

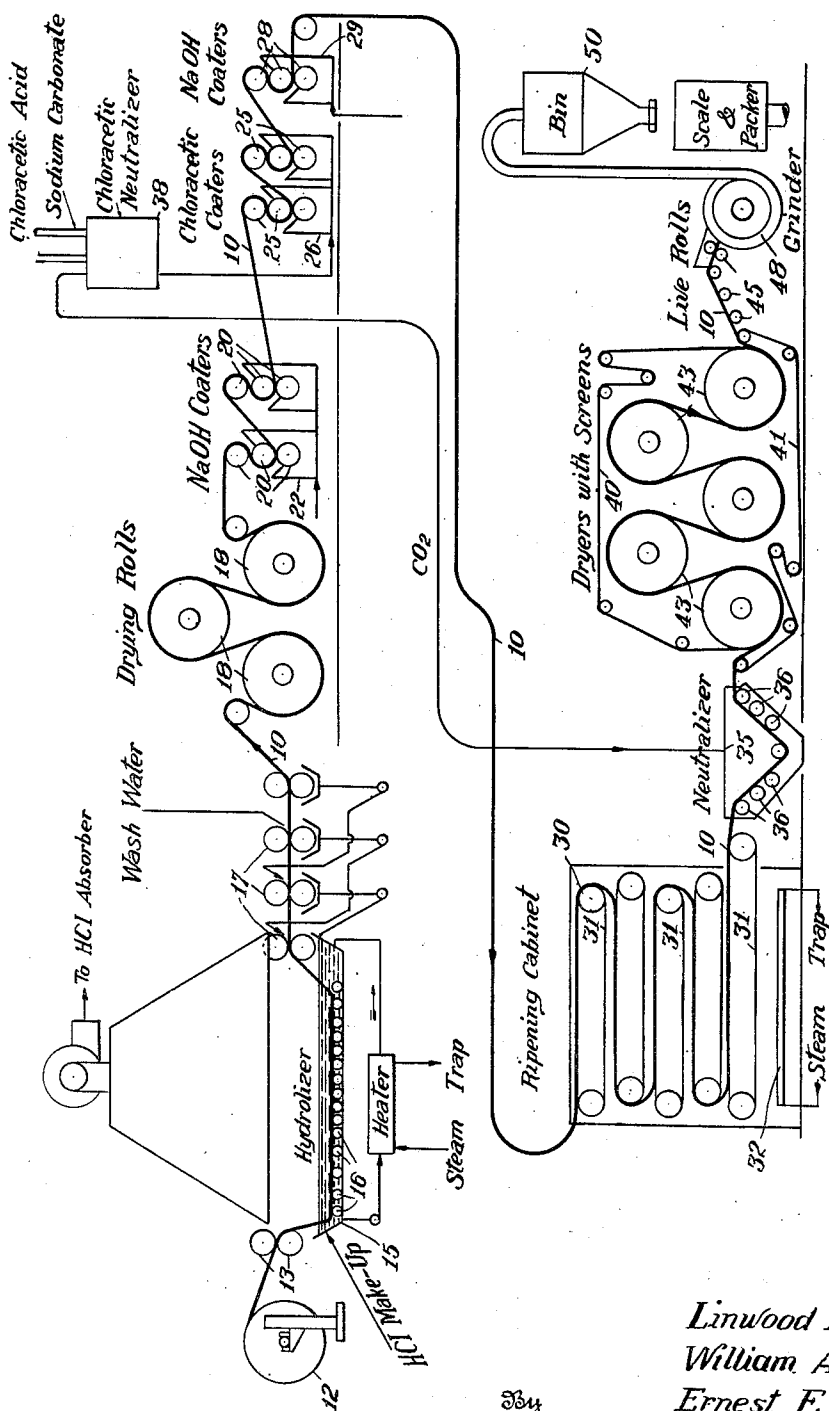
May 22, 1951

L. N. ROGERS ET AL

2,553,725

PROCESS OF PREPARING CELLULOSE DERIVATIVES

Filed Sept. 10, 1948



Inventors

Linwood N. Rogers

William A. Mueller

Ernest E. Hembree

Watson, Cole, Grindle & Watson

ATTORNEYS

UNITED STATES PATENT OFFICE

2,553,725

PROCESS OF PREPARING CELLULOSE
DERIVATIVES

Linwood N. Rogers, William A. Mueller, and Ernest E. Hembree, Memphis, Tenn., assignors to Buckeye Cotton Oil Company, Memphis, Tenn., a corporation of Ohio

Application September 10, 1948, Serial No. 48,732

16 Claims. (Cl. 260—231)

1

This invention relates to an improved process for the preparation from cellulose pulp of salts of acidic ether derivatives of cellulose, and more particularly to a process for the preparation of salts of an acidic ether derivative of cellulose of the group consisting of cellulose ether derivatives of aliphatic carboxylic and alkyl sulfonic acids having not more than 4 carbon atoms, as for example water-soluble salts of carboxymethyl cellulose and of cellulose ethane sulfonic acid.

