

UNITED STATES PATENT OFFICE

2,101,263

CONTINUOUS PREPARATION OF CELLULOSE
DERIVATIVES

Robert W. Maxwell, Wilmington, Del., assignor
to E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

No Drawing. Application August 1, 1935,
Serial No. 34,133

19 Claims. (Cl. 260—152)

This invention relates to the manufacture of cellulose ethers and particularly to a continuous process therefor.

Heretofore the preparation of cellulose ethers has been confined to the action of etherifying agents on alkali cellulose in a loose or shredded state. These customary preparations of cellulose ethers from alkali cellulose are slow, expensive and inconvenient. It is necessary to steep the cellulose, press, shred, age, and then effect reaction in a shredder, barratte, autoclave, or other apparatus. Each of these are separate operations requiring large pieces of apparatus and extensive floor space. The mixing in the reaction vessel is generally poor and leads to a non-uniform product especially when low degrees of substitution are sought. While it has been proposed to etherify alkali cellulose in the form of pulp board by the action of gaseous etherifying agents, this method requires a gas tight reaction vessel and a careful separation of the pulp sheets to permit contact with the gas. Penetration of the gas into the alkali cellulose sheet is necessarily slow and is attended by poor uniformity. In addition, non-volatile etherifying agents are obviously not applicable.

While U. S. Patent 1,736,714 to Lilienfeld discloses the treatment of spun or woven fabric of cotton with etherifying agent in the presence of alkali, this process is contraindicative to the process of the present invention, and it would not be expected from the success of that process that a uniform etherification could be obtained by the present invention, inasmuch as the process of this Lilienfeld patent discloses a method of obtaining a surface effect, therefore an essentially non-uniform effect, on a fabric.

This invention has as an object the preparation of cellulose ethers from alkali cellulose in a simplified manner. A further object is a process whereby cellulose ethers of greatly improved uniformity are prepared from alkali cellulose. A still further object is a process for the preparation of improved low substituted cellulose ethers. A still further object is a continuous process of cellulose etherification. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein cellulose pulp in the form of individual sheets or a continuous roll is continuously impregnated with alkali, the excess removed and the alkali cellulose then continuously impregnated with a liquid etherifying composition, the excess removed and the impregnated sheet allowed to react. The impregnation with

the etherifying agent may be subsequent to or simultaneous with the impregnation with alkali.

In the simplest, most convenient and most preferred embodiment of the invention, the etherifying agent is dissolved in caustic alkali solution of the desired concentration and cellulose from a roll or in individual sheets is passed continuously through the steeping bath, then through press rolls to remove excess, then stored for a suitable length of time during which the reaction proceeds and thereafter the reaction is stopped by removal of the etherifying mixture, i. e. by washing with water.

This simplest procedure is, however, limited to etherifications with etherifying reagents soluble in and at least moderately stable towards caustic alkali. If the reagent is not stable to caustic alkali it becomes decomposed to an appreciable extent before mixing with the cellulose is accomplished.

In a further, likewise preferred, embodiment of the invention which is particularly desirable when the etherifying agent is rather sensitive to caustic alkali, the alkali cellulose is formed continuously by running cellulose pulp in continuous or individual sheet form through aqueous caustic alkali and then through rolls to squeeze out the excess. The alkali cellulose sheet or sheets is then impregnated continuously with the etherifying agent.

The impregnation may be effected in several ways. The simplest is to pass the alkali cellulose sheet through a bath containing the etherifying reagent and then through squeeze rolls to remove the excess. This procedure works best for those materials such as aqueous solutions which swell the alkali cellulose, thus penetrating rapidly. It would be expected that passing alkali cellulose into an aqueous solution would result in the extraction of much of the caustic. Surprisingly, however, the loss is very small, usually considerably less than 10%.

A second method of introducing the substituting reagent is to pass the alkali cellulose sheet through squeeze rolls which are provided with a means of supplying the reagent to the sheet. The roll may be covered with a felt or spongy material saturated with reagent or the roll may carry suitable engravings adapted to carry considerable liquid or in some instances a smooth roll itself may be satisfactory. The reagents can be fed to the roll by a spray or the roll may turn in a trough filled with reagent. Another procedure is to spray the reagents on the alkali cellulose pulp sheet before it passes through the rolls, the pres-

sure of the rolls forcing the liquid uniformly through the sheet.

