of the polyvinyl alcohol and the aldehyde precondensate.

The aldehyde compounds, although preliminarily condensed, so to speak, are nevertheless relatively readily reactable with polyvinyl alcohol, and with this consideration in mind, one aspect of the invention contemplates preparation of the impregnating solution from a substantially completely hydrolyzed polyvinyl alcohol (most desirably above about 90% hydrolyzed) and application of

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the solution to the fabric in accordance with the technique described herebelow, in order to ensure co-polymerization of the two resinous constituents in and on the fibers of the fabric, rather than at an earlier stage of the processing.

It is here pointed out that it is of importance to effect complete dissolution of the polyvinyl alcohol in the aqueous medium of the impregnating solution, but that with the substantially completely hydrolyzed polyvinyl alcohol (which is highly reactive with respect to the aldehyde precondensates), dissolution of the polyvinyl alcohol can only be effectively attained at relatively high temperatures such that, if the aldehyde precondensate is also present, interreaction will tend to occur, and in addition, the molecules of the precondensate would also tend to further polymerize, both of which effects result in the impairment of the desired ultimate reaction of the polyvinyl alcohol and precondensate on the fabric itself.

With all of the foregoing in mind, the invention contemplates initially dissolving the substantially completely hydrolyzed polyvinyl alcohol in a portion of the aqueous medium to be employed in making up the impregnating solution and the effecting of the dissolution of the polyvinyl alcohol at an elevated temperature, preferably above 185° F. After complete solution of the polyvinyl alcohol has been obtained, this portion of the impregnating solution is cooled, preferably to a temperature below 125° F., whereupon it is intermixed with an aqueous solution of the aldehyde precondensate, together with such other constituents as may be desired in the impregnating solution, for example, as a textile softener, a textile lubricant, or the like.

In formulating the impregnating solution from substantially fully hydrolyzed polyvinyl alcohol, the amount of polyvinyl alcohol in relation to the amount of the aldehyde precondensate may be varied over a wide range. Thus the polyvinyl alcohol may be used in an amount substantially equal to the amount of the aldehyde precondensate, or may comprise only a minor fraction of the amount of the precondensate, even down to 1 part of polyvinyl alcohol to 125 parts of the precondensate.

In the preferred practice of this aspect of the invention, where a solution pick-up of 60% to 70% is employed, the solution is prepared to contain a concentration of from .1% to about 3% of the polyvinyl alcohol and from about 3% to about 12.5% of the aldehyde precondensate, both by weight of the total solution.

The solution is then applied to the fabric while still at a temperature below about 125° F., for instance, by padding, and after impregnation, the fabric may be squeezed to yield a solution pick-up of from about 60% to 70% by weight of the fabric.

Other processing or finishing steps may then be employed, such as calendering, but whether or not such other processing steps are employed, the fabric is ultimately heated to effect co-polymerization of the polyvinyl alcohol and of the aldehyde precondensate in and on the fibers of the fabric. At the time of curing, the total amount of the precondensate and polyvinyl alcohol resin solids on the fabric should be between about 2% and 10% by weight of the fabric.

The curing is preferably effected by subjecting the fabric to a temperature of from about 250° F. to about 450° F. for a time of about 10 minutes to 1 minute.

During the curing, a catalyst promoting interreaction of the polyvinyl alcohol and the aldehyde precondensate should also be present. Such a catalyst is desirably incorporated in the impregnating solution and, if the conditions of preparation of the solution and its use, as described above, are observed, such presence of the catalyst in the impregnating solution will not impair the desired ultimate result, i. e., the co-polymerization of the resinous constituents.

ents on the fabric. However, as disclosed in U. S. Patent No. 2,242,218 and British Patent No. 450,225, the catalyst can be introduced in a separate operation.

Examples of catalysts which may be used are ammonium thiocyanate, stearamidomethyl pyridinium chloride, and 2-amino-2-methyl-1-propanol hydrochloride. Various other catalysts which are known in the art to promote condensation reactions of this general type may be used. These may be either acidic or alkaline, depending upon the nature of the resin precondensate employed.

By operating according to the foregoing technique, the invention assures that co-polymerization of the substantially fully hydrolyzed polyvinyl alcohol and the aldehyde precondensate is effected on the fabric itself, and I have found that maximizing this co-polymerization in this way minimizes the total quantity of resinous constituents which need be applied to the fabric to secure given finishing results, especially with respect to the durability of the finish effect. This is of advantage since, in general, the use of increasing quantities of resinous constituents tends to tender or weaken the fabric.

Moreover, the technique of the present invention also substantially completely overcomes the tendency for the development in the impregnating solution, on the impregnated fabric, and on fabric handling and finishing equipment, such as calender rolls, of granular deposits of partially polymerized resinous constituents or of interreaction products of the polyvinyl alcohol and the aldehyde precondensate.

Figure 1 schematically illustrates this aspect of the invention.

