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**TREATED FIBROUS PRODUCT AND METHOD**

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This invention relates to the preparation of materials with improved wet strength and to useful articles which can be made from such materials. Specifically, the invention relates to a process and composition suitable for use in the manufacture of high wet strength papers or other nonwoven fibrous materials.

In general, manufacturers employ any of three different methods of imparting wet strength to paper.

One method obtains increased wet strength by purely mechanical means. This method involves forming the sheet from highly beaten pulp by using special types of beaters, Jordans, pulpers, and pumps. Pulp is obtained which is finely divided and which assumes a semigelatinous state. Such pulp is referred to as being slow or as having low freeness. Papers produced this way have increased wet strength over freer pulp papers and are usually more transparent. Glassine paper is an example of material resulting from this type of treatment. This process suffers from the disadvantage of requiring large specific expensive equipment whose output is very slow compared to the output obtained from the machinery producing freer pulp papers. The resulting wet strengths of these papers are still not as high as usually desired.

A second method enjoying wider usage consists of parchmentizing the paper in varying degrees by any of several chemicals. The method does not require as much additional expensive equipment as the entirely mechanical method described above, since the chemicals are usually applied to the formed sheet. The parchmentizing reagents used include zinc chloride, strong sodium hydroxide, sulphuric acid, etc. These parchmentizing methods are still costly, however, due to the concentrated reagents which are required and to the strict control and washing techniques which are necessary. While these methods do give better wet strength papers than the first method, they cannot impart this wet strength without greatly and seriously altering the texture of the papers so treated.

The third method in common usage designed to increase wet strength in paper consists in sizing the paper in either of two ways by the use of various materials. The size material may be natural gums, chitin, or resins such as urea-formaldehyde or melamine derivatives. It may be incorporated into the beater sizing or it may be surface sized on the sheet during one of the drying operations or in calendering. This method is the best which has been found to date. However, it requires the use of expensive resinous materials and precise control of the various reactants such as formaldehyde, acids, coupling agents, etc., some of which always remain entrained in the cellulose fibers of the pulp in the unreacted or uncured state. Aside from these disadvantages, resinous materials are highly colored, especially when fully cured, and thereby produce very dark papers, such as butcher paper. When the resin content is reduced to produce minimum discoloration, the wet strength suffers.

As far as we have been able to determine, there is no clearly defined system of applying size materials by either

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surface sizing or beater sizing which will economically produce a high degree of wet strength in free paper stock using small amounts of size materials, which does not simultaneously produce a parchmentizing effect, leave undesirable unreacted reagents entrained in the cellulose fibers, or cause pronounced discoloration.

One object of the present invention is to develop a high wet strength nonwoven fibrous product and devise a method for its production, for example, by either surface or beater sizing, which product does not necessarily contain an excessive amount of size materials, is not unduly parchmentized, does not contain undesirable unreacted reagents entrained in the fibers, and is not undesirably disclosed.

A further object of the invention is to obtain a product having a wet strength which is a major proportion, at least about 60% expressed percentage-wise, of the untreated dry strength without resorting to incorporation of an excessive amount of sizing material in the fibers.

The products of the present invention which possess marked advantages as compared to prior art materials are nonwoven fibrous articles containing as impregnant free acid cellulose glycolic acid ether (also called free acid carboxymethyl cellulose) or free acid cellulose hydroxypropionic acid ether (also called free acid carboxyethyl cellulose) having degree of polymerization within a certain range, and heat treated in the dry state at elevated temperature to convert the free acid cellulose ether to an insoluble or "refractory" form. Free acid carboxymethyl cellulose is the preferred impregnant. In the specification terminology, the term cellulose glycolic acid ether (or carboxymethyl cellulose) includes both the free acid cellulose glycolic acid ether and its salts. Similarly, cellulose hydroxypropionic acid ether (or carboxyethyl cellulose) includes both the free acid cellulose hydroxypropionic acid ether and its salts.

Particular advantages of the invention flow from the manner of heating the cellulose derivative (ether) treated materials. Further important characteristics, developed more fully below, of the impregnant of this invention are the degree of substitution (number of carboxymethyl or carboxyethyl groups per anhydroglucose unit) and the degree of neutralization (percentage of total carboxyl hydrogens replaced by salt-forming cations such as ammonium and alkali metals).

