METHOD OF MAKING PULP
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The present invention relates generally to a method of making improved pulp for the manufacture of paper, and more particularly, it relates to a method of making improved cellulosic pulp, by chemically treating said pulp, for the manufacture of paper having increased tensile strength and fold endurance.

A pulp has been manufactured in any one of the several methods which are known to the paper art, it is generally further processed to develop "freeness" or reduce "freeness"; that is, the pulp is processed to increase the amount of beating necessary to provide a desired degree of hydration of the pulp. Furthermore, the method may be carried out at ambient temperature, if desired. Such method involves subjecting the pulp, under substantially anhydrous conditions, before beating to treatment with a selected reagent so as to bring about a low degree of substitution of hydrophilic groups for hydroxyl-containing radicals in the cellulose of the pulp. The method provides a pulp which is capable of making sheets of increased tensile strength and fold endurance.

Accordingly, the main object of this invention, therefore, is to provide a method of improving paper-making pulp, by increasing the sorptivity of the pulp without substantially damaging the fibers in the pulp. It is also an object of the present invention to provide a method whereby improved paper products can be manufactured. It is a further object of the present invention to provide a method for treating cellulosic pulp in situ to improve its papermaking characteristics, which method is readily carried out at a relatively low temperature and at a relatively rapid rate.

As will become more clearly described hereinafter, the method of the present invention involves treating cellulosic-containing pulp with substantially anhydrous reagent comprising a selected acid in dimethyl sulfoxide so as to introduce into the cellulose of the pulp, to a low degree, hydrophilic groups comprising short chain organic radicals. The treatment provides the pulp with improved papermaking properties, including low freeness. Moreover, in the beater operation, the time and power required to achieve the desired degree of freeness in the pulp are considerably reduced, if the pulp has been treated with the reagent in accordance with the present invention before beating.

The pulp may be any papermaking materials which contain cellulose, for example, cotton linters pulp, rag stock, Douglas fir pulp, or the like or mixtures thereof, with or without noncellulosic-containing constituents. The pulp, after being subjected to the described treatment in accordance with the present invention, may, if desired, be blended in various degrees with other pulp prior to or subsequent to beating.

Paper sheets produced from pulp treated in accordance with the method of the present invention exhibit a tensile strength which is increased as much as 100 percent or more in tensile strength over that of handsheets made from conventionally processed pulp. In addition, the zero-span tensile strength may be increased more than 20 percent over that for conventional sheets. Moreover, the fold endurance of such sheets has been greatly increased, by the use of the method of the present invention, up to 400 times that of the sheets made from conventionally processed pulp, further indicating that higher quality paper products are produced in accordance with the present invention.

The observed increase in strength characteristics for the paper products is obtained without accompanying decrease in other desirable characteristics of the paper products and without the production of undesirable characteristics. Such improvement in strength characteristics appears to result from the substitution of a short chain hydrophilic radical, to a low degree, for hydroxyl groups on some of the cellulose molecules of the pulp. This permits the pulp fibers to be more readily separated from,
each other without breakage during beating and also to more readily sorb water, i.e., hydrate. The degree to which the hydrophilic groups are to be added should be limited and, in this connection excessive addition of hydrophilic groups results in solubilization of the cellulose with consequent loss in yield. In general, the degree of substitution should be less than 0.08 and, for most practical purposes, not more than 0.07. The degree of substitution (D.S.) is defined as follows:

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\text{D.S.} = \frac{\text{molecular equivalents of hydrophilic radicals substituted}}{\text{molecular equivalents of anhydroglucose units}}
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The anhydroglucose unit is the basic structural unit of the cellulose. At 0.07 to 0.10 D.S. cellulose fibers become partially soluble in water. Moreover, no further improvement in the tensile strength and fold endurance can be obtained with such high D.S. Any lower D.S. provides some improvement in the papermaking properties of the pulp but below about D.S. 0.009, the improvements are minimal. It is preferred that the degree of substitution be kept within the range of from about 0.03 to 0.05 for optimal results. The degree of substitution is inversely proportional to freeness of the pulp, which has been previously described.

The hydrophilic groups which may be substituted in the cellulose comprise carboxyalkyl groups having carbon chains of less than four carbon atoms in the alkyl chain, so as to provide ethers of cellulose having a hydrophilic character. In general, longer chains in the alkyl groups result in reduced hydrophilic properties so that the improved properties of the present invention do not result. The ethers, which are formed by the substitution reaction, comprise only a small portion of the pulp, so as not to unduly increase the water solubility of the pulp, while still providing a large increase in the hydration of the cellulose fibers.