As schematically illustrated in Figure 2, another aspect of the invention is especially concerned with production of durable calender finish effects, and particularly with calendering operations employing so-called high pressure calenders.

This aspect of the invention is also applicable to woven or knitted textile goods made of cellulosic materials, particularly cotton, regenerated cellulose, linen, and mixtures thereof.

It is known in the production of calender finishes that durability may be imparted if the fabric is impregnated with certain resins or resinous materials, prior to the calendering operation, such resinous materials being cured or set to thereby retain the finish effect.

This aspect of the invention has several general objectives in view, including making possible the attainment of a given type of high pressure calender finish effect of high durability with less total resinous materials on the fabric. This is important since the presence of the resinous materials cured on the fabric has a tendency to weaken the fabric.

In addition, it is common in most prior calender finishing operations to preliminary size the fabric by applying thereto some agent adding stiffness or body to the fabric. In accordance with the present invention, such pre-sizing is not needed, since the process of the present invention, especially by virtue of the selection and application to the fabric of certain particular resinous materials, produces a fabric of good hand and body, notwithstanding the absence of presizing.

The foregoing and other objects and advantages of this aspect of the invention will appear more fully from the following description in which reference is first made to a typical or illustrative operation according to the invention.

A woven cotton fabric, for example, 80/80-3.50 yd./lb., in the "pure" state, i. e., without pre-sizing materials to stiffen or add body to the fabric, is first impregnated with an aqueous solution containing the finishing agents to be permanently retained by the fabric. According to the invention, this impregnating solution contains certain interreactable resinous finishing constituents, as defined more fully hereinafter, the fabric is then dried to a moisture content below a value referred to herebelow. The dried

fabric is then passed to and through a high pressure calender, for example, a schreiner calender, following which the fabric is heated to cure or set the resinous materials, in this instance to effect copolymerization of the interreactable constituents present in the impregnant.

With the foregoing general outline of the processing procedure in mind, attention is now directed to various criteria and conditions which are to be observed in the practice of this aspect of the invention.

First with respect to the "pure" state of the fabric referred to above, the invention contemplates application of the several treatment steps to a fabric which has been subjected to the usual treatments employed in preparation of the fabric for finishing, except for the omission of the pre-sizing with stiffening agents. Thus, in preparing the fabric, it is subjected to singeing, usually also to a de-sizing operation to remove starch or lubricant applied during weaving or the like. Scouring is usually also used to saponify and remove waxes and oils. The fabric is also usually bleached and may be either dyed or undyed. The reference herein to "pure" fabric refers to fabric prepared by application of these known treatment steps.

The pure fabric is then impregnated with the aqueous impregnating solution containing the interreactable resinous constituents above mentioned.

With respect to the polyvinyl alcohol to be employed, it is preferred to utilize a polyvinyl alcohol having a degree of hydrolysis of at least about 50%. If the polyvinyl alcohol used is the highly reactive, substantially fully hydrolyzed (e. g. over about 90%) form which can only be dissolved at relatively high temperatures, the solution should be prepared and applied as previously described. The more soluble, less reactive forms of polyvinyl alcohol can of course be incorporated in the solution in the usual manner. Further, in connection with the polyvinyl alcohol constituent, it is to be observed that it is essential to employ polyvinyl alcohol itself, because various other alcohol compounds do not afford the multiple hydroxyl groups which are essential to effect the formation of the co-polymer with the aldehyde precondensate also employed.

In formulating the impregnating solution for use in calender finishing operations, the amount of the polyvinyl alcohol should be from about 33% to about 0.8% of the amount of the aldehyde precondensate present. For an impregnating operation when 60 to 70% solution pick-up is used, the resinous precondensate should be employed in an amount from about 3% to about 12.5% by weight of the solution, and the polyvinyl alcohol should be employed in an amount from .1% to 1% by weight of the solution. However, as is well understood in the art, if it is desired to operate in a different pick-up range, the solution concentration should be varied so as to provide the fabric with a total resin solids concentration of from about 2% to about 8% of the weight of the fabric.

Other constituents may also be present in the solution, but it is preferred that the sum of the precondensate and the polyvinyl alcohol should constitute at least 90% by weight of the interreactable constituents of the solution. Moreover, it is further preferred that the sum of the precondensate and the polyvinyl alcohol should constitute at least the major part of the total of those finishing agents incorporated in the solution which are to be retained permanently on the fabric. These limitations are of importance in order to ensure that the influence and effect of the co-polymer to be produced on the fabric predominates, and is not impaired by adverse influences such as have been encountered heretofore.

After formulation of the impregnating solution, it should be retained at a temperature below 125° F. and should be applied to the fabric without elevation of temperature beyond about 125° F. in order to minimize formation of the co-polymer until after the mechanical finishing has at least been initiated, i. e., until the goods

enter the calender. This is most important where the substantially fully hydrolized form of polyvinyl alcohol is used.