Cellulose derivatives of the character indicated are highly useful in laundry operations, in which they enhance the action of the detergent, apparently by retaining in suspension the dirt particles removed from the fabrics, whereby gray- ing of the fabric on repeated washing with the detergent composition is reduced. This ability of a detergent composition to maintain the whiteness of white fabrics on repeated washing is sometimes referred to as "whiteness maintenance." Furthermore, these cellulose derivatives tend to prevent the deposition on the fabric of insoluble salts, and thus tend to reduce the harsh feel so imparted to the fabrics, especially when the detergent is of low grade. For this and related purposes, the solubility of the cellulose derivatives in water is quite important to effective results, and clarity is desirable. When, as is often the case, the derivative is to be mixed with the detergent while fluid, derivatives having low viscosity, adapted for use in conventional mixing equipment such as crutchers and the like, are preferable. Moreover, there has been some indication that those cellulose derivatives, which give low-viscosity aqueous solutions, have greater efficiency in improving the whiteness maintenance of detergent compositions.

It is accordingly an object of the invention to provide a novel process for the efficient low-cost production of salts of acidic ether derivatives of cellulose, which salts form clear solutions in water, are highly effective, and which have a viscosity sufficiently low to facilitate handling with convenient detergent making equipment.

It is a feature of the instant process that the cellulose derivatives may be produced continuously; in the preferred process the cellulose pulp is conveyed through each of the treatment zones in the form of a continuous sheet, emerging in sheet form after conversion to the ether salt for delivery to crushing and grinding equipment. It is particularly important to pass the material through the etherifying zone in the form of a continuous sheet in order that the final product may have the desired properties, as hereinafter more fully explained.

2

It is a further object of the invention to provide a method of forming cellulose derivatives of the character described which includes the step of etherifying a sheet of cellulose by the application to the sheet of liquid reagents in amount which is at no time greater than the amount of liquid which the sheet is capable of absorbing.

It is a further object of the invention to provide a process of etherifying cellulose which includes the steps of applying thereto in succession, and in the order named, an alkaline agent, a halogenated lower fatty acid, or halogenated lower alkyl sulfonic acid, and an alkaline agent, in total amount not greater than that which the sheet is capable of absorbing.

More specifically, it is an object of the invention to provide a new and improved process for the manufacture of carboxymethyl cellulose which involves feeding the pulp continuously in sheet form in succession, and in the order named, through a hydrolyzing zone, a washing zone, a drying zone, an etherifying zone, a ripening zone, and drying zone.

Further objects and features of the invention will be apparent from the following description taken in connection with the accompanying drawing, in which the single figure illustrates diagrammatically a preferred form of equipment for the practice of the process of the invention.

In order to facilitate an understanding of the invention, the process is described with reference to its application to the manufacture of low viscosity, water soluble carboxymethyl cellulose. It will be understood, however, that the process is readily applicable to the preparation of cellulose ethers of other aliphatic carboxylic acids having not more than 4 carbon atoms per molecule and of lower alkyl sulphonic acids having not more than 4 carbon atoms per molecule by appropriate substitution of reagents, and that the use of specific language describing the preferred embodiment of the invention is not intended to limit its scope.

The following specific examples are illustrative of preferred methods of processing cotton linters in sheet form to produce the acidic ethers of cellulose.

Example I

A 10-pound roll of cotton linters sheet, 10 inches wide and 0.040 inch thick, and a viscosity of 11 seconds when 2.5 grams are dissolved in cuprammonium according to the A. C. S. Standard Method, was passed continuously through a hydrochloric acid bath at 70° C. and containing 15% hydrogen chloride. The speed was so regu-

lated that the contact time of the paper with the acid was 60 seconds. During this time the viscosity was reduced to 20 seconds, as measured by the A. C. S. method, using a 5-gram sample, but other characteristics of the paper such as strength and absorbency remained practically unchanged. The sheet was then passed through squeeze rolls to remove the excess acid, and then alternately through three successive water washes and squeeze rolls to remove the remaining acid, and finally through a roll dryer and partially dried to about 20% moisture.

The dried sheet was passed through a series of saturating rolls (coating rolls) to spread uniformly over both sides of the sheet 10 pounds of 35% aqueous sodium hydroxide. The resultant sheet, showing very little shrinkage, was immediately passed through a second set of saturating rolls to coat onto the paper 8.9 pounds of an aqueous solution prepared by adding to 10 pounds of 80% chloracetic acid solution 1.8 pounds of dry soda ash, and finally through a third set of saturating rolls to coat 7 pounds of 35% sodium hydroxide.