Consequently, the necessity for long periods of beating in the papermaking operation to bring about hydration of the pulp at the expense of strength characteristics in the pulp is substantially eliminated. The mechanism by which the desired result is accomplished is not completely understood, but it is evident that pulp which has been treated in accordance with the present invention has greatly increased hydrophilic properties and may be formed into paper sheets which have increased tensile strength and fold endurance.

The method of the present invention involves carboxyalkylation of the cellulose pulp in situ and under selected conditions, preferably in substantially anhydrous environment. This latter condition prevents mercerization of the pulp during its treatment. It has been found that mercerization of the pulp is undesirable, particularly where relatively short fibers, such as those of cotton linters, are utilized in the pulp, since mercerization results in a decrease in fiber length, with consequent decrease in fold endurance when the pulp is manufactured into paper.

The limited carboxyalkylation of the pulp in situ is accomplished by reacting the pulp with a selected acid in dimethyl sulfoxide. A species of the carboxyalkylation is carboxymethylation in which a carboxymethyl group is substituted in the cellulose for a few of the free hydroxyl groups of the cellulose molecule. This type of reaction may be obtained by reacting monochloroacetic acid with alkaline cellulose. In this manner, some of the hydroxyl groups of the cellulose molecules react to form a glycolic acid ether having the general formula ROCH₂COOH, where R represents the remaining large portion of the cellulose molecule or modified cellulose molecule to which the particular OCH₂COOH group is attached.

It should be noted that the improved sorbing qualities of the cellulose pulp obtained in situ carboxyalkylation of the pulp are not achieved by the addition of commercially available substances such as carboxymethyl cellulose (CMC) to the pulp before or during the beating operation for the following reasons: (1) if CMC is merely added to the pulp, it is difficult to control the degree of retention of CMC in the pulp because of its solubility in water; (2) the CMC which is sorbed on the pulp may be removed by washing; (3) the hydrophilic groups provided by the CMC do not appear to be very uniformly distributed in the pulp; (4) it has been found that in certain pulp beating operations the improvement in strength characteristics brought about by the addition of the CMC undergoes substantial decreases while during the same beating operations the strength characteristics of the partially substituted cellulose fibers treated in accordance with the present invention improve.

Now referring more particularly to the method of the present invention, cellulose-containing pulp is obtained in the usual way from various cellulose sources. The pulp is then dried in any suitable manner, as for example, air drying and/or drying by solvent exchange technique to drastically reduce the water content thereof. The dried pulp is then subjected to in situ carboxyalkylation to a low degree by soaking it in at least substantially anhydrous reactant comprising at least substantially anhydrous liquid dimethyl sulfoxide and a small but effective amount of an acid selected from the group consisting of monochloroacetic, monobromoacetic, monooiodooacetic, monochlorobutyric, and monochloropropionic acids and mixtures thereof. The particular acid is selected from the group on the basis of the particular type of carboxyalkylation it is desired to effect. However, it is generally preferred to carry out in situ carboxymethylation, utilizing monochloroacetic acid.

Dimethyl sulfoxide has the formula C₄H₇OSO₂H and is normally an oil or thick syrup with a melting point of 6° C. and a decomposition point of about 100° C. It is commercially available. It has been found that the enhanced results obtained by the method of the present invention are, to a considerable extent, due to the use of the dimethyl sulfoxide as solvent for the carboxyalkylation. It is not known in what manner the dimethyl sulfoxide operates to bring about such improved results. However, the improved results afforded by the use of the dimethyl sulfoxide in place of other anhydrous or substantially anhydrous organic solvents is demonstrable. Thus far, solvents exerting the same effect the pulp as dimethyl sulfoxide have not been found.

The acids above-listed are also commercially available and are normally liquid at room temperature. The selected acid or acids may be utilized for the carboxyalkylation in any suitable concentration in the dimethyl sulfoxide as, for example, 2 to 4 percent by weight, which is sufficient to bring about the desired low degree of substitution in the pulp, within the range of from about 0.009 to 0.08, preferably .03 to .05, and within a reasonable period of time. The reagent is preferably present in a volume at least as great as the pulp which is soaked therein, in order to facilitate suspending the pulp in the reagent and to ensure uniformity of reaction throughout the pulp. Preferably, the reagent-to-pulp ratio is at least about 2:1, on a volume basis.