The impregnation of the fabric with the prepared solution may be effected by any of the well known impregnating techniques, for instance, by padding.

Following the impregnating operation, the fabric is desirably subjected to a drying operation of sufficient extent to reduce the moisture content of the fabric to below 14% by weight, and the fabric should be fed to the calender at a moisture content below the 14% limit just mentioned. In the preferred operation according to the invention, the fabric, at the time it is fed to the calender, should have a moisture content of from between 7% to 14%. It is important not to exceed a moisture content much above 14% because under those conditions, resinous constituents may be squeezed out of the fabric and onto the rolls of the high pressure calenders here contemplated for use. It is desirable not to reduce the moisture content much below 7% because there is a possibility of prematurely initiating co-polymerization of the interreactants mentioned prior to calendaring unless some moisture is present to prevent excessive rise in temperature. As will be pointed out hereinafter, when a fragile fabric is to be calendered, "a generally higher moisture content" should be utilized.

At the time of feeding the fabric to the calender, it is preferred that the total amount of the aldehyde precondensate and the polyvinyl alcohol resin solids be from about 2% to about 8% by weight of the fabric.

The invention, as already mentioned, is particularly concerned with treatments involving calendaring by means of high pressure calenders, i. e., calenders operating at a roll pressure upwards of about 10 to 15 tons, this pressure being calculated by addition of the pressure applied to the roll bearings, at the two ends of the roll.

Calenders of the high pressure type operate at roll pressures running up from about 15 tons to well above 100 tons, and include such calenders as glazing calenders, schreiner calenders, chasing calenders, rolling calenders, and embossing calenders.

With the high pressure calenders generally, and especially with certain of them, the high pressure has a tendency to increase the stiffness or boardlike character of the finish, but I have found that by maintaining the content of the polyvinyl alcohol at a relatively low value, preferably below about 1% of the impregnating solution (based on 65% solution pick-up), desirable fabric finishes may be obtained with the use of high pressure calenders, even where the pressure is very high and even when employing certain particular types of calenders which heretofore have a tendency to undesirably exaggerate the stiffness of the fabric. This is especially true with respect to the schreiner calender, which is operated above a roll pressure of about 25 tons, and when employing the schreiner calender the invention contemplates limiting the polyvinyl alcohol content of the impregnating solution to a maximum of about .5% (with 65% solution pick-up).

It is here further pointed out that when operating according to the invention, high pressure fabric finishes of good hand and of a given degree of durability may be obtained with appreciably less total content of resinous constituents in the impregnating solution and on the fabric than has been possible heretofore where resinous precondensates alone have been employed in the impregnating solution.

With respect to the heating to be applied in order to cure or set the resinous constituents, it is first noted that it is important according to the present invention that the polyvinyl alcohol and also the aldehyde precondensate be present in form or state capable of ready interreaction during the heating operation. Thus, for this purpose, it is not only of importance to employ polyvinyl alcohol having a degree of hydrolysis of at least about 50%, but

also to employ aldehyde precondensates which are not condensed to an extent impairing ready reactivity with the polyvinyl alcohol.

In many processes heretofore known for the resin treatment of textile fabrics, it has been regarded as permissible to use materials which will react to form a precondensate. Thus for example, urea and formaldehyde have been regarded as being the full equivalent of a urea-formaldehyde precondensate. That is not true of the present operation. If substantial quantities of free formaldehyde are present, the formaldehyde will preferentially react with the polyvinyl alcohol to produce an insoluble reaction product and thereby preclude pro tanto the formation of the co-polymer which is the intended reaction product of the present invention.

With further reference to the heating, it should be kept in mind that at least some of the heating to effect co-polymerization of the polyvinyl alcohol and the aldehyde precondensate may occur during the calendaring operation itself, especially in the case of chasing calenders, or other equipment in which the fabric requires some appreciable time to pass therethrough and in which elevated temperatures are employed. Similarly, in the case of certain friction glazing treatments where the fabric is passed through the glazer a plurality of times, at least some appreciable extent of the desired co-polymerization may occur during the calendaring operation itself and, in fact, depending upon the operating conditions and the number of passes through the equipment, it is even possible to substantially completely co-polymerize or set the resinous constituents without the necessity for applying a subsequent and separate heat treatment.

Regardless of the manner in which the heating is effected, it is desirable that the fabric be subjected to a temperature of from about 250° F. to about 450° F. for a time of about 10 minutes to 1 minute.

Other ingredients may be added, in conventional amounts, to the solution, such as a conventional textile softener, a conventional textile lubricant (or a softener which is also a lubricant), depending upon the particular hand and feel desired and/or to lubricate calender surfaces. A conventional textile water repellent may also be added. Where such an additional ingredient is employed, I may use Zelan (stearamido-methyl pyridinium chloride, manufactured by E. I. du Pont de Nemours & Co., Wilmington, Delaware) along with the polyvinyl alcohol and the aldehyde precondensate for the reason, among other things, that the Zelan in this process is a catalyst, a softener, a water repellent, and a lubricant.