The sheet was then passed (a) through a non-drying oven at 100° C. for a period of 4 minutes of ripening, (b) through a tank containing carbon dioxide gas (15 seconds), (c) over a second roll dryer to dry to 3% moisture and, (d) into crushing and grinding equipment.

The product dissolved readily in water to form a free flowing 2% solution which, when adjusted to pH 7, was substantially water clear.

Example II

The procedure was the same as Example I except that the sheet was coated first with 12 pounds of 35% aqueous sodium hydroxide then 8 pounds of 80% chloracetic acid, and finally 8 pounds of sodium hydroxide. The product was similar to that of Example I.

Example III

The procedure was the same as Example I except that the hydrolysis, washing, and partial drying were omitted. The product formed a gel when prepared into 0.5% solution.

Example IV

A 10-pound roll of absorbent cellulose sheet, 10 inches wide and 0.040 inch thick, was passed continuously through a hydrochloric acid bath at 67° C. and containing 20% hydrogen chloride. The speed was so regulated that the contact time of the paper with the acid was 45 seconds. During this time the viscosity was reduced to 25 seconds, as measured by A. C. S. method using a 5-gram sample, but other characteristics of the paper such as strength and absorbency remained practically unchanged. The sheet was then passed through squeeze rolls to remove the excess acid, and then alternately through three successive water washes and squeeze rolls to remove the remaining acid, and finally through a roll dryer and partially dried to about 32% moisture.

The dried sheet was passed through a series of coating rolls to spread uniformly over both sides of the sheet 7.2 pounds of 29% aqueous sodium hydroxide. The resultant sheet, showing very little shrinkage, was immediately passed through a second set of saturating rolls to coat onto the paper 7.3 pounds of a solution prepared by adding 2.0 pounds of sodium carbonate to 10 pounds of a 70% aqueous solution of mono-

chloracetic acid, and finally through a third set of saturating rolls to coat 8.4 pounds of 29% sodium hydroxide.

The sheet was then passed (a) through a non-drying oven at 120° C. for a period of 3 minutes of ripening, (b) through a tank containing carbon dioxide gas (11 seconds), (c) over a second roll dryer to dry to 3% moisture and, (d) into crushing and grinding equipment.

Over 97% of the product was soluble in water when dissolved to make a 2% solution and adjusted to pH 7. This solubility was less than that of Example I, but the product was eminently suitable as a detergent acid.

Example V

A 10-pound roll of absorbent cellulose sheet, 10 inches wide and 0.022 inch thick, was passed continuously through a hydrochloric acid bath at 70° C. and containing 15% hydrogen chloride. The speed was so regulated that the contact time of the paper with the acid was 90 seconds. During this time the viscosity was reduced to 15 seconds as measured by A. C. S. method using a 5-gram sample, but other characteristics of the paper such as strength and absorbency remained practically unchanged. The sheet was then passed through squeeze rolls to remove the excess acid, and then alternately through three successive water washes and squeeze rolls to remove the remaining acid, and finally through a roll dryer and partially dried to about 9.0% moisture.

The dried sheet was passed through a series of two or more saturating (coating) rolls to spread uniformly over both sides of the sheet 12 pounds of 34% aqueous sodium hydroxide. The resultant sheet, showing very little shrinkage, was immediately passed through a second set of saturating rolls to coat onto the paper 12 pounds of a solution prepared by adding 1.8 pounds of sodium carbonate to 10 pounds of 80% aqueous solution of monochloracetic acid, and finally through a third set of saturating rolls to coat 7.1 pounds of 34% sodium hydroxide.

The sheet was then passed (a) through a non-drying oven at 90° C. for a period of 6 minutes of ripening, (b) through a tank containing carbon dioxide gas (22 seconds), (c) over a second roll dryer to dry to 3% moisture, and (d) into crushing and grinding equipment.

The product was readily and completely soluble in water when dissolved to make a 2% solution, and when adjusted to pH of 7 this solution was water clear.

Example VI

The procedure was the same as Example I except that the paper was coated first with 9.5 pounds of 35% sodium hydroxide, then with 11.5 pounds of an aqueous solution containing 75% alpha chloro propionic acid which was 40% neutralized with soda ash, and finally with 8.6 pounds of 35% sodium hydroxide.

Example VII

The procedure was the same as Example VI except that the acid used in the second coating step was 10.2 pounds of chloro-ethane sulfonic acid. The product was very similar to carboxymethyl cellulose, and had excellent properties as a detergent added.