The soaking or immersion step can be carried out at any desired temperature above the melting point of the dimethyl sulfoxide and acid and below the boiling point or decomposition point thereof. The soaking step can be conveniently carried out at room temperature (65°–70° F.) or below. It is preferred to carry out the soaking steps at ambient temperature, usually within the range from about 55° to 90° F., so that heat need
not be added to the system. The carboxyalkylation reaction is sufficiently rapid at low temperatures utilizing the reagent of the present invention, so that temperatures within the above-described range can be readily utilized. The soaking step is carried out until a predetermined period of time has passed which, depending on the type of pulp, concentration and type of acid in the reagent, temperature and other conditions, will assure that the desired low degree of carboxyalkylation, that is, substitution of the hydrophilic groups in the cellulose, has occurred. For example, soaking cotton linter pulp in 2 parts by volume of dimethyl sulfoxide containing 4 percent by weight of monochloroacetic acid 1 hour at room temperature is usually sufficient to bring about the desired low degree of substitution of from about 0.009 to 0.07.

After the soaking step, the pulp can be processed in any suitable manner to the final product. In this connection, it is preferred that the excess reagent be removed, as by filtering or thioketone, and that whatever residual acid is present in the pulp be then neutralized with a suitable base, such as sodium hydroxide, potassium hydroxide or the like.

Since it is desired to avoid mercerization of the pulp, the alkali neutralization treatment of the pulp with the base should be carried out under at least substantially anhydrous conditions. For example, the base can be placed in a non-aqueous solvent, such as dimethyl sulfoxide or methanol, or a mixture thereof, or other suitable organic solvent can be employed. It is preferred to utilize dimethyl sulfoxide as the medium, with or without another organic solvent. Neutralization can be carried out at any suitable temperature, for example, ambient temperature. The pulp can then be separated from the base and non-aqueous medium, and can be subjected to treatment at any desired temperature with an aqueous solution of a basic water-soluble salt, for example, sodium bicarbonate, to convert the compound formed from cellulose by the carboxyalkylation reaction into the corresponding salt. After such treatment, the pulp is ready for conventional beating operations to hydrate the pulp to the desired degree and prepare it for conventional paper-making processes.

It has been found that the fold endurance and tensile strength of paper made from the treated pulp can be further enhanced, subsequent to the soaking treatment, when the alkaline neutralization step is carried out utilizing an excess (above that required for neutralization) of base, preferably sodium hydroxide. The excess base should be present in an amount sufficient to provide an excess base concentration of at least about 0.3 percent, by weight of the total amount of the base, preferably between about 0.3 percent and about 1.0 percent, to obtain the enhanced results. Furthermore, higher percentages within the range set forth have been found to be preferable.

Subsequent to such alkaline neutralization, the base and non-aqueous medium may be removed from the pulp, as by filtering or the like. The residual excess base in the pulp may then be neutralized by contacting the pulp with acid, as by immersing it in an aqueous solution containing a small amount of acetic acid or other suitable acid. Thereafter, the pulp may then be washed with water to remove the formed salts and residual acid. The pulp is not soluble in alkaline solution at low or high temperature. Treatment of the pulp with a basic salt solution, for example sodium bicarbonate, to form the corresponding salt of the cellulose derivative formed by carboxyalkylation can then be carried out, as previously described.

Refining subsequent to the described pulp treating steps is carried out to beat the pulp to a given freeness. Such beating can be completed in less time than when untreated pulp is beaten, and furthermore, provides the treated pulp with enhanced physical characteristics. The pulp is then ready for conversion into paper having greatly improved tensile strength and fold endurance over paper made from conventionally processed pulp. The following example more particularly sets forth certain features of the present invention.

**EXAMPLE**

Cotton linters pulp, was solvent exchange dried in the conventional manner utilizing a mixture of water, methanol and benzene. The pulp was then air dried to remove the residual benzene therefrom, after which the pulp was separated into portions A, B, C and D of equal weight. Portion A was the control and was left untreated prior to beating and conversion to paper. Portions B, C and D were each soaked in two parts by weight of anhydrous reagent to one part by weight of pulp. In the case of portion B, the reagent comprised dimethyl sulfoxide, with 2 percent, by weight of dimethyl sulfoxide, of anhydrous monochloroacetic acid added, while in the case of portions C and D the reagent comprised dimethyl sulfoxide, with 4 percent, by weight of dimethyl sulfoxide, of anhydrous monochloroacetic acid added.