The use of a lubricant is particularly desirable in certain operations, especially where a calender, such as a glazing calender, is employed in which a roll surface is caused to slip on the surface of the fabric.

Among the various treatment conditions and factors of importance in achieving the various objectives already mentioned, the co-polymerization of the polyvinyl alcohol and the aldehyde precondensate on the fabric itself is of great importance. Certain of the reasons for this are brought out just below.

Polyvinyl alcohol will not itself insolubilize or lose its dispersibility on curing. Generally considered, it is a long carbon chain with hydroxyl or other groups attached to every second carbon, the number of hydroxyl groups depending on the degree of hydrolysis. One of the functions of the aldehyde precondensate is to insolubilize or destroy the dispersibility of the polyvinyl alcohol by forming a co-polymer therewith on curing.

It may also be mentioned that polyvinyl alcohol alone or in percentages substantially above 1% would tend to give a leathery hand which would be destroyed on washing, whereas the aldehyde precondensate alone would normally tend to give a somewhat brittle hand. With the co-polymer which is formed on curing, there is a tendency for these two constituents to modify one another so as to give a somewhat tough but flexible hand,

not brittle or harsh. The polyvinyl alcohol is a mixture of molecules of various sizes, only the smaller ones of which will enter into the fibers of the fabric. On the other hand, the aldehyde precondensate comprises relatively small molecules, a large proportion of which will enter into the fibers of the fabric. The co-polymer formed will, therefore, be partly within and partly on the surface of the fibers. In any event, the co-polymer provides a high degree of durability of the mechanical finish effect contemplated according to the invention. It has been supposed that direct reaction with the aldehyde precondensate with the cellulose may also occur, for instance, by replacement of some hydroxyl groups of the cellulose and a cross-linkage between cellulose molecules, but whatever may be the actual mechanism of the reaction, the effect is to render the cellulose non-swelling to water, and to provide highly durable finishes.

As schematically illustrated in Figure 3, still another aspect of this invention relates to the production of durable finish effects on fabrics and is especially concerned with the production of effects on fragile fabrics made of cellulosic materials, particularly cotton, regenerated cellulose, linen and mixtures thereof. What are herein referred to as fragile fabrics are fabrics of relatively light weight per square yard, i. e., weighing not more than about 4 ounces per square yard, and especially those weighing less than 2.5 ounces per square yard, examples of such fragile fabrics being voile, mouseline, lawns, etc.

It has been known in various fabric finishing operations, such as, for example, crease proofing, calendering, etc., to apply to the fabric certain resinous materials for the purpose of fixing and rendering durable the finish effect. Various of the prior art finishing techniques, while resulting in a relatively durable effect, have a tendency to weaken or tender the fabric. This weakening effect tends to increase with the quantity of resinous material applied to the fabric, and I have found that this is especially true with respect to fragile fabrics of the kind above mentioned.

According to this aspect of the present invention, the particular interreactable resinous materials previously described are used in combination and I have found that thereby a given degree of durability of the finish applied to fragile fabrics may be obtained with considerably smaller total quantities of resinous materials applied, in view of which a given degree of durability may be obtained with much less tendering or weakening of the fabric than has been possible heretofore.

In cases where it is desired to impart a mechanical finish effect to fragile fabrics, there has heretofore been a tendency, especially with certain of the calender effects, for example, glazing (where roll slippage is present) for the fabric to be damaged, as by excessive distortion of the weave or even tearing or chewing the fabric. In accordance with the present invention, however, when employing the combination of resinous materials contemplated, it is practicable and preferred to employ a somewhat increased moisture content in the fabric at the time of the calendering, and as a result of this the tendency to damage the fragile fabric by the calendering operation is greatly reduced.

In a typical illustrative treatment according to this aspect of the invention, a cotton lawn weighing about 2½ ounces per square yard is impregnated with a solution containing a water soluble resinous precondensate and polyvinyl alcohol, together with a catalyst. The impregnated fabric is dried to a moisture content below about 20% by weight of the fabric and while the fabric is at a moisture content between about 12% and 20%, it is passed to and through a glazing calender. After glazing, the fabric is heated at a temperature and for a time sufficient to effect interreaction of the two resinous constituents and thus form a water insoluble co-polymer in and on the fibers of the fabric.

With certain exceptions, as will be pointed out hereinafter, the foregoing discussion in connection with calender finishing aspects of the invention and with respect to the preparation of the impregnating solution, its components, its application to the fabric, and the ultimate setting of the finish effect, also apply to the application of the invention to the finishing of fragile fabrics.