Other halogenated acids which may be employed to form acidic ether derivatives of cellulose are chlorobutyric acid, chloropropane sulfonic acid, bromobutane sulfonic acid and chlorohydroxy propane sulfonic acid.

The apparatus shown in the drawing may be used to carry out the processes just described. Thus the fibrous sheet which is designated throughout by the reference character 10, initially constituted by absorbent cellulose sheet having the characteristics set forth in the example, is drawn continuously from a roll 12 by draw rolls 13 and passed through hydrochloric acid in tray 15, being supported therein by rollers 16. Following depolymerization or hydrolysis in the acid bath and consequent reduction of viscosity, the sheet is led between squeeze rolls 17 and is washed with water, to remove the acid. It is then led over heated drying rolls 18, or through any conventional roll dryer, where it is dried to the specified moisture content.

The partly dried sheet of depolymerized cellulose is then passed through a series of two or more sets of saturating or coating rolls, two sets being shown in the drawings, to apply caustic to the sheet. Each set of coating rolls may comprise three superposed rolls 20, the sheet being fed between the several rolls so as to absorb the caustic which is fed onto the rolls from troughs on side of rolls similar to those used in the paper industry for saturating paper. It will be noted that the sheet is not submerged in the solution. By suitable selection of the number of sets of rolls and their diameters, the amount of caustic supplied can be determined with exactness.

From the caustic rolls the sheet is fed directly to coating rolls 25, of which several sets are similarly provided, whereby the halogenated acid is supplied to the sheet from troughs, on side of rolls same as above. From these rolls the sheet is passed directly to one or more sets of rolls 28, functioning similarly to the coating rolls hereinbefore described, by which the final application of caustic from troughs are effected.

The sheet is then fed into a ripening cabinet 30 in which it is supported on a series of superposed continuous conveyors 31, alternate conveyors being driven in opposite directions, whereby the sheet is passed along each conveyor from the uppermost to the lowest of the series. Cabinet 30 is heated from steam coils 32 in bottom of cabinet. High humidity is maintained.

Upon leaving the ripening cabinet, the sheet is fed into a neutralizing chamber 35 which is supplied with carbon dioxide gas, the sheet being supported on rolls 36. The gas may be derived from a chamber 38 in which chloroacetic acid to be supplied rolls 25 is partially neutralized with sodium carbonate, as described more fully hereinafter.

The sheet is then passed between screen conveyors 40, 41 which are entrained over drying rolls 43, and is then fed by positively driven rolls 45 to a conventional grinding or pulverizing mill 48, the ground material being delivered to a bin 50.

The type of pulp used may vary widely, the processing conditions being altered to treat effectively the selected pulp. Cotton linters is the preferred material, but wood, straw, bagasse or other cellulosic material may be employed. The viscosity of the initial pulp obviously affects materially the selection of processing conditions for the production of a derivative having specified characteristics.

The strength of the pulp sheet should, of course, be sufficient to ensure against breakage as the sheet is passed through the various treatment zones, but the mullen (tear) value should be low, for ready penetration. Values of the order of 25

to 40 mullen, measured on a sheet 0.040 inch thick, are satisfactory, this being the optimum thickness of sheet. However, the sheet thickness may vary substantially, cotton linters sheets of thickness as low as 0.0125 inch and as high as 0.06 inch being processed satisfactorily. The sheet width is immaterial, but fairly wide sheets, for instance of the order of 40 inches, are preferable from the standpoint of output.

As has been pointed out, processing conditions may be varied rather widely depending upon the initial pulp and the nature of the final product. The following more detailed discussion of the several steps of the process are indicative of the variations in processing conditions which are possible.

Acid hydrolysis

The hydrolysis or depolymerization of the cellulose may be effected with a wide variety of acids, inorganic mineral acids such as hydrochloric, sulfuric, nitric, and phosphoric being commonly used. Hydrochloric acid is preferred, and the limits and conditions specified herein relate to this acid.

In order to produce carboxymethyl cellulose having a viscosity in a 2% aqueous solution (pH 7) of less than 100 centipoises, for example 25 to 50 centipoises, the hydrolyzed sheet should have a viscosity of 12 to 36 seconds, when measured by the standard method of the American Chemical Society, using a 5-gram sample. When pulp such as described in the foregoing specific example, having a viscosity of 11 seconds (2.5-gram sample) is employed, the concentration of hydrochloric acid should be from about 5% to about 30% by weight, preferably between 13% and 17%. If the acid concentration is 15%, the time of contact between acid and pulp may vary from 30 to 90 seconds. If the acid concentration is held at 15% and the contact time to 60 seconds, the temperature of the bath may vary between 60° and 80° C. It is the primary purpose in conducting this step to hydrolyze the fiber without reducing the fiber strength materially and without substantial swelling of the sheet, and temperatures from about 50° C. to about 100° C. and time from about 15 to about 200 seconds and other processing conditions are selected with this end in view. Excellent results are achieved, using the pulp of Example I, by the use of 15% hydrochloric acid at a temperature of 70° to 80° C., the sheet being immersed for a period of 60 seconds.

