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PROCESS FOR IMPROVING THE PROPERTIES OF REGENERATED CELLULOSE FIBROUS MATERIAL

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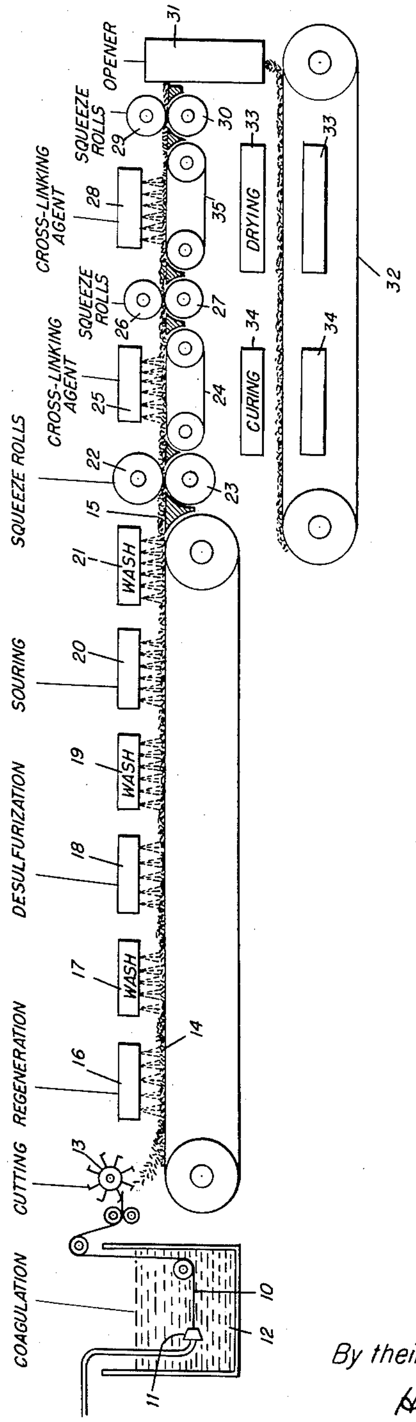

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PROCESS FOR IMPROVING THE PROPERTIES OF REGENERATED CELLULOSE FIBROUS MATERIAL

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This application relates to a new and improved method of cross-linking regenerated cellulose fibrous materials with permanently soluble cross-linking agents.

This application is a continuation-in-part of our application Serial No. 635,695, filed January 23, 1957, and now Patent No. 2,902,391. In that patent a process is described and claimed in which regenerated cellulose fibrous materials are impregnated with heat hardenable resinous materials by a process which comprises treating the fibrous material while it is still in the gel state and before it has ever been dried sufficiently to convert it from the gel state with an aqueous liquid containing the resinous material and then mechanically reducing the liquid content of the treated fiber to less than the normal water imbibition value of the fiber in the gel state.

As pointed out in our earlier application, prior processes for impregnating cellulosic fibers with heat hardenable resins had not been commercially satisfactory because the fibers tended to stick together on drying and curing, making it difficult and often impossible to process the fibers into yarn and cloth. By mechanically reducing the liquid content of the fibers to below the gel imbibition value in accordance with our prior invention this difficulty is overcome.

The purpose of treating regenerated cellulose fibers with heat hardenable resinous materials is in general to improve the properties of the fiber, particularly by decreasing its water imbibition. This is accomplished by a cross-linking of the cellulose chains through the resin or resin derived groups.

In place of heat hardenable resinous materials, permanently soluble cross-linking agents have been used to improve the properties of regenerated cellulose fibers.

In general these compounds are characterized in having two or more functional groups which are reactive with the hydroxyl groups of the cellulose and in remaining water-soluble when dried and heated to the temperatures required to effect cross-linking of the cellulose.

When such compounds are applied to regenerated cellulose fiber there is no particular problem in keeping the fibers from sticking together, or forming clots, since, although some of them may solidify, these compounds do not form into infusible, insoluble masses upon drying and curing. Thus, there was no apparent reason to use the process of our copending application with these permanently soluble cross-linking agents.

Contrary to what might have been expected, however, it has not been found that fiber of greatly improved quality can be obtained if in impregnating regenerated cellulose material with a permanently soluble, cross-linking agent, the technique described in our copending application as applicable to heat hardenable materials, is used. Thus when our process is used with permanently soluble cross-linking materials, the resulting fibers show better break factors (wet and dry), elongation (wet and dry) and uniformity of dyeing than do identical fibers impregnated by conventional means.