In formulating the impregnating solution for the finishing of fragile fabrics, somewhat different resin ratios and concentrations are employed. The amount of the polyvinyl alcohol should be from about 33% to about 1.5% of the weight of the aldehyde precondensate present. For an impregnating solution where 60% to 70% solution pick-up is used, the polyvinyl alcohol should be employed in an amount from 0.1% to 1% by weight of the solution, and the resinous precondensate should be employed in an amount from 3% to 6% by weight of the solution.

Following the impregnating operation, the fabric is desirably subjected to a drying operation of sufficient extent to reduce the moisture content of the fabric to below 20% by weight, desirably between 7% and 20%. When calendering is employed, it is preferred to feed the fabric to the calender, at a moisture content of from between 12% and 20%.

At the time of feeding the fabric to the calender, it is preferred that the total amount of the aldehyde precondensate and the polyvinyl alcohol be from about 2% to about 4.5% by weight of the fabric.

Whether or not mechanical finishing is used, the fabric should be heated to effect the interreaction of the resinous constituents in order to form a reaction product of the aldehyde precondensate and the polyvinyl alcohol in and on the fibers of the fabric, as previously described.

Since as previously described, the co-polymer formed will be partly within and partly on the surface of the fibers, it provides a high degree of crease resistance and of durability of the finish effect contemplated according to the invention, notwithstanding the use of relatively small total amounts of resinous materials.

When employing the technique of the present invention, it is possible to obtain a given degree of durability of the finish effect (crease resistance and/or calender finish) with appreciably less total resinous material applied to the fabric, in many cases the reduction being of the general order of 15 to 20%. With such reduction in the total amount of resinous material applied, it is found that weakening of the fabric is greatly reduced in many instances by as much as 25%, i. e., 25% less than has been encountered heretofore with other resinous finishing operations adapted to obtain comparable durability. At the same time, the hand of the fabric is unusually good and quite distinctive.

Various of these improvements contemplated by the various aspects of the invention will be illustrated in examples given hereinafter.

Example I

A dyed cotton fabric having a construction of 80/80 and 4 yards per pound was impregnated with the following solution and thereafter squeezed to provide a solution pick-up of 65% by weight of the fabric:

	Parts
Methylated methylol melamine (100% solids)-----	7½
Polyvinyl alcohol-----	0.5
Aerotex softener H (mixed anionic and cationic long chain resinous fatty acid derivatives)-----	2.8
Ammonium thiocyanate-----	1.2
Ammonia 26° Bé-----	0.5
Water to make 100 parts.	

The fabric was then dried to moistness (about 8% free moisture) and was passed twice through a friction calender operating at a speed of 30 yards per minute,

with the steel rolls heated to 370° F. and a pressure of 25 tons was applied, using a friction ratio of 2.5 to 1. The fabric was then cured at about 265° F. for about 2½ minutes, and was washed and dried.

This treatment provided a fabric having a highly durable, highly glazed mechanical finish, with excellent strength, and of very good hand, notwithstanding the fact that the total resin content employed was very substantially less than what would be required to give similar durability without the presence of polyvinyl alcohol. Moreover, this result was achieved without substantial loss in strength, notwithstanding the fact that the fabric was not pre-sized before the treatment.

Example II

The same fabric as referred to in Example I was treated in the same way as in Example I except that the following impregnating solution was used, instead of that employed in Example I.

	Parts
Methylated methylol melamine (100% solids) -----	6¾
Polyvinyl alcohol -----	0.18
s-Dil 1-(2-stearamidoethyl) urea monoacetate -----	2.5
Methylhydroxypropanolamine hydrochloride -----	1.2
Water to make 100 parts.	

The finish obtained by this treatment was similar to that obtained in Example I, notwithstanding the fact that the polyvinyl alcohol content was much less than in Example I, but in Example II the finish was somewhat softer.

Example III

A dyed cotton fabric having a construction of 80/80 and 4 yards per pound was impregnated in the following solution and squeezed so that the fabric retained a 65% solution pick-up:

	Parts
Methylol melamine (100% solids) -----	5.4
Methylated methylol melamine (100% solids) -----	2.5
Polyvinyl alcohol -----	1.0
Sulfonated castor oil -----	2.1
Methylhydroxypropanolamine hydrochloride -----	1.2
Water to make 100 parts.	

The fabric was then dried to approximately 8% total moisture, and was passed once through an embossing calender operating at a speed of 18 yards per minute, with the steel roll heated to 400° F. and a pressure of 18 tons was applied. The fabric was then cured at about 285° F. for about 2½ minutes.

A very sharply defined pattern was obtained and the finish was permanent, of good hand, strength, abrasive resistance and stabilization against shrinkage. The presence of the polyvinyl alcohol substantially eliminates tendency for the resinous materials to stick on the engraved roll and as a result, sharper definition of the design is obtained than in a similar treatment in the absence of polyvinyl alcohol, even with an increase in the quantity of the aldehyde precondensates.