Washing and drying

It is an important feature of the invention that etherification of the cellulose is effected by absorption of the reagents in the fibrous sheet, no excess of reagent being applied at any time. It is therefore necessary to remove the hydrolyzing acid and at least partially dry the sheet prior to etherification. Washing may be effected by dipping, spraying, absorption or in any other convenient manner by which most of the acid can be removed. An amount of water approximately equal in weight to the weight of the cellulose has been found adequate. Drying may be accomplished on conventional open paper dryer rolls. Preferably drying is continued until the moisture of the sheet is from 10% to 25% by weight of the sheet when dry.

Etherification

A significant feature of the instant invention is the application of the alkaline agent, for in-

stance caustic soda, in two steps which respectively precede and follow the application of the esterifying agent, such as chloracetic acid, bromacetic acid or other halogenated aliphatic carboxylic acid or alkyl sulfonic acid having not more than 4 carbon atoms, chloracetic acid being most generally applicable, however. The chief effects of the double causticization are to ensure more uniform penetration, less swelling of the pulp, and less heating and therefore less decomposition of the chloracetic acid; for example, and to effect corresponding improvements in solubility and clarity of the product. The caustic serves to further the reaction between chloracetic acid and cellulose, either by combining with the halogen of the chloracetate and causing the resultant free radical to combine with the hydroxyl of the cellulose, or by combining with the hydrogen chloride formed in the reaction. Mercerization (i. e. conversion of all of the cellulose to alkali cellulose) is undesirable in the instant process, and is effectively avoided by the absorption of all of the caustic in the cellulose sheet, there being no unabsorbed solution in contact with the cellulose at any time. For instance, the contraction of the sheet (a measure of the amount of swelling) when processed by the present invention is less than 3%, whereas a similar sheet dipped in caustic of the same strength contracts from 15 to 20%. Since swelling tends to close the interstices of the sheet, the initial application of caustic as proposed herein results in a sheet which is quite porous and absorptive, and which therefore can absorb and distribute uniformly a relatively viscous solution of halogenated acid of high concentration. It is therefore desirable to limit the amount of caustic initially applied so as to eliminate swelling before application of halogenated acid, and to add thereafter an additional amount of caustic. In the case of the use of caustic soda and chloracetic acid this additional amount is preferably sufficient to bring the total weight of NaOH to substantially the weight of actual chloracetic acid introduced.

While any alkaline agent of adequate strength may be employed, alkali metal hydroxides function most satisfactorily, and caustic soda is preferred. When using caustic soda, the concentration may vary from 25% to 40% and the temperature from 15° to 40° C. In the initial causticization step, we prefer to add slightly over half of the total amount of caustic required, for instance 60%, or about 1.2 to about 2.2 mols per glucose unit, the balance of about 1.0 to about 1.4 mols being added in the second causticizing step. By applying the caustic on a plurality of sets of rolls, more uniform distribution is obtained and the product correspondingly improved. A higher concentration of caustic can be used if the temperature of the solution is raised sufficiently to avoid viscosity difficulties; a concentration of less than 25% should be avoided, however, because introduction of too much water retards subsequent reaction by formation of a gel, mercerization or swelling.

The acid preferably used in the preparation of carboxymethyl cellulose is an aqueous solution of monochloracetic acid (ClCH_2COOH), the acid concentration ranging from 60% to 80% and the temperature from 15° to 40° C. An 80% solution of chloracetic acid corresponds to the solubility of the acid at room temperature, and at higher temperatures the acid tends to hydrolyzed. Lower concentrations than 60% introduce suffi-

cient water to result in gellation of the product and reduce the workability of the sheet. The amount of actual chloracetic acid used may vary between about 50% and 100% by weight of the pulp being treated. Preferably we employ from about 0.8 to about 1.5 mols of acid per glucose unit or from about 0.45 lb. to about 0.88 lb. of actual chloracetic acid per pound of hydrolyzed cellulose, the ratio selected depending upon the degree of substitution and the clarity of the product desired.

The acid may be partially neutralized with an alkaline agent, before application to the sheet to decrease the heat of neutralization liberated in the sheet and to reduce corrosion of equipment. As hereinbefore indicated, the employment of sodium carbonate for this purpose is helpful since the carbon dioxide gas which is liberated may be used in the final neutralization step, as indicated hereinbefore.