The reagent should preferably be applied in as small excess as possible to prevent washing out the caustic when the excess is expressed. However, an excess must be applied to make sure that each fibre of the sheet is flooded with reagent for an instant.

The pressure applied at the impregnation roll will depend on the quantity of reagent to be introduced and the nature of the reagent. With water insoluble substances such as methyl sulfate, the excess is removed with moderate force but where the reagent is applied in water solution, considerably more pressure is necessary. The force applied at the impregnation roll should be so regulated that minimum expression of steeping caustic will take place. The quantity of liquid taken up may be controlled by the pressure on the impregnation rolls and the concentration of reagent in the impregnating solution. Since an excess of water is usually undesirable in cellulose reactions, when the reagent is added in aqueous solutions the concentration should be as high as other conditions will permit. The press weight of the sheet after passing the rolls is between 2.5 and 6 times and preferably 3-4 times that of the original cellulose sheet.

An important feature of the process is the introduction of the reagent into the sheet at the place where it is to react. Too high mobility, i. e. rapid evaporation or diffusion, of the reactant is undesirable. Accordingly, reagents which are not easily lost by volatilization under the conditions of the reaction are preferably used. Also since the alkali cellulose is wet most readily by aqueous solutions and thus aqueous reagents are taken up very uniformly, when convenient those reagents which are water soluble are preferably used. Wetting agents such as salts of acids prepared from primary branch chain alcohols of 6-8 carbon content prepared by catalytic hydrogenation of carbon oxides at elevated temperatures and pressures are of great assistance both in the impregnation of the cellulose with alkali and in the impregnation of the alkali cellulose with reagents. The large area and uniform texture of chemical cellulose in pulp form permits impregnation of the alkali cellulose sheet with reagent with a degree of uniformity which cannot be equalled by cellulose in any other form.

The treatment of the impregnated sheets depends upon the nature of the reaction. In some instances it is sufficient to allow them to stand at room temperature, i. e. 20-30° C. in a vessel protected from the air. In other instances, temperatures as high as 150° or as low as 0° may be desirable depending on the nature of the material. Although aging of the alkali cellulose impregnated sheets takes place more slowly than aging of shredded alkali cellulose, in some instances it is desirable to replace the air about the sheets with nitrogen to preserve viscosity.

The concentration of the steeping caustic varies with the nature of the reaction and the quantity of reagent used. Solutions of from 10 to 70% concentration may be used successfully, but the preferred concentration in the freshly impregnated sheet is 15-25% calculated on the water and caustic present.

The concentration of etherifying agent may vary from 100% as in the case of a liquid reagent added directly, down to a much lower concentration. In general, the reagent should be present

in the pressed sheet in an amount equal to 0.1 to 2 mols of reagent per glucose unit of the cellulose for the formation of those ethers in the production of which the present invention is so particularly advantageous—namely, the alkali soluble low substituted cellulose ethers, i. e. those containing up to 1 mol. substituent and preferably up to ½ mol. substituent per glucose unit of the cellulose. The process of the present invention is applicable to the preparation of cellulose ethers in general so that more than 2 mols even up to 5, 10, or more mols of reagent per glucose unit of the cellulose may be introduced into the alkali cellulose sheet, depending on the degree of substitution desired.

The process is also particularly suited for preparation of cellulose ethers of extremely low degrees of substitution such as the methyl celluloses made from as little as .005 mols. of reagent.

Having outlined the general principles and purposes of the invention, the following exemplifications thereof are added in illustration but not in limitation of the invention.