The treatment of this example was repeated with changes in the type of calender employed, in one instance a shallow engraved embossing calender was used, in another instance a moire calender was used, and in a third instance a schreiner calender was used. Comparable results were obtained in each instance and in no case was there tendency for the resin to stick to the calender rolls, so that the rolls could be run for long periods of times between cleanings.

The treatment above described was repeated with different curing temperatures and times. In one repetition, a temperature of 450° F. and a time of 1 minute was used, and in another instance a temperature of about 250° F. and a time of 10 minutes was used. In all cases the results were comparable.

Example IV

The same fabric was treated in the same manner as in Example III, except that the impregnating solution was as follows:

	Parts
Dimethylolethyleneurea (50% solids) -----	9.3
Polyvinyl alcohol -----	0.36
Tetraalkylquaternary ammonium chloride -----	1.7
Methylhydroxypropanolamine hydrochloride -----	1.2
Water to make 100 parts.	

The results obtained were similar.

Example V

A printed-cotton fabric having a construction of 80/92 and 3.50 yards per pound was impregnated in the following solution and was then squeezed to a solution pick-up of 65%:

	Parts
Methylol melamine (100% solids) -----	5.4
Methylated methylol melamine (100% solids) -----	2.5
Polyvinyl alcohol -----	1.0
Sulfonated castor oil -----	2.1
Methylhydroxypropanolamine hydrochloride -----	1.2
Water to make 100 parts.	

After drying to moistness, the fabric was passed through a chasing calender, the metal rolls of which were heated to about 300° F. and operated at a pressure of substantially 25 tons on the bearings, the calender operating at a speed of 120 yards per minute. After the calendering, the fabric was cured at about 300° F. for about 2½ minutes. A substantially permanent finish of excellent hand and strength with deep seated luster was obtained.

The treatment above described was repeated with different curing temperatures and times. In one repetition, a temperature of 450° F. and a time of 1 minute was used, and in another instance a temperature of about 250° F. and a time of 10 minutes was used. In all cases the results were comparable.

Example VI

An all spun regenerated cellulose fabric 46/40 and 3.50 yards per pound was impregnated in the following solution and squeezed to a solution pick-up of 65%:

	Parts
Dimethylol ethylene urea (50% solids) -----	2.5
Stearamido methylpyridinium chloride -----	1.4
Sodium acetate -----	0.24
Methylhydroxypropanolamine hydrochloride -----	1.2
Polyvinyl alcohol -----	0.36
Water to make 100 parts.	

After drying to moistness, the fabric was passed through a chasing calender, the metal rolls of which were heated to about 300° F., and a pressure of about 25 tons was applied, the speed of the calender being 120 yards per minute. Following the calendering, the fabric was cured at about 300° F. for about 2½ minutes.

A permanent finish was obtained with good full-bodied hand and strength and of good abrasion resistance and stabilization.

Example VII

A linen fabric was impregnated in the following solution and was squeezed to a solution pick-up of 65%:

	Parts
Dimethylol ethyleneurea (50% solids) -----	9.3
Polyvinyl alcohol -----	0.36
Tetraalkylquaternary ammonium chloride -----	1.7
Methylhydroxypropanolamine hydrochloride -----	1.2
Water to make 100 parts.	

After drying to a moisture content approximating 8% total moisture, the fabric was passed once through a calender operating at a speed of 18 yards per minute, with the steel roll heated to about 400° F., and a pressure of

18 tons was applied. After calendering, the fabric was cured at about 285° F. for about 2½ minutes.

This procedure was repeated using several different types of calenders. In one instance a shallow engraved embossing calender was used, in another instance a moire calender, and in a third, a schreiner calender. In all instances a permanent finish was obtained with good full-bodied hand and strength.

Example VIII

A white cotton fabric, 40"-88/80 and 6.9 yards per pound, was impregnated in the following solution and then squeezed to give approximately a 65% solution pick-up:

	Parts
Methylated methylol melamine (100% solids) ----	6
Polyvinyl alcohol -----	0.18
s-Di[1-(2-stearamidoethyl)]urea monoacetate ---	4.1
Methylhydroxypropanolamine hydrochloride ----	1.2
Water to make 100 parts.	

The fabric was then dried to moistness (about 8% free moisture or about 13% total moisture), and was passed twice through a friction calender operating at a speed of 30 yards per minute, with the steel roll heated to 370° F. and a pressure of 25 tons was applied, using a friction ratio of 2.5 to 1. The fabric was then cured at about 265° F. for about 2½ minutes and then washed and dried.

A finish of high glaze was obtained and the fabric had excellent strength being only slightly less than that obtained in Example XI. The abrasion resistance and stabilization were excellent.

Similar permanent finishes with similar strength and other characteristics were secured by the same treatment as here described, except for varying the number of runs through the calender. With only one run through the calender, the gloss was good, though not as high as with two runs, and with three runs through the calender, the gloss was higher than with two. In all cases, the degree of gloss was higher than with a comparable finishing operation employing the other resin constituent in the absence of polyvinyl alcohol.