Complete neutralization of the chloracetic acid at this point is undesirable, and there are a number of factors to consider in determining the most desirable extent of neutralization. Thus when large quantities of salt are formed, much of the salt fails to go into solution, the viscosity of the solution is increased, and there is a greater tendency toward foaming. On the other hand, as the extent of neutralization is decreased, the aforementioned advantages of neutralizing are realized in less degree. We prefer to neutralize from 30% to 50% of the chloracetic acid, neutralization of about 40% giving optimum results.

In order to produce carboxymethyl cellulose which is readily soluble in water, the final product should contain as an average at least 0.4 and preferably 0.6 to 1.0 glycolic acid groups per glucose unit, and the reagents and conditions should be selected accordingly.

Following halogenated acid impregnation, caustic is again applied to the sheet in amounts sufficient to make up the total required. It should be noted, however, that when the halogenated acid has been partially neutralized before application to the cellulose, the amount of caustic required for each application may be reduced proportionately. At no time is there excess caustic in the sheet to allow conditions of steeping required for the formation of alkali cellulose.

It is important to the effective practice of this step of etherification that the total amount of reagents supplied to the sheet is always less than that which the sheet is capable of absorbing. Consequently the final caustic application results in prompt absorption and uniform distribution of reagent.

The reagents used in the etherification step may be applied in immediate sequence, and the time required for the material to pass through the entire set of coating rolls is usually only about one minute, rapid application of caustic and acid being essential to prevent swelling and other difficulties.

In describing the application of the reagents as a coating step, it will be appreciated that the term "coating" is not intended in a limited sense; the cellulose is promptly impregnated with the reagent by absorption, for the reason stated above.

Ripening

It is a feature of the invention that the etherification reaction is completed in a non-drying

or humid atmosphere, and to this end the impregnated sheet may be conveyed through a ripening cabinet which may be humidified by the introduction of steam. This is desirable in order to eliminate any substantial drying with resultant lack of control of the degree of substitution. A relative humidity of 90% is found to be entirely adequate for the purpose.

The conveyors in the ripening chamber are designed to retain the sheet in the chamber for a period of time which varies with the temperature selected. If a temperature of 100° C. is established in the chamber, a period of 4 minutes is satisfactory, and the ripening time may be decreased to 3 minutes at a temperature of 120° C. As the temperature is lowered, the time increases rapidly, 15 minutes being required at 80° C. The time and temperature may vary considerably, periods of ripening of from one to 20 minutes and temperatures of from 60° to 130° C. being satisfactorily employed. Only very slight drying is permissible during ripening.

Neutralization

In order to prevent the formation of yellow color in the product on drying, it is desirable to neutralize the etherified product. Carbon dioxide gas, preferably derived from partial neutralization of the halogenated acid, with sodium carbonate or other alkali metal carbonate for example, may be employed, or Dry Ice may be introduced in the neutralizing chamber to supply the gas. Hydrogen chloride gas, aqueous hydrogen chloride, or other acidic gas such as sulphur dioxide may also be used. The gas penetrates the sheet rapidly and only a loop dip is required. This step may, of course, be omitted, where neutrality is not desired, and color control is not needed, or where the product is not to be dried.

Drying

Any type of dryer, such as an ordinary open or closed roll dryer may be employed to dry the neutralized sheet. The dry product is flexible when hot, and brittle when cold, so that no crushing occurs in the dryer. However, the sheet is easily crushed in any conventional grinder to the desired particle size.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. In the process of preparing salts of acidic ether derivatives of cellulose from cellulose pulp, the steps which comprise (1) contacting the pulp in the form of a continuous sheet, while feeding the sheet through a hydrolyzing zone, with a mineral acid at elevated temperature for a period of time sufficient to effect substantial depolymerization of the pulp, (2) washing and drying the sheet while feeding the sheet through an acid removal zone, and (3) impregnating the sheet, while feeding the sheet through an etherifying zone, with an aqueous solution of a halogenated acid of the group consisting of halogenated aliphatic carboxylic and halogenated alkyl sulfonic acids having not more than 4 carbon atoms in the molecule and an alkaline agent in total amount not greater than that which the sheet is capable of absorbing.

2. In the process of preparing salts of cellulose ether carboxylic acids from cellulose pulp, the steps which comprise (1) contacting the pulp in the form of a continuous sheet, while feeding the sheet through a hydrolyzing zone, with a mineral acid at elevated temperature for a period of time

sufficient to effect substantial depolymerization of the pulp, (2) washing and drying the sheet while feeding the sheet through an acid removal zone, and (3) impregnating the sheet, while feeding the sheet through an etherifying zone, successively and in the order named, with an aqueous alkali metal hydroxide, a halogenated lower fatty acid of not more than 4 carbon atoms per molecule, and an aqueous alkali metal hydroxide, in total amount not greater than that which the sheet is capable of absorbing.