The present invention therefore comprises a method for impregnating regenerated cellulose fibrous material with a permanently soluble cross-linking agent, which comprises treating the fibrous material while it is still in the gel state and before it has ever been dried sufficiently to convert it from the gel state, with an aqueous liquid containing a permanently soluble material and then mechanically reducing the liquid content of the treated fiber to less than the normal water imbibition of the fiber in the gel state.

Following impregnation of the fiber with the cross-linking agent, the impregnated fiber is normally dried and heated at a suitable temperature to effect reaction of the cross-linking agent with the cellulose chains.

As indicated above, the term "permanently soluble cross-linking agent," means a compound which will react with the hydroxyl groups of the cellulose to link two cellulose chains together. It must therefore be polyfunctional, i.e. it must contain at least two functional groups or two labile atoms in the same functional group which will react with the cellulose hydroxy groups. It may be monomeric or polymeric, and it may or may not undergo polymerization under the conditions required for the cross-linking reaction, but if it is a polymer or if polymerization does occur concurrently with or prior to cross-linking, the resulting polymer, though it may be a solid, will normally be linear, rather than three dimensional, and remain water-soluble.

Of course, when we speak of the cross-linking agent or its polymers as remaining water-soluble, we refer to such portions of the agent or of its polymer, as are not linked to the cellulose. Once the agent has reacted with the cellulose, a new molecule is formed which is neither cellulose nor agent and which, of course, is not water-soluble.

Cross-linking agents of the type described are well known in the industry. Many of them are presently used to make so-called "wash and wear" garments, and in other finishing processes. They include, for example, formaldehyde, dialdehydes such as glutaraldehyde and adipaldehyde; hydroxy aldehydes such as hydroxy adipaldehyde; mixed aldehydes such as acrolein; glycidyl aldehydes; polyacetals (including diacetals) of polyhydroxy compounds, for example, the products described in Patent No. 2,786,081 which have been defined as polymeric acetal condensation products of at least one dialkylene glycol in which the alkylene radical has 2 to 4 carbon atoms in a straigth chain and at least one aliphatic monoaldehyde containing 1 to 8 carbon atoms, said condensation products containing, per molecule, at least two dioxyalkylene radicals derived from said dialkylene glycol and at least two alkylidene radicals derived from said aldehyde; divinyl sulfone; dihalohydrins, for example, dichlorohydrin; and di- and tri-aziridinyl phosphine oxides and sulfides such as are described in Patent No. 2,859,134. Also of interest are the so-called reactant type resins. These are heat hardenable resinous materials, but under the conditions required for cross-linking remain water soluble. They include, for example, modified urea resins, i.e. methylol compounds such as methylated methylol urea, methylated and unmethylated methylol ethylene ureas, such as dimethylol ethylene urea, and methylated and unmethylated methylol 1,2-propylene ureas as well as dimethylol triazines, triazones and the like.

Other possible cross-linking agents will readily occur to those skilled in the art.

If desired, mixtures of two or more cross-linking agents may be used. It will be understood that the precise structure of the cross-linking agent is not a part of the present invention, so long as it remains soluble under the conditions required to effect cross-linking of cellulose chains.

It is characteristic of the present process that the regenerated cellulose fibrous material is treated with the cross-linking agent while the fiber is still in the initial gel or swollen state after its formation. It has been discovered that in this initial gel or swollen state, fibers have their highest degree of absorptive power, much higher than at any other time in their existence. Furthermore, it has been found that by reducing the liquid content of the fibers to below their normal water imbibition value in the gel state, there is in effect created a kind of negative pressure inside the fibers. If the fibers have been previously immersed in or contacted with a solution containing a cross-linking agent, they draw the liquid remaining on the fibers after squeezing, evenly into the interior of the fibers.

The absorptive power of regenerated cellulose fiber is measured by what is known in the industry as "the water imbibition value" which is defined as the percent by weight of water retained in saturated material after centrifuging a 0.5 gm. sample for five minutes at 1,000 G and is expressed as percent of the oven-dry weight of the fiber (see Journal of the Society of Dyers and Colorists, October 1948, page 331).