The impregnants, whose structure and properties are described in greater detail below, may be added to the nonwoven fibrous material according to the invention by a variety of procedures. Each of the procedures involves incorporating, by one way or another, free acid carboxymethyl or free acid carboxyethyl cellulose into the nonwoven fibrous material. The free acid cellulose ether may be so incorporated by way of any of its soluble salts, soluble forms of the acid itself, or by synthesis of the cellulose ether in situ on cellulose fibers. A preferred procedure utilizes the ammonium salt of the cellulose derivative, which may be made by direct contact of free acid carboxymethyl or carboxyethyl cellulose powder with concentrated aqueous ammonium hydroxide solution. The latter solution is used at least in amount to supply NH<sub>3</sub> equivalent to the free COOH groups on the selected free acid cellulose derivative. The ammonium salt is then diluted with water to any desired concentration and used directly as a treating agent added to the fibrous material either as a beater size or surface size. If desired, the free acid carboxymethyl cellulose used for preparation of the ammonium salt may be synthesized by acidification of the sodium salt, using aqueous mineral acid if the free acid cellulose ether has degree of substitution (described below) in the insoluble range, and mineral acid plus alcohol if the free acid cellulose ether is soluble in water, and filtration of the free acid cellulose ether.

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Free acid carboxymethyl cellulose was prepared, for example, by steeping 20 parts (by weight) of sodium carboxymethyl cellulose in 500 parts of a mixture of 1000 parts isopropanol to 200 parts concentrated hydrochloric acid for two hours. The liquid was then removed and steeping repeated with an equal and fresh amount of isopropanol-HCl. The solid material was then washed with a mixture of 80 parts isopropanol and 20 parts water until free of mineral acid and sodium chloride. The converted free acid carboxymethyl cellulose powder was then filtered and dried in air at room temperature. The dried powder was treated with ammonium hydroxide solution containing  $\text{NH}_3$  in amount equivalent to the carboxyl groups in the free acid carboxymethyl cellulose. The resulting solution of ammonium carboxymethyl cellulose was then diluted with water to 2 percent by weight strength.

The ammonium salt is incorporated into the fibrous material in amounts and aqueous solution concentrations indicated below. After treating and drying, the fibrous material is heated at temperature to bring about decomposition of the ammonium salt into  $\text{NH}_3$  and the free acid cellulose ether and further transformation of the free acid cellulose ether into a form which has been found to be quite insoluble in water and other solvents, and may be properly described as "refractory." The formation of refractory free acid carboxymethyl cellulose or carboxyethyl cellulose impregnant is accompanied by a remarkable increase in wet strength and is brought about by carefully controlling the temperature at and time during which the treated material is heated. In general, elevated temperatures are necessary to bring about the transformation. Formation of refractory acid impregnant begins to take place at an appreciable rate at about  $175^\circ\text{F}$ . At this temperature it takes at least about 30 minutes to effect an appreciable increase in wet strength of the impregnated material and a decrease in the solubility of the acid as compared with the acid-treated and dried but non-heat treated material. Conversion takes place at a substantially faster rate at temperatures of at least about  $200^\circ\text{F}$ . Heating time in each case is preferably at least about 30 minutes. Within the heating time of about  $2\frac{1}{2}$  to 3 hours optimum wet strength and insolubility is obtained.

On rapid and continuously operating paper and other textile machinery treatment times in excess of about 10 minutes are generally not permissible. It is a particular advantage of this invention that temperature may be so adjusted to produce reaction rates sufficiently rapid and reaction time correspondingly short so that the desired refractory properties and high wet strength may be obtained in time sufficiently short to be compatible with the operation of such high speed machinery. Temperatures above about  $235^\circ\text{F}$ . generally afford these higher reaction rates. Preferably, for fast operation and correspondingly short heating times, temperatures are maintained above about  $300^\circ\text{F}$ . The temperature in any case is maintained below levels at which excessive degradation of the cellulose ether treating agent or the base fabric occurs within the minimum time in which the material can be handled at the elevated temperatures in question. Preferably, temperature is held below about  $350^\circ\text{F}$ .

Any source of heat is suitable for practicing the invention. Hot air or infra-red ovens, induction heating devices, steam, hot plates, or heated irons may be used. For small scale work involving surface sizing of formed sheets, the use of hot plates or flat irons is preferred, whereas in larger scale, e. g., continuous operation, hot air ovens, which are standard equipment in paper manufacture, are preferred.