3. In the process of preparing carboxymethyl cellulose, the steps which comprise (1) contacting cellulose pulp in the form of a continuous sheet, while feeding the sheet through a hydrolyzing zone, with a mineral acid at elevated temperature for a period of time sufficient to effect substantial depolymerization of the pulp, (2) washing and drying the sheet while feeding the sheet through an acid removal zone, and (3) impregnating the sheet, while feeding the sheet through an etherifying zone, with caustic soda and an aqueous solution of chloracetic acid, the amounts by weight of actual chloracetic acid and caustic being substantially equal, and the molar ratio of chloracetic acid to glucose unit being in the range of about 0.8:1 to about 1.5:1.

4. In the process of preparing a water-soluble carboxymethyl cellulose, having a viscosity of less than 100 c.p. in a 2% aqueous solution of pH 7, the steps which comprise (1) contacting cellulose pulp in a continuous sheet of thickness 0.0125-0.06 inch, while feeding the sheet through a hydrolyzing zone, with an aqueous solution of hydrochloric acid of concentration of 5-30% by weight, maintaining within the zone a temperature of 50-100° C., the rate of feed being such that the period of hydrolysis varies from 15-200 seconds, (2) alternately washing and pressing the sheets, adding after each pressing an amount of water equal in weight to the weight of the pulp while feeding through a washing zone, (3) drying at elevated temperatures until the moisture content of the pulp is from 10-25% by weight while feeding through a drying zone, (4) impregnating the sheet while feeding through an etherifying zone, first with an aqueous solution of caustic soda of concentration 25-40% by weight in quantity of about 1.2 to about 2.2 mols of caustic alkali per glucose unit, then with an aqueous solution of chloracetic acid of concentration of 60-80% by weight in quantity of 0.8 to 1.5 mols of acid per glucose unit, and finally with an aqueous solution of caustic soda of concentration of 25-40% by weight in quantity sufficient to yield with the caustic soda added previously an amount of sodium hydroxide equal in weight to the weight of ClCH_2COOH employed in the etherification, and maintaining throughout the etherification process a temperature of 15° to 40° C.

5. In a process for the manufacture of salts of cellulose ether carboxylic acids, the steps which comprise continuously feeding a cellulose sheet while applying to the sheet, in succession and in the order named, an alkaline agent, a halogenated lower fatty acid having not more than 4 carbon atoms, and an alkaline agent, in total amount not greater than that which the sheet is capable of absorbing.

6. In a process for the manufacture of carboxymethyl cellulose, the steps which comprise continuously feeding a cellulose sheet while applying to the sheet, in succession and in the order named, aqueous solutions of caustic soda, chloracetic acid, and caustic soda, the acid and caustic

being supplied in substantially equal quantity by weight and the acid being in the molar proportion of about 0.8 to about 1.5 mols acid per glucose unit.

7. In a process for the manufacture of carboxymethyl cellulose, the steps which comprise continuously feeding a cellulose sheet while applying to the sheet, in succession and in the order named, aqueous solutions of caustic soda, chloracetic acid, and caustic soda, the acid and caustic being supplied in substantially equal quantity by weight and the acid being in the molar proportion of about 0.8 to about 1.5 mols acid per glucose unit, approximately 60% of the total caustic being supplied in the initial application.

8. In a process for the manufacture of carboxymethyl cellulose having a degree of substitution of 0.4-1.0 glycolic acid groups per glucose unit, the steps which comprise feeding a cellulose sheet while applying to the sheet in succession and in the order named, an aqueous solution of caustic soda of concentration of 25-40% by weight in quantity of about 1.2 to about 2.2 mols of caustic per glucose unit, an aqueous solution of chloracetic acid of concentration of 60-80% by weight in quantity of about 0.8-1.5 mols of acid per glucose unit, and caustic soda of concentration of 25-40% by weight in quantity of about 1.0-1.4 mols of caustic per glucose unit.

9. In a process for the manufacture of salts of cellulose ether carboxylic acids, the steps which comprise continuously feeding a cellulose sheet through an etherifying zone and a ripening zone, impregnating the sheet while in said etherifying zone with aqueous solutions of a halogenated lower fatty acid and an alkali metal hydroxide, and maintaining in said ripening zone a temperature of from about 60° C. to about 130° C. and a humid atmosphere, the rate of feed in said ripening zone being such that the period of ripening is from about one to about 20 minutes.

10. In a process for the manufacture of salts of cellulose ether carboxylic acids, the steps which comprise continuously feeding through an etherifying zone a cellulose sheet while applying to the sheet, in succession and in the order named, aqueous solutions of an alkaline agent, a halogenated lower fatty acid, having not more than 4 carbon atoms, and an alkaline agent, in total amount not greater than that which the sheet is capable of absorbing, and thereafter feeding the sheet through a ripening zone while maintaining in said zone a temperature of from about 60° C. to about 130° C. and a humid atmosphere, the rate of feed in said zone being such that the ripening is completed in from about one to about 20 minutes.