The water imbibition values for once dried normal textile rayon fibers are in the range of 90% to 115%. When fabrics made from such fibers are treated in the usual fashion with cross-linking agents for effects such as crease resistance and dimensional stability, even with the high mangle pressures used in conventional equipment, liquid retention of the padded fabric is in this approximate range. On the other hand, the water imbibition values of never-dried normal textile rayon fibers are in the range of 120% to 150%. It has been found that by squeezing never-dried rayon fiber while still in the gel state it is possible to reduce the moisture content of this material much below the water imbibition range cited. Thus, fibers having a gel water imbibition value of 145% may be squeezed to contain as little as 60% moisture on the oven-dry weight of the fiber. When this is done after the fiber is brought into contact with a cross-linking solution, it acts like a sponge which has newly been squeezed out and evenly draws in the excess liquid.

The invention is applicable to regenerated cellulose made by any of the conventional techniques, i.e. by the viscose, cuprammonium or nitrate processes. However, it is preferred to use regenerated cellulose which has been made by the viscose process.

By certain variations in coagulating and spinning technique, well-known to the art, it is possible to obtain viscose rayon having never dried imbibition values from 60% to say 150%. The lower the water imbibition, the more pressure must be exerted to squeeze the fiber to a liquid content below the water imbibition value. For this reason, while the invention is applicable to fibers of all water imbibition values, best results are obtained from fibers having high gel water imbibition values and especially those having gel water imbibition values of 120% to 150%.

The invention is applicable to all forms of fibrous regenerated cellulose, to both staple and continuous filament fibers. However, it is of particular importance in the treatment of staple fibers.

The cross-linking agent is preferably applied as an aqueous solution containing from about 0.5 to about 20% by weight of the cross-linking agent. The concentration of agent used will depend on the nature of the agent. In general it will vary inversely with the molecular weight of the agent. Thus for a material such as formaldehyde a concentration of say 0.5 to 10% will be sufficient whereas for agents of higher molecular weight, such as dimethylol ethylene urea or glycol acetal, concentrations of say 3 to 20% would normally be used. In order to insure penetration of the agent into the interior of the fiber its molecular weight should not normally be more than about 1000. Obviously there is no minimum molecular weight. Formaldehyde, with a molecular weight of about 30 has the lowest molecular weight of cross-linking agents in general use.

The impregnating solution may contain various ingredients other than the cross-linking agent. For example, it may contain from 2 to 150% on the weight of the agent of a catalyst to aid in carrying out the cross-linking reaction. Obviously the type of catalyst used will depend on the particular cross-linking agent. Moreover, it may be pointed out that the catalyst does not have to be put into the same bath as the cross-linking agent. For example, the cross-linking reaction with certain agents such as divinylsulfone and the chlorohydrins is catalysed by alkali. In such cases the fiber may advantageously be first impregnated with the agent, then squeezed to below its water imbibition and then subjected to a second bath containing the alkali, followed by another squeeze to reduce the liquid content to below the water imbibition value. In some instances the alkali may be applied before the cross-linking agent.

In addition to a catalyst and the cross-linking agent the impregnating liquid may contain from 0.1% to 4% on the weight of the liquid of a finishing agent. The finishing agent may be selected to add lubricity, cohesion, water repellancy, scroop or other desired properties to the fiber. Materials well-known to the art, such as polyglycol stearate, lauryl ketene dimer, silicone emulsions, stearamido methyl pyridinium chloride, octadecyl pyridinium sulfate and others may be used alone or in combination for this purpose.

The temperature of the impregnating solution is not a critical factor and will vary with the particular cross-linking agent being applied. Normally, it will be between about 15° C. and about 50° C., preferably between about 20° C. and about 40° C.

The manipulative steps which are used in carrying out the invention depend to a certain extent upon the form of the fibrous material which is being treated. Thus, a different mechanical technique would be used in applying a cross-linking solution for a continuous filament than would be used in treating staple fiber. Staple fiber is in general treated in the form of a mat or blanket in which the fiber is arranged more or less at random. The thickness of the blanket is, in general, not a critical factor and the process may be employed with blankets of various thickness, although normally the blanket thickness will be between about one-half inch and about two and one-half inches.

The technique used in carrying out this invention is to pass the blanket between squeeze rollers to remove a large portion of the final wash water, then bring it into contact with the solution containing the cross-linking agent which is usually applied as a heavy spray onto the blanket.