Example 1—Methylcellulose

Cellulose in roll or sheet form was run continuously through a bath containing 480 parts of 18% sodium hydroxide and 102 parts of sodium methylsulfate. The steeped material was run through squeeze rolls which reduced the weight to 3.34 times that of the original pulp. The product was aged for 96 hours at 30° and was then purified by washing with water. The methylcellulose product when dissolved to give 5% methylcellulose and 7% sodium hydroxide at -8° C. gave a viscous, stable and clear solution. It filtered a great deal better and was much stronger in acid film casting baths than products of the same viscosity and methyl content prepared by the action of methylating agents on alkali cellulose from the same cellulose in batch processes.

Example 2—Methylcellulose

The procedure was the same as in Example 1 except that the sodium methylsulfate-alkali cellulose sheets were aged in an atmosphere of nitrogen for ten days. The product was much more viscous than the product of Example 1 but was of the same degree of solubility.

Example 3—Cellulose glycolic acid

Cellulose in sheet or roll form was steeped continuously in a small volume of a solution of sodium chloroacetate in sodium hydroxide. The solution was prepared by mixing together at temperatures below 10°, 162 parts of 36% sodium hydroxide solution with a solution of 59 parts of sodium chloroacetate in 162 parts of water. The freshly mixed caustic—sodium chloroacetate solution was fed constantly into the steeping tank at the same rate as it was removed by the steeping process. The temperature of steeping the liquor was held below 10° to minimize hydrolysis on the sodium chloroacetate. The sheets after steeping were passed through squeeze rolls under such pressure that the pressed sheets were 3.36 times the weight of the original cellulose. This gave one-half mol. of sodium chloroacetate per mol. cellulose (glucose unit). The sheets were stored in a closed container below 30° C. for two days. The product was purified by washing with hot water and drying. It dissolved at 5° C. in 6% sodium hydroxide to give solutions of high viscosity which contained very little insoluble

fiber and which filtered readily. Solutions of the product contained much less insoluble fibre and filtered more readily than glycolic acid ethers of cellulose of the same degree of etherification and viscosity made from alkali cellulose from the same cellulose using batch processes.

Example 4—Cellulose glycolic acid

Cellulose in roll or sheet form was steeped continuously in 28% sodium hydroxide solution. It was then run through squeeze rolls which reduced the weight of the sheet to three times that of the original cellulose. The alkali cellulose sheet was next run through wringer rolls, the lower member of which was covered with an alkali resistant felt which dipped in a 30% aqueous sodium chloroacetate solution. The felt was of such a nature that it carried sufficient of the solution that, as the alkali cellulose sheet passed through the squeeze rolls sodium chloroacetate solution was forced through the alkali cellulose sheet in such quantity that a very small ripple of the solution was to be seen between the sheets passing through the rolls and the upper roll. The appearance of the ripple was an indication that thorough impregnation was taking place. The pressure on the rolls was so adjusted that the impregnated sheet weighed four times that of the original cellulose. The sheet was then rolled onto a core or if in the form of separate sheets, these were piled in a closed container and set aside at 25° C. to react. After 48 hours the product was washed caustic free with hot water and was then dissolved to 6% cellulose and 7% sodium hydroxide in water at -7° C. The product was of much better solubility, containing fewer undissolved fibers and filtering with much greater ease than products of the same degree of substitution and viscosity made from the same alkali cellulose with batch processes. The quantity of sodium chloroacetate used equalled approximately one-half mol. per glucose unit of cellulose.

Example 5—Cellulose glycolic acid

The procedure was the same as in Example 4 except that the pressure on the impregnation rolls was increased so that the impregnated sheet weighed 3.5 times the weight of the original cellulose. The product after purification dissolved in 7% sodium hydroxide at -10° C. to give viscous, almost fibre free solutions. This procedure utilized $\frac{1}{4}$ mol. of sodium chloroacetate per glucose unit of the cellulose. Using batch processes with the same alkali cellulose, to obtain a product of the same viscosity and solubility, it was necessary to use $\frac{1}{2}$ mol. of sodium chloroacetate.

Example 6—Cellulose glycolic acid

The procedure was the same as in Example 4, except that a 15% solution of sodium chloroacetate was used as the impregnating bath. The quantity of sodium chloroacetate used equalled $\frac{1}{4}$ mol. per glucose unit of the cellulose. The product resembled that of Example 5, except that it was of slightly poorer solubility and was of somewhat higher viscosity.