11. In a process for the manufacture of salts of cellulose ether carboxylic acids, the steps which comprise continuously feeding a cellulose sheet through an etherifying zone and a ripening zone, impregnating the sheet while in said etherifying zone with aqueous solutions of a halogenated lower fatty acid having not more than 4 carbon atoms and an alkali metal hydroxide, and maintaining in said ripening zone a temperature of from about 60° C. to about 130° C. and a humid atmosphere, the rate of feed in said ripening zone being such that the period of ripening is from one to about 20 minutes.

12. In a process for the manufacture of carboxymethyl cellulose, the steps which comprise continuously feeding a cellulose sheet through an etherifying zone and a ripening zone, impregnating the sheet while in said etherifying zone with

a partially neutralized aqueous solution of chloracetic acid and an aqueous solution of an alkali metal hydroxide, and maintaining in said ripening zone a temperature of from about 60° C. to about 130° C. and a humid atmosphere, the rate of feed in said ripening zone being such that the period of ripening is from about one to about 20 minutes.

13. In a process for the manufacture of carboxymethyl cellulose, the steps which comprise continuously feeding a cellulose sheet in succession through an etherifying zone and a neutralizing zone, reacting chloracetic acid with an alkali metal carbonate to effect partial neutralization of the acid with liberation of carbon dioxide gas, contacting the sheet while in said etherifying zone with the partially neutralized acid and an aqueous alkali metal hydroxide, and passing the liberated gas into said neutralizing zone to effect neutralization of unreacted hydroxide in the cellulose.

14. In a process for the manufacture of carboxymethyl cellulose, the steps which comprise continuously feeding a cellulose sheet in succession through an etherifying zone and a neutralizing zone, reacting chloracetic acid with an alkali metal carbonate to effect neutralization of about 40% of the acid with liberation of carbon dioxide gas, and contacting the sheet while in said etherifying zone with the partially neutralized acid and an aqueous alkali metal hydroxide.

15. In a process for the manufacture of carboxymethyl cellulose from cellulose pulp, the steps which comprise continuously feeding cellulose pulp in the form of a continuous sheet through a hydrolyzing zone, an acid acid removing zone, an etherifying zone, a ripening zone, and a neutralizing zone, contacting said sheet while in said hydrolyzing zone with a strong mineral acid to partially degrade the cellulose, washing the sheet with an aqueous liquid and heating the washed sheet to effect removal of washing liquid, applying to the sheet in said etherifying zone aqueous solutions of a halogenated lower fatty acid having not more than 4 carbon atoms and an alkaline agent and maintaining an elevated temperature in said etherifying zone to effect substitution of glycolic acid groups on the cellulose chain, and contacting the sheet in said neutralizing zone with a neutralizing agent for the unreacted remainder of the alkaline agent.

16. In a process of preparing water soluble salts of cellulose ether alkyl sulfonic acids where the alkyl radical contains no more than 4 carbon atoms the steps which comprise continuously feeding the cellulose in the form of a continuous sheet, through a hydrolyzing zone, an acid removal zone, a drying zone, and then impregnating the sheet while feeding through an etherifying zone successively and in the order named (1) with an aqueous solution of caustic alkali of concentration of 25-40% by weight in quantity of about 1.2 to 2.2 mols sodium hydroxide per glucose unit of cellulose, (2) with an aqueous solution of a halogenated alkane sulfonic acid having not more than 4 carbon atoms in concentration of about 60% to about 80% by weight in quantity of about 0.8 to 1.5 mols of acid per mol of glucose unit, (3) with an aqueous solution of caustic alkali of concentration of 25-40% by weight in quantity of 1.0 to 1.4 mols sodium hydroxide per mol glucose unit, maintaining throughout the etherifying zone a temperature of 15° to 40° C., then continuing the process while feeding the

sheet continuously through a ripening zone, a neutralizing zone, and a drying zone.

LINWOOD N. ROGERS.
WILLIAM A. MUELLER.
ERNEST E. HEMBREE.

5

REFERENCES CITED

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

Number
1,503,604
1,864,554
2,060,056
2,101,263
2,159,375
2,278,612

UNITED STATES PATENTS

Name	Date
Seel -----	Aug. 5, 1924
Reid -----	June 28, 1932
Ellsworth -----	Nov. 10, 1936
Maxwell -----	Dec. 7, 1937
Freeman et al. -----	May 23, 1939
Collings et al. -----	Apr. 7, 1942