Example IX

Exactly the same procedure as described above in Example VIII was employed except for a change in the amount of the polyvinyl alcohol in the impregnating solution. In this example .625 part of polyvinyl alcohol were used instead of 0.18 part. The results were comparable to those of Example VIII but the hand was firmer.

Example X

A white cotton fabric, 40"-88/80 and 6.90 yards per pound, was impregnated in the following solution and then squeezed to give approximately a 65% solution pick-up:

	Parts
Methylated methylol melamine (100% solids) ----	3
Polyvinyl alcohol -----	12
Sulfonated castor oil -----	2.00
Methylhydroxypropanolamine hydrochloride ----	1.2
Water to make 100 parts.	

The fabric was then dried and cured in an oven having an atmosphere at approximately 275° F. with a residence time of approximately 2½ minutes. The fabric was then washed and dried.

A very durable crease-resistant finish was obtained with good hand and strength, with good abrasion resistance, and fairly good stabilization.

Example XI

A white cotton fabric, 40"-88/80 and 6.90 yards per pound, was impregnated in the following solution and then squeezed to give approximately a 65% solution pick-up:

	Parts
Methylol melamine (100% solids) -----	4.3
Methylated methylol melamine (100% solids) ----	.8
Urea -----	2.4
s-Di[1-(2-stearamidoethyl)]urea monoacetate ----	.6
Methylhydroxypropanolamine hydrochloride -----	1.2
Polyvinyl alcohol -----	.3
Water to make 100 parts.	

The fabric was then dried and cured in an oven at a temperature of approximately 275° F. with a residence time of approximately 2½ minutes. The fabric was then washed and dried.

A substantially permanent crease-resistant finish was obtained with negligible loss in tensile strength, from substantially 41 warp and 26 filling in the untreated control to substantially 38 warp and 25 filling, representing an exceptionally small strength loss. The tear strength of the fabric actually was increased, from substantially 586 warp and substantially 425 filling in the control, to substantially 611 warp and 480 filling. To obtain a similar substantially permanent finish in the absence of polyvinyl alcohol, the other resin constituent would have to be increased at least 20%, in which case the strength would be approximately 25% less, and the hand would be markedly inferior. The hand or feel obtained in accordance with this example (XI) is quite distinctive, being full-bodied, but nevertheless soft. It will be noted that this finish effect was secured notwithstanding the use of very small amounts of both polyvinyl alcohol and of the other resinous material. The combined effect of these two constituents, which become co-polymerized in and on the fibers of the fabric, thus produces a highly desirable finish with low loss of strength, as compared with a similar treatment employing the other resin constituents in the absence of the polyvinyl alcohol. The stabilization against shrinkage is also substantially as good if not better, and the abrasion resistance is much better than would be obtained in the absence of polyvinyl alcohol but employing a larger amount of the other resinous constituents. The procedure of this example was repeated with variation in curing, temperature and time, with comparative results. Thus in one repetition, the curing was done at a temperature of about 450° F. with a residence time of about one minute; and in another repetition, the curing was done at about 250° F., with a residence time of about ten minutes.

Example XII

Example XI was repeated on a different cotton fabric of the same construction as in Example XI, with the sole exception that the impregnating solution contained 0.625 part of polyvinyl alcohol instead of .3 part.

The crease-resistant finish thus obtained was for all practical purposes permanent; the strength was even better than in Example XI; and the distinctive hand, while of still fuller body, was nevertheless still soft and pleasing. In other respects, the results were comparable to those obtained in Example XI.

Example XIII

The treatment procedure described above in Example XI was applied to the same cotton fabric, but a different impregnating solution was employed, as follows:

	Parts
Dimethylol ethylene urea (50% solids) -----	9.3
Polyvinyl alcohol -----	0.36
Tetraalkylquaternary ammonium chloride -----	1.7
Methylhydroxypropanolamine hydrochloride -----	1.2
Water to make 100 parts.	

The results were, in most respects, very similar to those obtained in Example XI, but the stabilization against shrinkage was even better.

Example XIV

The procedure of Example XI fully described above was repeated but applied to a dyed cotton fabric having a construction of 80/80 and 4 yards per pound. Similar results were obtained.

Example XV

The procedure of Example XII fully described above was repeated but applied to a dyed cotton fabric having a construction of 80/80 and 4 yards per pound. Similar results were obtained.

Example XVI

The procedure of Example XIII fully described above was repeated but applied to a dyed cotton fabric having a construction of 80/80 and 4 yards per pound. Similar results were obtained.

In all of the foregoing examples, the polyvinyl alcohol is at least 50% hydrolyzed, and polyvinyl alcohol which is substantially completely hydrolyzed can be used provided the previously described special techniques for the preparation and application of impregnating solutions prepared from such grades of polyvinyl alcohol are observed.