Example 7—Cellulose glycolic acid

The procedure was the same as in Example 5, except that the impregnating solution contained 15% of sodium chloroacetate. The product dissolved in 8% sodium hydroxide at -10° to give almost fibre free, viscous solutions. The quantity of reagent used was $\frac{1}{8}$ mol. per glucose unit

of the cellulose. These solutions differed from those of the higher substituted products in that they are much more opalescent. However, the material cast to brilliantly clear films with excellent wet strength in acid baths. The solutions contained fewer undissolved fibres and filtered better than products of the same viscosity made from the same cellulose with one-fourth mol. of sodium chloroacetate per glucose unit using alkali cellulose and batch processes.

Example 8—Cellulose glycolic acid

Cellulose in roll or sheet form was steeped continuously in 28% sodium hydroxide solution and was then passed through pressure rolls which reduced the weight of the sheet to 2.8 times the weight of the original cellulose. The sheets were then passed through a bath containing 40% sodium chloroacetate solution at such a rate that a very low degree of swelling occurred. The impregnated sheets were immediately passed through squeeze rolls which reduced the weight of the sheets to 3.8 times the weight of the original cellulose. The quantity of reagent left in the alkali cellulose was one-half mol. of sodium chloroacetate per glucose unit of the cellulose. The product was stored in a closed container for 48 hours at 25° C. It resembled the product of Example 4 closely.

In this procedure a small quantity of sodium hydroxide is expressed from the alkali cellulose sheet. To counteract its effect in saponification of the sodium chloroacetate, the bath may be replenished constantly with a sodium chloroacetate solution containing enough free chloroacetic acid or other acid to react with the caustic present.

Example 9—Cellulose glycolic acid

Alkali cellulose in roll or sheet form was passed continuously under a spray of 40% sodium chloroacetate solution. The sheets were then passed through squeeze rolls which reduced the weight of etherifying solution to that of the original cellulose. The product resembled that of Example 4. In lieu of supplying the sodium chloroacetate solution by a spray, it may be fed to the sheets by means of brushes.

Example 10—Methylcellulose

One hundred sixty-two parts of wood cellulose were steeped in an aqueous 28% sodium hydroxide solution for one hour and then pressed to 480 parts. The pressed sheets were run rapidly through squeeze rolls which were covered with a spongy material saturated with a 45% aqueous solution of sodium methylsulfate. The pressure on the rolls and the quantity of sodium methylsulfate on the roll were so adjusted that 147 parts of the sodium methylsulfate solution were taken up by the alkali cellulose. The sheets were set aside to age for 5 days at 30° C. and then purified and the product dried. It gave a high viscosity solution in 7% sodium hydroxide when cooled to -10°.

Example 11—Methylcellulose

Alkali cellulose was prepared continuously in roll or sheet form by steeping in 18% sodium hydroxide solution and pressing to a weight three times that of the original cellulose. The sheets were next run through squeeze rolls covered with a spongy material which was saturated with dimethyl sulfate under such pressure that dimethyl sulfate was squeezed through the sheets. The

pressure was so adjusted that the impregnated sheets weighed 3.75 times the weight of the original cellulose. The impregnated material was stored in the form of a roll or piled in sheets in a closed vessel for 30 minutes. The product was then purified by washing in a beater. It dissolved readily in 8% sodium hydroxide at room temperature to give solutions containing a small quantity of fibre. The solutions contained considerably less fibre than solutions of methylcellulose of the same methyl content and viscosity prepared from the same cellulose by the action of dimethyl sulfate on alkali cellulose in batch operations.

Example 12—Ethylcellulose

The procedure was the same as in Example 11, except that the impregnating material was diethyl sulfate. A quantity of diethyl sulfate equivalent to the weight of the original cellulose was introduced. This was one mol. of alkylating agent per glucose unit of the cellulose. The sheets were set aside and allowed to react for 48 hours at 30° C. The product dissolved in 7% caustic at -5° C. to give fibre free solutions which filtered much better than products of the same viscosity and degree of substitution made from the same alkali cellulose using batch processes.