When the blanket has been wet thoroughly with the cross-linking liquid, it is removed between another pair of rollers where it is squeezed to remove excess liquid. This process may be repeated several times to obtain uniform distribution and increase the total pickup of cross-linking agent. While there is no limit on the number of times the contacting step may be repeated, it has been found that four baths are usually sufficient.

The blanket, thoroughly wet with the cross-linking liquid then passes through squeeze rollers adjusted to remove enough liquid from the blanket so that the remaining liquid content is less than the normal water imbibition value of the fiber (in the gel state). In most cases, when the invention is applied to textile grade fibers, the liquid content is reduced to 10 to 65% below the gel water imbibition value which is equivalent to a liquid content of 60% to 120% on the weight of the oven-dry impregnated fiber. The pressure required to accomplish this will vary with the past history of the fiber and with the thickness of the blanket, but will, in general, be between about 500 and about 3500 pounds per linear inch of nip.

A convenient way to determine the liquid content is to weigh the fiber immediately after squeezing and then dry it in the manner outlined below. During drying, water and a certain amount of other volatile material may be driven off. The dried fiber is weighed and the difference in the two weights taken. The liquid content of the squeezed fiber, for purposes of the present invention, may then be calculated as

$$\frac{\text{Weight of squeezed fiber} - \text{weight of dried fiber}}{\text{Weight of dried, treated fiber}} \times 100$$

After passing through the final squeeze rollers, the blanket may be opened by conventional methods, spread on a moving conveyor belt, dried and cured. The temperatures and conditions of drying and curing will depend on the particular agent being employed. However, in general the impregnated fiber will be dried between about 50° C. and about 100° C. for whatever time is required to bring the moisture content of the fiber into equilibrium with its environment. Normally this will be between about 10 and about 45 minutes.

Curing, i.e. the cross-linking reaction, is usually conducted by heating the impregnated fiber at a temperature of between about 110° C. and about 160° C. for between about 3 and about 30 minutes. The precise time and temperature will vary with the particular cross-linking agent being used.

The invention will be further described in connection with the accompanying FIGURE which is a schematic flow diagram illustrating treatment of viscose staple fiber in accordance with the invention.

Referring to the figure, a regenerated cellulose tow **10** is formed in conventional fashion by extruding viscose from a spinnerette **11** into a coagulating bath **12**. The bath **12** may be of any conventional composition comprising, for example, between about 7% and about 12% H_2SO_4, between about 14% and about 25% Na_2SO_4, from 0 to about 8% $ZnSO_4$ and from 0 to about 10% $MgSO_4$. Other ingredients well-known to the art such, for example, as surface-active agents for preventing spinnerette incrustation, may also be present. The temperature of the bath will normally be from say 40° C. to 60° C.

The tow is withdrawn from the coagulating bath **12** and, in accordance with conventional practice, is cut up into staple fiber by a cutting device **13**. The staple falls on a continuous belt **14** and forms a mat or blanket **15** thereon. It may then be subjected to an aqueous spray **16** containing from 1% to 2% H_2SO_4 at a temperature of from 60° C. to 92° C. Following this, it may be given a neutral or slightly alkaline wash **17** (pH 7.5–9.5) at a temperature of say 75° C.–90° C.

Following the neutralizing wash **17**, the blanket may be treated with a desulfurization wash **18** containing from say 0.1% to 0.4% Na_2S at a temperature of between about 55° C. and about 70° C. This wash may also contain up to about .4% of sodium carbonate or sodium hydroxide together with sequestering or wetting agents, if desired.

The desulfurization treatment is then normally followed with a sulfide wash **19** comprising neutral water at 70° C.–90° C. to remove sulfide liquors. In accordance with usual practice, a sour or acid wash **20**, containing between about 0.2% and about 0.5% H_2SO_4 or HCl at a temperature of 20° C.–25° C. is then employed. An additional water wash **21** at a temperature of say 60° C.–85° C. follows to remove acid. The blanket **15** is then squeezed to remove excess water by passing it between squeeze rolls **22** and **23**.

In accordance with the invention the squeezed gel fiber is now passed over another endless belt **24** where it is subjected to an aqueous liquid **25** containing between about 0.5% and about 20% by weight of a permanently fusible cross-linking agent, at a temperature of between about 20° C. and about 40° C. The liquid may also contain a catalyst, the amount of catalyst being in general from about 2% to about 20% on the weight of the resinous material, the exact amount depending upon the concentration and kind of resin used. The liquid may further comprise from say 0.1% to 4% of a finishing agent of any of the types customarily used in the art.