This application discloses and claims subject matter disclosed in applicant's pending applications as follows: Serial No. 287,590, filed May 13, 1952; Serial No. 294,491, filed June 19, 1952; Serial No. 296,090, filed June 27, 1952; Serial No. 647,191, filed March 20, 1957; or Serial No. 647,194, filed March 20, 1957.

I claim:

1. In the art of applying textile finishing agents to and fixing such agents on textile fabrics, the method for effecting co-polymerization on a cellulosic fabric of inter-reactable finishing agents consisting essentially of polyvinyl alcohol and a water-soluble aldehyde resin precondensate, which method comprises dissolving polyvinyl alcohol, at least 90% of which is hydrolyzed, in water at a temperature between about 185° F. and 212° F., cooling the polyvinyl alcohol solution thus formed to a temperature below about 125° F., intermixing the cooled solution with a water-soluble aldehyde resin precondensate selected from the group consisting of methylol ureas, methylol melamines and ketone aldehydes, the quantities of the intermixed resins providing a solution in which the ratio of polyvinyl alcohol to said precondensate is from 1:1 to 1:125, maintaining the resin solution at a temperature below about 125° F. until it is applied to the fabric, applying the solution to deposit on the fabric from 2 to 10% total resin solids by weight and after application of said solution to the fabric, heating the fabric in the presence of a catalyst at a temperature and for a time sufficient to effect the formation of a water-insoluble co-polymer of said inter-reactable finishing agents.

2. In the art of imparting durable mechanical finishes to cellulosic fabrics involving impregnating the fabric with an aqueous solution containing a mixture of resinous finishing agents to be retained by the fabric wherein said resinous mixture includes a water-soluble thermosetting resin precondensate as one resinous component and polyvinyl alcohol as a second resinous component, drying the fabric, calendering the dried impregnated fabric and heating the fabric in the presence of a resin curing catalyst to fix the resinous finishing agents, the improvement characterized in that the polyvinyl alcohol is at least 50% hydrolyzed, the water-soluble thermosetting resin precondensate is selected from the group consisting of methylol ureas, methylol melamines, and ketone aldehydes, the weight ratio of the polyvinyl alcohol to the thermosetting resin precondensate ranges from 1:3 to 1:125, the total combined weight of the polyvinyl alcohol and the thermosetting resin comprises at least

90% of the inter-reactable materials present in the impregnating solution, and comprises the major portion of the finishing agents to be retained by the fabric, the total resin concentration of the impregnating solution and the solution pick-up are adjusted to provide for applying to the fabric a total combined weight of the resin solids of from 2 to 8% of the weight of the fabric and the heating of the fabric is sufficient to effect the formation of a water insoluble copolymer of polyvinyl alcohol and the thermosetting resin.

3. A process according to claim 2 and further characterized in that the fabric to be treated is a pure fabric, i. e. substantially free of fabric stiffening sizing materials.

4. A process according to claim 2 and further characterized in that the moisture content of the fabric at the time the fabric is fed to the calender constitutes from 7 to 14% of the weight of the fabric.

5. A process according to claim 2 and further characterized in that the weight of the fabric to be treated runs not more than 4 ounces per square yard; the weight ratio of the polyvinyl alcohol to the thermosetting resin precondensate of the impregnating solution and the solution pick-up are adjusted to provide for applying to the fabric a total combined weight of the resin solids which constitute from 2 to 4.5% of the weight of the fabric; and the moisture content of the fabric at the time the fabric is fed to the calender constitutes from 12 to 20% of the weight of the fabric.

6. In the art of imparting durable finishes to cellulosic fabrics involving impregnating the fabric with an aqueous solution containing a mixture of resinous finishing agents to be retained by the fabric wherein said resinous mixture includes a water-soluble thermosetting resin precondensate as one resinous component and polyvinyl alcohol as a second resinous component, and heating the fabric in the presence of a resin curing catalyst to fix the resinous finishing agents, the improvement characterized in that the weight of the fabric to be treated runs 4 ounces per square yard and less; the polyvinyl alcohol is at least 50% hydrolyzed; the water soluble thermosetting resin precondensate is selected from the group consisting of methylol ureas, methylol melamines and ketone aldehydes, the weight ratio of the polyvinyl alcohol to the thermosetting resin precondensate ranges from 1:3 to 1:67, the total combined weight of the polyvinyl alcohol and the thermosetting resin comprise at least 90% of the inter-reactable materials present in the impregnating solution and comprise the major portion of the finishing agents to be retained by the fabric and the total resin concentration of the impregnating solution and the solution pick-up are adjusted to provide for applying to the fabric a total combined weight of the resin solids which constitutes from 2% to 4.5% of the weight of the fabric and the heating of the fabric is sufficient to effect the formation of a water insoluble copolymer of polyvinyl alcohol and the thermosetting resin.

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