Although the ammonium salt affords a convenient way of incorporating the free acid cellulose derivative agent into the material to be treated, the invention is not limited to the use of the ammonium salt. An alternative procedure is to treat the fibrous article with the sodium salt, for example, in an aqueous solution, and thereafter form

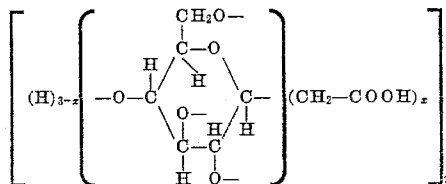
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the free acid cellulose derivative in situ on the fibers by the addition of a stronger acid, such as hydrochloric acid or a mixture of such acid and alcohol. The acidified material is then washed thoroughly with water to remove excess reagents and dried. The treatment described is then followed by heating to form the refractory free acid carboxymethyl cellulose just as described in the case of the ammonium salt.

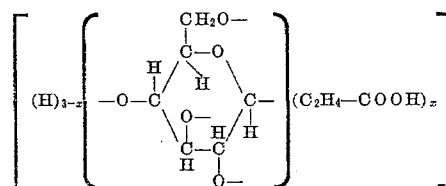
As a further alternative procedure, a water solution of the free acid cellulose derivative may be prepared (if cellulose derivative water soluble in acid form is used) by adding an excess of HCl to a 2 percent solution of the sodium salt. This can be dialyzed using a semi-permeable membrane to remove the excess mineral acid and NaCl and leave free acid cellulose ether in solution. This free acid carboxymethyl cellulose solution is then used to treat the fibrous material. The material is dried and heated at the elevated temperatures indicated above to obtain an invention product having refractory cellulose derivative impregnant and high wet strength.

Another method for incorporating the invention sizing agents into cellulosic materials comprises first treating the cellulosic material with caustic soda or potash to form the alkali metal derivative, when reacting this derivative with an alkali metal salt of chloroacetic acid. The conditions of the reaction can be controlled to maintain the physical state of the reacted fibrous cellulosic material, which can then be washed free of reagents and converted to the free carboxymethyl cellulose acid by treatment with a solution of a mineral acid. Washing, drying, and heat treatment to form the refractory cellulose derivative follow.

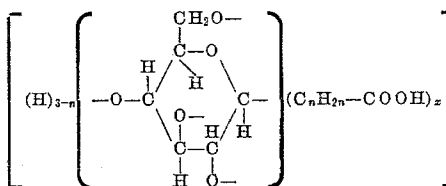
The carboxymethyl cellulose, also known as cellulose glycolic acid ether, which is used to prepare the products of the invention, may be described structurally as:



where  $x$  is not greater than 3 and  $y$  is a large whole number. The ring structure represents the anhydroglucose residue which is linked in known manner to similar residues on either side to form the long chain cellulose structure. The bracketed H atoms are attached to oxygen atoms in the anhydroglucose residue in known fashion. Similarly, the  $(\text{CH}_2-\text{COOH})$  groups are attached to the residue through oxygen linkage by substituting for the aforementioned H atoms. The carboxyethyl cellulose (cellulose hydroxy propionic acid ether), which is an alternate to the carboxymethyl cellulose, may be described structurally as:



$x$ , again, being not greater than 3 and  $y$  a large whole number. The  $\text{C}_2\text{H}_4$  group is preferably  $-\text{CH}_2-\text{CH}_2-$ . The general formula of the starting materials of the invention is, therefore:



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where  $x$  is not greater than 3,  $n$  is 1 or 2, and  $y$  is a large whole number.

The degree of substitution (D. S.), a term commonly employed in connection with cellulose derivatives of the nature of the invention starting materials, is an important property and indicates the average number of substituent groups per glucose unit in the cellulose molecular chain (i. e., the value of  $x$  in the above formulae). Since there are three hydroxyl groups and hence three possible points of substitution per glucose unit, the maximum D. S. is 3.0. For the purpose of the present invention, material having D. S. which will afford water solubility of the salts (such as the ammonium or sodium salt) to produce suitable sizing solution may be employed. Solubility will generally be adequate in compounds having D. S. at least about 0.25. Compounds having D. S. above about 0.5 are generally soluble in the acid form. As D. S. approaches 3.0, water solubility of the salts may generally be found to be adequate. The preferred maximum D. S. is about 2.0.

For invention purposes, consideration is given to the degree of polymerization (D. P.), of the cellulose derivatives (the value of  $y$  in the above formulae). At very low molecular weights, water solubility may become quite high with corresponding increase in difficulty of producing, by the heat treatment described above, an impregnant which is desirably insoluble in water and which imparts wet strength to fibers. This degree of polymerization expressed as viscosity reading in seconds on a modified Ostwald-Fenske viscosimeter pipette ASTM D-445 #300 of a 0.5% by weight aqueous solution of the free acid in a 0.50 N NaOH solution at 25.50° C. should be at least about 5.7 seconds and may be as high as 36 seconds or greater, as compared with a zero pipette reading of 5.0 seconds for a 0.50 N NaOH solution at the same temperature.