If desired, the blanket can be taken directly from treatment at **25**, squeezed until its liquid content is below the gel water imbibition value and passed to a curing and drying stage. However, in the embodiment of the invention shown in the figure there is an additional impregnation step. Thus the blanket, having been treated at **25**, is again subjected to a squeezing between rollers **26** and **27**, then delivered to another endless belt **35** where it is contacted with additional cross-linking solution at **28**, the solution at **28** being preferably the same as that at **25**. Further cross-linking treatments may be added, as desired, although these are not shown in the figure.

After the final cross-linking treatment the blanket is passed through final squeeze rolls **29** and **30** where it is squeezed with sufficient pressure to reduce the amount of liquid in the fibers to below the water imbibition value of the gel fiber. When the blanket leaves this set of squeeze rolls, substantially all of the liquid and the cross-linking agent dissolved therein is drawn into the fibers leaving only the larger molecular size finishing agents on the surfaces of the fibers. The total liquid in the treated fiber is now between about 60% and 120% on the weight of the oven-dry treated fiber. The blanket is then delivered to a conventional opening device **31** where the blanket is pulled apart. The resulting fibers are delivered to another endless belt **32** which carries them through to a drying oven **33** where they are dried at a temperature which is normally between about 50° C. and about 100° C. The dried fibers are then passed through a curing oven **34** where they are cured at a temperature of say 110 to 160° C.

The fibers obtained from the process have low water inhibition. They may be processed without difficulty on conventional cotton spinning machinery without the danger of excessive fly or breaking of the fibers. The material has a good hand and is altogether satisfactory for all textile purposes. In particular it is evenly treated, so that the variation in water imbibition from fiber to fiber is very low, much lower than with fibers impregnated by other techniques. This permits even dyeing. Moreover, fiber made in accordance with the invention has higher break factor and higher elongation, wet and dry than when other impregnating processes are used.

The invention will be further described in reference to the following specific examples. It is understood that these examples are given for purposes of illustration only and are in no way intended as restricting the invention beyond the scope of the appended claims.

Example I

A blanket of 1½ x 1⅜₁₆ bright never-dried regenerated cellulose staple fiber still in the gel-state and having a water imbibition value of 127% was squeezed between pressure rolls to a liquid retention of 100% on the weight of the oven-dried cellulose. The blanket was 2½" thick and the pressure of the rolls was 700 pounds per lineal inch of nip. The squeezed blanket was then passed under a spray of an aqueous solution containing 12% of Kaurit G (an aqueous solution containing 50% of a glutaraldehyde-urea precondensate in which the mol ratio of glutaraldehyde to urea is about 2:1, sold by the Putnam Chemical Co.), 1.2% magnesium chloride hexahydrate catalyst and 0.4% of a polyglycol stearate softening agent. The impregnation was carried out in two stages with an intermediate light squeeze and a final heavy squeeze between pressurized roll (750 pounds/lineal inch or 60 pound gauge pressure) to a final liquid retention of 80% on the oven-dry weight of the cellulose.

The fibrous blanket was then opened and dried at a temperature of 200° F. and cured at a temperature of 310° F. for 7 minutes.

The water imbibition values of four random samples of the product were 53, 52, 55, 51, respectively.

The fiber dyed uniformly without dark or light spots with 2% Sky Blue FF direct dyestuff. It processed without difficulty to yarn which had the following properties:

Single strand dry break factor[1]	264
Single strand dry elongation .... percent	13.4
Single strand wet break factor	163
Single strand wet elongation .... percent	16.6
Skein break factor	2187

The yarn produced a strong fabric with uniform dyeing properties.

The above experiment was repeated using the same bath reduced in concentration by dilution with water to give the equivalent pickup of Kaurit G at increased wet pickup resulting from reduced squeeze pressure. The final squeeze roll pressure was reduced (10 pound gauge pressure) to give a wet pickup of 130%.

As expected, there were no stuck fibers; however, random samples of the product had water imbibition values of 95, 48, 79, 69%, respectively. As would be expected from these values, dyeing was grossly non-uniform. While the sample was processable, the yarn (20/1) was uneven and had the following properties:

Single strand dry break factor	243
Single strand dry elongation .... percent	11.5
Single strand wet break factor	151
Single strand wet elongation .... percent	14.2
Skein break factor	2035

The fabric was also uneven, weak, and dyed non-uniformly.