Example 13—Hydroxyethylcellulose (glycol cellulose)

The procedure was the same as in Example 11, except that the impregnating material was ethylene chlorohydrin. The quantity of reagent introduced in the impregnating step equalled one-half the weight of the original cellulose. This was one mol. of ethylene chlorohydrin per glucose unit of the cellulose. The product after aging for one day at 20° C. dissolved in 6% sodium hydroxide to give solutions which were practically free from fiber.

Example 14—Hydroxyethylcellulose

The procedure was the same as in Example 13, except that the impregnating medium was a 50% solution of ethylene chlorohydrin in benzene. The quantity of solution introduced was equal to one-half the weight of the cellulose. This gave one-half mol. of etherifying reagent per glucose unit of the cellulose. The impregnated sheets were set aside to age at 25° for 72 hours. The product dissolved in 7% sodium hydroxide at room temperature to give practically fibre free solutions.

Example 15—Hydroxypropylcellulose

The procedure was the same as in Example 13, except that the impregnating medium was a 70% solution of propylene oxide in benzene. The weight of the etherifying solution introduced equalled the weight of the starting cellulose. The operation was carried out at 10° C. and the impregnated sheets were stored at 10° for 48 hours after which the temperature was allowed to rise to 30° for 24 hours. The product was almost completely soluble in water especially below 15° C. and was completely soluble in the presence of a small quantity of sodium hydroxide. After once being dissolved in the presence of caustic the product became completely water soluble.

Example 16—Dihydroxypropylcellulose (glyceryl cellulose)

The procedure was the same as in Example 11, except that the impregnating material was glyceryl

monochlorohydrin. The quantity of etherifying agent introduced into the alkali cellulose sheet equalled 70% of the weight of the starting cellulose. This gave one mol. of glyceryl monochlorohydrin per glucose unit of the cellulose. The product after aging for 48 hours at 30° C. dissolved readily in 7% sodium hydroxide at room temperature to give viscous, fibre free, solutions.

Example 17—Dihydroxypropylcellulose

A solution was prepared of 49 parts of sodium hydroxide, 56 parts of glyceryl monochlorohydrin and 220 parts of water. In this was steeped continuously in roll or sheet form cellulose pulp which was pressed between rolls to three times the original weight of the cellulose. The pressed material was stored in a closed container at 30° C. for 72 hours. The product dissolved in sodium hydroxide 7% at -8° C. to give viscous fibre free solutions. The solutions were of better solubility and filtered more readily than products of the same viscosity and degree of substitution made from the same cellulose by batch processes.

Example 18—Benzylcellulose

Cellulose in roll or sheet form was steeped in 18% sodium hydroxide solution and pressed to 2.7 times the original weight of the cellulose. The alkali cellulose sheets were then fed through rolls provided with a means as described in Example 4 for introducing benzyl chloride into the sheet. The pressure on the rolls was so adjusted that the weight of benzyl chloride introduced equalled 79% of the weight of the original cellulose. The sheets were stored at 85° C. for 18 hours and were then purified by washing with water in a beater, followed by extraction with methanol. The product was insoluble in all solvents and was somewhat water repellant.

In place of the methyl and ethyl sulfates, sodium methylsulfate, glycerol chlorohydrin, ethylene chlorohydrin, propylene oxide, and sodium chloroacetate, other liquid etherifying agents, i. e. liquid as such or by solution in water, may thus be employed. The agents are preferably substantially non-volatile under the conditions of the reaction.

The term, improved solubility, as used in the examples refers to the greater freedom from fibre of solutions of the product. In the preparation of low-substituted derivatives it is necessary to mix a small quantity of reagent with a large quantity of fibrous cellulose. This is difficult to do uniformly and in the processes of the prior art some of the fibres receive more reagent than is necessary to make them soluble and some do not receive enough. Upon dissolving the product therefore some of the fibres dissolve completely while others remain undissolved. The uniformity of the product is greatly increased by the process of the present invention and therefore the discrepancy in solubility between different batches of fibres is greatly decreased while the average degree of substitution of the materials might be approximately the same.