It is important to retain in the cellulose ether impregnant an adequate number of carboxyl groups whose hydrogen atoms are not replaced by salt-forming radicals such as ammonium or alkali metal. In other words, the degree of neutralization (D. N.) should be maintained below certain limits. These free carboxyl groups are necessary to bring about formation of the highly insoluble and refractory impregnant in the treated fibrous article according to the invention. D. N. is maintained not greater than about 50%, preferably 25% or lower. As indicated above, however, the sizing agent used to treat the fibrous material may be highly or even completely neutralized, so long as the D. N. is reduced in the final impregnant.

The cellulose derivative (ether) impregnant of the invention is incorporated in the fibrous material in amount sufficient to impart to the material the degree of wet strength desired. Greater amounts of impregnant in general will impart greater wet strengths. Some increase in wet strength may be noted in amounts above about 0.1% based on the dry fibrous material, particularly in the case of highly beaten (i. e. low freeness) pulps. In ordinary usage where a material having an appreciable degree of flexibility, such as paper, is desired, the content of solid impregnant will generally be below about 10% by weight based on the dry material. For the manufacture of stiffer material, however, such as paper board, the content of the sizing agent may run much higher, possibly about 50%. Preferred amounts of impregnant affording the advantages of maximum flexibility and optimum hand consistent with high wet strength lie in the approximate range 1 to 8%.

The concentration of impregnant in the sizing solution will be influenced largely by the point at which the agent is incorporated into the process stream. In paper manufacture, for example, the water content of the pulp in the beater is quite high and decreases progressively as it is passed through the paper forming and drying machine. Accordingly, concentration of sizing agent to

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effect a given increase in wet strength would ordinarily be lower in the beater pulp than farther along in the process, for example, in or about the drier (where the agent may be applied as a surface size). In general, it is preferred to practice the invention in the range of 0.05% to 10% by weight solids in the size solution. The pickup of size solution, i. e. proportion thereof to the weight of dry fibrous material will be controlled, as by calendering or surface sizing, in coordination with the concentration of the size solution to produce the desired incorporation of agent into the material. For example, if 3% solids is desired and the sizing solution has 2% solids, sizing solution pickup will be about 150%.

The various procedures illustrated above for incorporating carboxymethyl cellulose or carboxyethyl cellulose into nonwoven fibrous material each involve forming an aqueous solution of the cellulose derivative in one chemical form or another and treating the fibrous material with this aqueous solution. Other procedures may be used, however, if desired. For example, the carboxymethyl or carboxyethyl cellulose in suitable form may be dissolved in organic solvents in cases where it is soluble therein, and the formed solutions used to treat the fibrous material just as in cases where aqueous solutions are employed. After converting the cellulose ether to the free acid form, the fibrous material is dried and heat treated.

The size material of the invention can be used to impart wet strength to materials other than paper, and enhances the value of articles made from such other materials. For example, the invention is specifically advantageous for imparting wet strength to materials such as paper board, tissues, toweling, disposable diapers and underpads, sheets formed of nonwoven fibers either isotropic or oriented in one or more directions, rovings, slivers, and special wrappers used in the food industry. The invention is not limited to fibers of cotton or even of cellulose. Materials formed of silk, linen, ramie, polyacrylonitrile fibers, polyamide fibers, vinyl polymer fibers, glass wool, asbestos, jute, or the like, may be imbued with enhanced wet strength in the same general fashion as cotton. Articles having improved wet strength properties find use as wrappings for food products such as meat, frozen vegetables, etc.; tea bags; filter discs and mats; wallpaper; paper bags; cleansing tissues; and toilet tissue.

Following are examples, in which parts are expressed on a weight basis, which are intended to illustrate the invention but not to limit the scope thereof.