Example II

The procedure of Example I was followed to treat textile grade gel-state cellulose staple fiber with a solution containing 8% of 1,3-dimethylol, 5-ethyl perhydrotriazone, 1.6% (Rohm and Haas) catalyst H-7 (buffered zinc nitrate solution) and 0.4% of a polyglycol stearate softener. The final squeeze pressure was 750 pounds/lineal inch (60 pound gauge pressure). The impregnated blanket was squeezed sufficiently to reduce the liquid content to 80% on the weight of the cellulose. The treated fiber blanket was opened, dried and cured as before.

Random samples had water imbibition values of 42, 44, 43, 42%, respectively, and the fiber dyed uniformly.

Processing to 20/1 yarn was accomplished without difficulty and the yarn had the following properties:

Single strand dry break factor	252
Single strand dry elongation .... percent	12.4
Single strand wet break factor	151
Single strand wet elongation .... percent	14.2
Skein break factor	2270

The procedure of the above experiment was repeated except that the final squeeze roll pressure was reduced to 10 pounds (gauge) or approximately 250 pounds/lineal inch to give a wet pickup of 135%.

Random samples of the fiber product had water imbibition values of 48, 36, 52, 39%, respectively, and dyed unevenly with direct or acid dyestuffs. The fiber processed with some difficulty to 20/1 yarn and had the following properties:

Single strand dry break factor	207
Single strand dry elongation .... percent	10.2
Single strand wet break factor	138
Single strand wet elongation .... percent	12.5
Skein break factor	1576

A weak fabric with uneven dyeing properties was produced from this yarn.

Example III

The experiment in Example II was repeated using an

impregnating liquid containing 6% by weight of the same cross-linking agent, with squeeze pressures adjusted to give 90% wet pickup and 140% wet pickup using 700 pound and 200 pound/lineal inch pressure, respectively. The following results were obtained:

	700 pound squeeze	200 pound squeeze
Fiber water imbibition values, percent	47, 47, 48, 47	36, 42, 49, 52
Yarn single strand dry break factor	285	219
Yarn single strand dry elongation, percent	13.0	12.0
Yarn single strand wet break factor	189	152
Yarn single strand wet elongation, percent	15.1	13.4
Skein break factor	2,421	1,775
Dyeing	Even	Uneven

Example IV

The procedure of Example I was followed to treat textile grade gel-state regenerated cellulose staple fiber (water imbibition value of 128%) with a solution containing 8% of an N,N-dimethyl, tetramethylol triazine precondensate, 1.2% magnesium chloride hexahydrate and 0.4% of a polyglycol stearate softener. The final squeeze pressure was adjusted to give a liquid content in the blanket of 80% on the weight of the cellulose. The squeeze roll pressure was reduced for a second sample to give a liquid content of 130% on the weight of the cellulose.

The samples were opened, dried and cured as before. The following results were obtained:

	Heavy Squeeze	Light Squeeze
Wet pickup, percent	80	130
Fiber water imbibition value range, percent	47–51	40–49
Yarn single strand dry break factor	266	203
Yarn single strand dry elongation, percent	13.0	10.2
Yarn single strand wet break factor	177	140
Yarn single strand wet elongation, percent	14.5	12.5
Skein break factor	2,266	1,495
Dyeing	Even	Uneven

Example V

The experiment in Example IV was repeated at reduced levels of triazine precondensate concentrations. Again, heavy and light squeeze pressures were used to make two samples. To insure that the same amount of cross-linking agent would be taken up with both light and heavy squeezes, the liquor used with the heavy squeeze contained 7% agent and that used with the light squeeze, 6% agent. The following results were obtained:

	Heavy Squeeze	Light Squeeze
Wet pickup, percent	80	130
Fiber water imbibition value range, percent	47–50	40–61
Yarn single strand dry break factor	258	223
Yarn single strand dry elongation, percent	12.1	11.3
Yarn single strand wet break factor	189	154
Yarn single strand wet elongation, percent	14.6	13.3
Skein break factor	2,219	1,718
Dyeing	Even	Uneven

Example VI

The procedure of Example I was followed to treat textile grade, gel-state regenerated cellulose staple fiber (water imbibition value 128%) with a solution containing 9% dimethylol ethylene urea, 1.35% magnesium chloride hexahydrate and 0.4% of a polyglycol stearate softener. The final squeeze pressure was adjusted to give a liquid content in the blanket of 84% on the weight of the cellulose. The squeeze roll pressure was reduced for a second sample to give a liquid content of 130% on the weight of cellulose.