The soaking treatment was carried out in the absence of agitation and over a period of one hour at ambient temperature (about 70°F.), after which the reagent was separated from each portion of pulp by filtering and pressing the pulp portion.

Portions B, C and D were then each suspended in two parts of a mixture of anhydrous dimethyl sulfoxide and anhydrous methanol. The dimethyl sulfoxide was present in the mixture in a volume ratio to the methanol of 7 to 1. The mixture also contained sufficient sodium hydroxide to neutralize all of the acid remaining in the pulp and to provide an excess sodium hydroxide concentration. In the case of portions B and C, this excess concentration of sodium hydroxide was about 0.3 percent, by weight of the pulp on a bone dry basis. In the case of portion D, the excess sodium hydroxide concentration was about 1.0 percent, by weight of the pulp on a bone dry basis. The neutralization was carried out at about 86°F., for a period of between about one and about two hours, the suspension being occasionally stirred to aid the neutralization. Mercerization of the pulp did not take place, due to the substantial absence of water in the suspension.

Following the alkaline neutralization step, the mixture was then filtered from each of portions B, C and D of the pulp and each portion B, C and D was suspended in a separate portion of a dilute aqueous acetic acid solution (1 N acetic acid at ambient temperature) to neutralize the excess sodium hydroxide. After a few minutes (10 minutes), the dilute acetic acid solution was filtered from each of portions B, C and D of the pulp, which portions were then water washed several times to remove residual salts and acetic acid.

Portions B, C and D were then suspended in separate portions of a 6 percent, by weight, aqueous sodium bicarbonate solution to convert the formed carboxymethyl cellulose in the pulp portions to the sodium salt thereof. This step was carried out at ambient temperature over a period of about 12 hours. The sodium bicarbonate solution was then drained from each of portions B, C and D, which were then washed until neutral in pH.

Portions A, B, C and D were subsequently refined in a conventional Jokro refining mill, samples thereof being taken at various intervals of time during the refining. Each of the samples was made into standard TAPPI handsheets which were tested for endurance on the standard MIT fold tester. Conventional tensile strength tests were also run on the handsheets, and corrected zero-span tensile strengths were determined in the usual manner for paper handsheets. The results of the various tests on the sample handsheets made from treated and untreated pulp portions are set forth in the following table.
The results set forth in the above table clearly illustrate the greatly improved fold endurance obtained by treating cellulose pulp with the reagent of the present invention in accordance with the method of the present invention, before refining the pulp and converting it to paper. In this connection, handsheets made from the treated portions B, C and D demonstrated average fold endurance increases of 50%, 112.5% and 10.800%, respectively, over the average fold endurance of handsheets made from untreated portion A. Handsheets made from treated portion D pulp had a maximum fold endurance increase of 49.025% over the control handsheets made from portion A. It should also be noted that there was a direct correlation between refining time and increased fold endurance when pulp treated in accordance with the present invention was utilized. The longer the refining time the greater the increased fold endurance. This was not the case with the control pulp portion A, which exhibited no increased fold endurance with increased refining time.

Significant increases in corrected tensile strength were also obtained with the method of the present invention, as will be noted from a comparison of the values listed in the table for handsheets made from treated portions B, C and D, with those for handsheets prepared from untreated pulp portion A. In this connection, TAPPI handsheets prepared from treated pulp portions B, C and D exhibited average corrected tensile strength increases of about 4%, 71% and 106% over the average corrected tensile strength of TAPPI handsheets prepared from untreated pulp portion A. The corrected tensile strength in each case increased with the length of refining time. TAPPI handsheets prepared from the treated pulp had a maximum corrected tensile strength increase of about 18%, 103% and 137% over the maximum corrected tensile strength for TAPPI handsheets prepared from the untreated pulp.

TAPPI handsheets prepared from treated pulp portions B, C and D also found to have average corrected zero-span tensile strength increases of about 10%, 23% and 17%, respectively, over the average corrected zero-span tensile strength of the TAPPI handsheets prepared from the untreated pulp portion A. Increased refining times, up to a limit, for the pulp portions generally resulted in increased corrected zero-span tensile strength for the TAPPI handsheets made from such refined pulp. However, it was found that such corrected zero-span tensile strengths passed through a maximum and that further increases in refining time resulted in slight decreases in the corrected zero-span tensile strengths for the various TAPPI handsheets tested. Accordingly, in refining pulp treated in accordance with the present invention, the refining time should be selected so as to provide the optimum overall results with respect to tensile strength and fold endurance.