In the conventional manufacture of low-substituted cellulose ethers, where solubility is poor, the proportion of insoluble fibre may be reduced by increasing the quantity of etherifying agent, because the larger quantity of reagent may be spread farther than a smaller quantity and thus more of the fibres receive sufficient etherifying agent to make them soluble. The product is, however, still non-uniform inasmuch as much of the fibre is more highly etherified than the rest.

The process of the present invention which gives a high degree of uniformity renders it possible to achieve the same degree of solubility (proportion of soluble fibre) with a smaller quantity of reagent than is necessary with the prior art processes which result in poor uniformity. Thus by impregnating alkali cellulose sheet, according to the process of the present invention, with 0.25 mol. of sodium chloroacetate, a product of the same solubility at -6° in 6% caustic resulted, as was obtained by treating alkali cellulose from the same cellulose in a high-speed shredded with 0.5 mol. of sodium chloroacetate. The first product contained 0.15 glycolic acid ether groups, while the second contained 0.25 groups. The solution of the first product when cast to films in acid film casting baths gave sheets of improved wet strength both in the casting bath and in the finished state. This distinct advantage is due to the lower number of solubilizing groups in the precipitated film.

This type of partial solubility above discussed is to be clearly distinguished from that type wherein the whole product is only partially soluble.

The usual process of making low-substituted cellulose ethers is by mixing the reagents together in a shredder or other agitator. The present process is an entirely new type of procedure involving the impregnation of pulp board without any mixing operation. While it would be expected that flushing an aqueous solution of etherifying agent through a sheet of alkali cellulose in pulp board form would result in substantial removal of alkali from the sheet, it has been found that, contrary to expectation, but little alkali is removed by the process of the present invention. From the somewhat similar process of Lilienfeld it would be expected that the process of the present invention would result in a mere surface treatment. It has been found, however, contrary to expectation, that a uniform effect throughout the sheet is obtained by following the principles laid down in the present application.

While one of the advantages of the present process is the fact that by a novel alteration in the etherifying process the same may be run in a continuous manner, the process affords a further advantage in the great improvement in the uniformity of the product.

Although the process works best for aqueous solutions of etherifying agents since these seem to give best penetration into the fibre, very good results are obtained with solutions of alkylating agents in organic solvents or mixtures of organic solvents with water, for example, glycerine monochlorohydrin in alcohol or aqueous alcohol, dimethylsulfate in benzene, benzyl chloride in gasoline or propylene oxide in dibutyl ether. Any solvent which will not react with the cellulose or alkylating agent under the conditions of the reaction, i. e. an inert solvent, may be used. The boiling point is preferably sufficiently low to permit easy purification but high enough that the solvent does not escape rapidly.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. Process for the preparation of cellulose ethers which comprises continuously impregnating

cellulose in sheet form with aqueous caustic alkali and an etherifying agent, the sheet being impregnated with the caustic alkali at least as soon as with the etherifying agent, continuously pressing out excess thereof, and allowing the thus impregnated sheet to react, and then stopping the reaction.

2. The process of claim 1 wherein the etherifying agent is water soluble.

3. The process of claim 1 wherein the etherifying agent is substantially non-volatile at the temperature of reaction.

4. The process of claim 1 wherein the etherifying agent is substantially non-volatile at the temperature of reaction and is water soluble.

5. Process for the preparation of cellulose ethers which comprises continuously impregnating alkali cellulose in sheet form with an aqueous solution of etherifying agent, continuously expressing the excess thereof, allowing the impregnated pulp sheet to react, and then terminating the reaction.

6. Process for the preparation of cellulose ethers which comprises continuously impregnating cellulose in sheet form with a solution of an etherifying agent in aqueous caustic alkali, continuously expressing the excess thereof, allowing the impregnated sheet to react and then terminating the reaction.

7. Process for the preparation of low substituted cellulose ethers which comprises continuously impregnating alkali cellulose in sheet form with an aqueous solution of etherifying agent, continuously expressing the excess thereof, allowing the impregnated pulp sheet to react, and then terminating the reaction.