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[1] Break factor is the cotton count of the yarn times the breaking load in ounces.

The samples were opened, dried and cured as before. The following results were obtained:

	Heavy Squeeze	Light Squeeze
Wet pickup, percent	84	130.
Fiber water imbibition value range, percent.	36–43	33–74.
Yarn single strand dry break factor	173	Would not process to yarn-excessive fly, brittle fibers.
Yarn single strand dry elongation, percent.	8.9	
Yarn single strand wet break factor	133	
Yarn single strand wet elongation percent.	11.7	
Skein break factor	1,336	
Dyeing	Even	Uneven.

Example VII

The experiment in Example VI was repeated at reduced levels of dimethylol ethylene urea concentrations. Heavy and light squeeze pressures were used to make two samples. To assure equal quantities of cross-linking agent being retained by the fiber, a solution containing 8% of cross-linking agent was used with the heavy squeeze and a 7% solution was used with the light squeeze. The following results were obtained:

	Heavy Squeeze	Light Squeeze
Wet pickup percent	81	132.
Fiber water imbibition value range, percent.	42–47	35–52.
Yarn single strand dry break factor	225	Would not process, excessive fly, brittle fibers.
Yarn single strand dry elongation, percent.	11.0	
Yarn single strand wet break factor	135	
Yarn single strand wet elongation, percent.	12.4	
Skein break factor	1,885	
Dyeing	Even	Uneven.

Example VIII

The procedure in Example I was followed to treat textile grade, gel-state 3 denier crimped, regenerated cellulose staple fiber (water imbibition value 130%) with a solution containing 3.5% formaldehyde, 3.5% magnesium chloride hexahydrate and 0.5% of a polyglycol stearate softener. The final squeeze pressure was adjusted to give a liquid content of 75% on the weight of the cellulose. The impregnated blanket was passed through an opener. The opened fiber was laid down on a conveyor which passed through a drier set at 180° F. and then through a cure zone at 320° F.

A separate sample was produced with reduced squeeze roll pressure which gave a liquid content of 135% on the weight of the cellulose.

The sample which had been squeezed below the gel-state water imbibition value had a water imbibition range after treatment of 34–37%, uniform dyeability and good processability. The sample which had been squeezed to a liquid content which was higher than the gel-state water imbibition value, had a water imbibition range after treatment of 32–50%, dyed non-uniformly and gave difficulties during processing because of brittle fibers and excessive fly. The treatment of cellulose with formaldehyde and curing agents such as magnesium chloride is claimed in the copending application of Daul et al. Ser. No. 81,956, filed January 11, 1961.

Example IX

The procedure in Example I was followed to treat textile grade, gel-state 1½ denier regenerated cellulose staple fiber (water imbibition value 127%), with a solution containing 4% of an acetal of ethylene glycol (Quaker Chemical Company, Reactant 53), 2% magnesium chloride hexahydrate and 0.4% of a polyglycol stearate softener. Two samples were produced using squeeze pressures designed to give 85% wet pickup in one and 135% wet pickup in the other sample. The samples were opened, dried and cured as in the previous examples. The sample which had been squeezed to 85% liquid retention (i.e., below the never-dried water imbibition value) dyed uniformly, had a water imbibition range of 54–56% and processed satisfactorily to make strong, even yarns and good fabric.

The sample which had a liquid content in excess of its gel-state water imbibition value, had a water imbibition range of 50–65% and dyed non-uniformly. Processability was poor, and weak, uneven yarn was produced.

We claim:

A method for cross linking regenerated cellulose fiber which consists essentially of impregnating a mass of said fiber while said fiber is still in the gel state after spinning and before it has ever been dried sufficiently to convert it from the gel state, with a liquid consisting essentially of water, formaldehyde and a catalyst for the cross linking reaction, squeezing the impregnated mass of fiber until the liquid content is between about 60 and about 120%, based on the weight of oven dry impregnated fiber and less than the water imbibition of the fiber in the gel state, and drying and curing the impregnated material to cross link the cellulose.

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