#### Example 1

Whatman #1 filter paper (a free pulp, high cellulose paper), having tensile strength when dry of 10.2 lbs. per inch width and a tensile strength when wet less than 0.2 lb. per inch, as determined on a standard Electro-Hydraulic Tensile Tester, model 35-4 of the Thwing-Albert Instrument Company with a jaw clearance of 2 inches, was treated with a 2% (based on free acid) solution of ammonium salt of carboxymethyl cellulose prepared from the sodium salt via the free acid as described above. The carboxymethyl cellulose had degree of substitution of 1.23 and degree of polymerization indicated by viscosity of the sodium salt in a 0.5 normal NaOH solution at 25.50° C. of 24.4 seconds as measured in a modified Ostwald-Fenske viscosimeter pipette ASTM D-445 #300. The treated paper contained about 300% of the sizing solution based on dry paper, corresponding with 6% added solids based on the dry paper. The paper was air-dried at about 75° F. and a portion tested for wet strength, which was found to be 7.0 lbs. per inch. Another portion of the same paper was heated under an iron at 320° F. for two minutes. Wet strength of the heat-treated paper was then determined and found to be 14.0 lbs. per inch.

*Example 2*

A portion of the free acid carboxymethyl cellulose-treated and air-dried (not heat treated) material prepared in Example 1 was placed in an air-heated oven and maintained therein to 240° F. for 10 minutes. At the end of this time, the wet strength of the impregnated material was found to be 8.2 lbs. per inch.

*Example 3*

Two parts by weight of free acid (0% neutralization) carboxymethyl cellulose (having degree of substitution of 1.17 and degree of polymerization indicated by viscosity as determined by Example 1 procedure of 18.3 seconds) were dissolved in 10 parts water and 4 parts of concentrated (28.3% by weight NH<sub>3</sub>) ammonium hydroxide. After solution of the acid had occurred, it was diluted to make a 2% solution based on free acid. Whatman filter paper #44 (dry strength 10 lbs. per inch, wet strength 0.8 lb. per inch) was then treated with the 2% solution to sufficient wet weight pickup to obtain 5.2 carboxymethyl cellulose ammonium salt on a dry basis. The treated paper was then dried in air and heated under an iron for 3 minutes at a temperature of about 290° F. One-inch wide strips of the impregnated material were then cut and immersed in water and tested for wet strength, which was found to be 12 lbs. per inch.

*Example 4*

Whatman filter paper of the type employed in Example 1 (i. e. #1) was treated with a 2% (based on free acid) solution of carboxymethyl cellulose ammonium salt to the extent of 6% ammonium salt based on the dry filter paper. The carboxymethyl cellulose had degree of substitution of 1.23 and degree of polymerization indicated by viscosity reading of the sodium salt of 7.0 seconds, as determined by the Example 1 procedure. The treated paper was dried at room temperature and then heated under an iron for 2 minutes at 320° F. The wet tensile strength was found to be 5.2 lbs per inch.

*Example 5*

A 2% (based on free acid) aqueous solution of carboxymethyl cellulose ammonium salt was prepared by acidification and washing of the sodium salt followed by treatment with aqueous ammonium hydroxide, as described above. The carboxymethyl cellulose had degree of substitution of 1.23 and degree of polymerization corresponding with sodium salt viscosity of 24.4 seconds as determined by the standard procedure set forth in Example 1. Filter paper of the type employed in Example 1 (i. e. Whatman #1) was then treated with a 2% solution to the extent of 6% sizing solids based on the dry filter paper. The treated paper was air-dried. One strip was maintained at 75° F. for one day. A second strip was heated for 10 minutes at 280° F. in an oven. A third strip was heated in the oven for 30 minutes at 280° F., and a fourth strip at the latter temperature for 2 hours. Wet strength was tested after one minute of immersion of the papers in water. The wet strength of the first sample (75° F. drying) was 6.2 lbs. per inch. Sample No. 2 (10-minute heating) was 8.2 lbs. per inch, sample No. 3 (30-minute heating) was 11.0 lbs. per inch, and sample No. 4 (2-hour heating) was 14.2 lbs. per inch.

*Example 6*

Filter paper of the type employed in Example 1 (Whatman #1) was treated with a 2% solution of carboxymethyl cellulose ammonium salt to the extent of 6% solids, and dried. The carboxymethyl cellulose had degree of substitution of 1.23 and degree of polymerization corresponding to sodium salt viscosity equal to 24.4 seconds. One sample of the dried material was heated in an oven at 180° F. for 10 minutes. Another sample was heated under the same conditions for 30 minutes, and a third sample under the same conditions for 2½ hours.

The wet strength of sample No. 1, as determined by standard procedure described above, was 6.2 lbs. per inch. Sample No. 2 showed wet strength of 7.8 lbs. per inch, and sample No. 3, 8.5 lbs. per inch.