8. Process for the preparation of low substituted lower alkyl celluloses which comprises continuously impregnating alkali cellulose in sheet form with a lower alkyl etherifying agent in liquid form, expressing excess etherifying agent until up to 2 mols per glucose unit remain in the sheet, allowing the thus impregnated sheet to react, and then stopping the etherification.

9. Process for the preparation of low substituted lower alkyl celluloses which comprises continuously impregnating cellulose in sheet form with a solution of a lower alkyl etherifying agent in aqueous caustic alkali, expressing excess etherifying agent until up to 2 mols per glucose unit remain in the sheet, allowing the thus impregnated sheet to react and then stopping the reaction.

10. Process for the preparation of low substituted alkyl celluloses which comprises continuously impregnating alkali cellulose in sheet form with an alkylating agent in liquid form, expressing excess etherifying agent, until up to 2 mols per glucose unit remain in the sheet, allowing the thus impregnated sheet to react, and then stopping the alkylation.

11. Process for the preparation of low substituted alkylcellulose which comprises continuously impregnating a sheet of cellulose pulp with a liquid composition comprising a solution of a lower alkyl etherifying agent in aqueous caustic alkali, continuously expressing excess reagents, allowing the impregnated pulp sheet to age and react, and then terminating the alkylation.

12. Process for the preparation of low substituted methylcellulose which comprises passing cellulose pulp in sheet form through an aqueous steeping bath containing sodium hydroxide and sodium methylsulfate, expressing excess etherification mixture continuously by passing through squeeze rolls to a press product containing up to 2 mols sodium methylsulfate, allowing the im-

pregnated sheet to age and react, and then stopping the etherification.

13. Process for the preparation of low substituted methylcellulose which comprises passing cellulose pulp in a continuous sheet form through an aqueous steeping bath containing approximately 15% sodium hydroxide and approximately 18% sodium methylsulfate, expressing excess etherification mixture by passing through squeeze rolls to a press weight of approximately $3\frac{1}{2}$ times that of the original cellulose aging for approximately 100 hours at 30° C. and stopping the etherification.

14. Process for the preparation of low substituted cellulose glycolic acid which comprises continuously impregnating alkali cellulose in sheet form with an alkali chloroacetate solution, expressing excess solution until up to 2 mols per glucose unit remain in the sheet, allowing the thus impregnated sheet to react, and then stopping the etherification.

15. Process for the preparation of low substituted cellulose glycolic acid which comprises continuously impregnating alkali cellulose in sheet form with sodium chloroacetate solution, expressing excess sodium chloroacetate solution until the impregnated sheet weighs approximately four times the weight of the original cellulose, allowing the thus impregnated sheet to react, and then stopping the etherification.

16. Process for the preparation of low substituted cellulose glycolic acid which comprises con-

tinuously impregnating alkali cellulose in sheet form with a liquid alkylating mixture comprising an alkali metal chloroacetate, continuously pressing the sheet to a press ratio of approximately 4 containing up to 2 mols chloroacetate per glucose unit, allowing the thus impregnated sheet to react and then stopping the etherification.

17. Process for the preparation of low substituted cellulose glycolic acid which comprises continuously impregnating a sheet of alkali cellulose pulp with a liquid composition comprising an alkali metal chloroacetate, continuously expressing excess alkali chloroacetate solution, allowing the impregnated pulp sheet to age and react, and then terminating the reaction.

18. Process for the preparation of low substituted hydroxyalkyl cellulose which comprises continuously impregnating a sheet of alkali cellulose pulp with a liquid composition comprising a hydroxyalkylating agent, continuously expressing excess hydroxyalkylating mixture, allowing the impregnated pulp sheet to age and react, and then terminating the hydroxyalkylation.

19. Process for the preparation of low substituted glyceryl cellulose which comprises continuously impregnating a sheet of alkali cellulose pulp with a liquid glycerylating composition, continuously expressing excess glycerylating mixture, allowing the impregnated pulp sheet to age and react, and then terminating the reaction.

ROBERT W. MAXWELL.