*Example 7*

Carboxymethyl cellulose sodium salt having degree of substitution of 0.74 and degree of polymerization corresponding with sodium salt viscosity of 36.0 seconds was made into a 1% aqueous solution (based on free acid). The solution was coated on a free pulp paper whose dry strength was 12.0 lbs. per inch and whose wet strength was 0.2 lb. per inch to the extent of 1 to 2% sizing solids based on the dry paper. After drying in air at room temperature overnight, the sized paper was steeped for 15 minutes in a solution of 80% ethyl alcohol and 20% HCl, followed by 15 minutes in a solution of 50% ethyl alcohol and 50% water, followed in turn by one hour in water. The paper was then dried in air at room temperature and heated under an iron at a temperature of about 300° F. for 3 minutes. After 2 minutes immersion in water, the wet strength of the heat-treated material was tested and found to be 5.1 lbs. per inch.

*Example 8*

Carboxymethyl cellulose acid having degree of substitution of 1.21 and degree of polymerization corresponding to sodium salt viscosity of 26.8 seconds was dissolved in water to form a solution having about 1% strength. Approximately 25% of the carboxyl groups substituted into the cellulose chain of the carboxymethyl cellulose were neutralized with sodium hydroxide; that is, degree of neutralization was about 25%. This solution was used to treat a piece of filter paper (Whatman #1) to the extent of about 2½% by weight solids based on the dry paper. The paper was then dried in air at about room temperature and heated under an iron for 2 minutes at about 290° F. The wet strength of the impregnated paper was 4.5 lbs. per inch as compared with 0.2 lb. per inch before treatment.

*Example 9*

Carboxymethyl cellulose sodium salt having degree of substitution of 1.21 and degree of polymerization corresponding with 26.8 seconds viscosity and degree of neutralization of about 45% was made into a 2% aqueous solution, which was then used to impregnate a sample of filter paper with dry strength of 16.4 lbs. per inch and untreated wet strength of about 0.2 lb. per inch to the extent of 3% by weight size solids based on the dry filter paper. The treated paper was dried in air at room temperature and heated under an iron for 1 minute at about 320° F. Wet strength was determined and found to be 9.0 lbs. per inch.

The foregoing description is presented as illustrative and it will be apparent that there are many modifications within the spirit and scope of the invention. Hence, the invention is to be limited only by the appended claims.

What is claimed is:

1. A flexible nonwoven fibrous sheet of improved wet strength, being substantially free of water soluble metallic compounds, and containing as the sole wet strength improving impregnant an amount in the range of about 0.1 to 8.0% by weight of a substantially water insoluble cellulose derivative of the group consisting of free acid cellulose glycolic acid ether and free acid cellulose hydroxypropionic acid ether having degree of polymerization indicated by viscosity of a 0.50% by weight solution of the free acid in a 0.50 N NaOH solution at 25.50° C. of at least 5.7 seconds as determined in a modified Ostwald-Fenske viscosimeter pipette ASTM D-445 #300, as compared with a zero pipette reading of 5.0 seconds for a 0.50 N NaOH solution at the same temperature, said cellulose derivative having degree of substitution above about 0.25, and degree of neutralization not greater than

about 50%, the wet strength thereof being at least 42.5% of its untreated dry strength.

2. A sheet of claim 1 wherein the cellulose derivative has a degree of substitution above about 0.50.

3. A sheet of claim 1 wherein the cellulose derivative is the glycolic acid ether.

4. A sheet of claim 3 having been heated at above about 235° F.

5. A sheet of claim 3 having been heated at above about 300° F.

6. A method of preparing a sheet of claim 1 which comprises incorporating in the initial sheet a water soluble salt of the cellulose derivative, which salt is unstable at elevated temperatures, and heating the so treated sheet at a temperature above about 175° F. to obtain the sheet of improved wet strength.

7. A method of claim 6 wherein the cellulose derivative is the glycolic acid ether.

8. A method of claim 6 wherein the salt is the ammonium salt.

9. A method of claim 8 wherein the cellulose derivative is the glycolic acid ether and the temperature is above about 235° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,033,481	Richter -----	Mar. 10, 1936
2,370,517	Bass -----	Feb. 27, 1945
2,422,572	Lillienfeld -----	June 17, 1947
2,474,700	Slifkin -----	June 28, 1949
2,502,782	Erickson -----	Apr. 4, 1950
2,502,783	Erickson -----	Apr. 4, 1950
2,542,784	Van Dueen -----	Feb. 20, 1951
2,655,864	Newman -----	Oct. 20, 1953