The preceding example clearly illustrates that paper products of improved properties, particularly greatly enhanced fold endurance and increased tensile strength, can be prepared from conventional cellulose pulps by treating the pulps in accordance with the method of the present invention. Selected acids are utilized in dimethyl sulfoxide under at least substantially anhydrous conditions to bring about substitution of hydroxyl groups in low degree in place of hydroxyl groups in the cellulose of the pulp before beating of the pulp. This facilitates hydration of the pulp and minimizes the heating necessary to prepare the pulp for manufacture into paper products. There is no necessity of introducing heat into the system in carrying out the treatment of the pulp before beating. Accordingly, the method of the present invention can be conveniently conducted utilizing relatively simple equipment with a minimum of expense. Various other advantages provided by the method of the present invention are as set forth in the foregoing. The present invention is a distinct improvement over conventional pulp treating and papermaking procedures.

Various modifications in the steps of the method of the present invention and in the materials and apparatus for carrying out such method as would be apparent to those skilled in the art are contemplated as being within the scope of the present invention.

The various features of the present invention which are believed to be new are set forth in the following claims.

We claim:

1. The method of making improved cellulose pulp for the manufacture of paper of increased fold endurance and tensile strength, said method comprising the steps of preparing dried cellulose pulp, treating said pulp in situ in an at least substantially anhydrous environment by immersing said pulp in an at least substantially anhydrous reagent comprising a mixture of dimethyl sulfoxide and a compound selected from the group consisting of monochloroacetic, monooiodoacetic, monobromoacetic, monochloropropionic and monochlorobutyric acids and mixtures thereof, said compound being present in an amount sufficient to bring about carboxyalkylation of the cellulose of said pulp to a low degree of substitution, less than 0.08, said pulp being maintained in said reagent until said low degree of substitution is obtained, and subsequently beating said pulp.

2. The method of making improved cellulose pulp for the manufacture of paper of increased fold endurance and tensile strength, said method comprising the steps of preparing dried cellulose pulp, treating said pulp in situ by immersing said pulp in an at least substantially anhydrous environment comprising an at least substantially anhydrous reagent comprising a mixture of dimethyl sulfoxide and a compound selected from the group consisting of monochloroacetic, monooiodoacetic, monobromoacetic, monochloropropionic and monochlorobutyric acids and mixtures thereof, said compound being present in an amount sufficient to bring about carboxyalkylation of the cellulose of said pulp to a low degree of substitution, less than 0.08 and more than about 0.009, said immersion being carried out for a time sufficient to obtain said low
degree of substitution in said pulp, and subsequently beating said pulp.

3. The method of making improved cellulose pulp for the manufacture of paper of increased fold endurance and tensile strength, said method comprising the steps of preparing dried cellulose pulp, treating said pulp in situ by immersing said pulp in an at least substantially anhydrous environment comprising an at least substantially anhydrous reagent comprising a mixture of dimethyl sulfoxide and a compound selected from the group consisting of monochloroacetic, monoiodoacetic, monobromoacetic, monochloropropionic and monochlorobutyric acids and mixtures thereof, said reagent being present in an amount of at least about one part by volume of part of pulp and said compound being present in a concentration of at least about 2 percent, by weight of said dimethyl sulfoxide, sufficient to bring about the substitution of hydrophilic groups for hydroxyl groups in the cellulose of said pulp to a low degree, less than 0.08, and at least about 0.009, said pulp being maintained in said reagent until said low degree of substitution is obtained in said pulp, and subsequently beating said pulp.

4. The method of making improved cellulose pulp for the manufacture of paper of increased fold endurance and tensile strength, said method comprising the steps of preparing dried cellulose pulp, treating said pulp in situ by immersing said pulp in an at least substantially anhydrous environment comprising an at least substantially anhydrous reagent comprising a mixture of dimethyl sulfoxide and a compound selected from the group consisting of monochloroacetic, monoiodoacetic, monobromoacetic, monochloropropionic and monochlorobutyric acids and mixtures thereof, said reagent being present in an amount of about two parts by volume per part of said pulp and said compound being present in said pulp in a concentration of between about 2 percent and about 1 percent, by weight of said dimethyl sulfoxide, sufficient to bring about carboxyalkylation to substitute hydrophilic groups for hydroxyl groups in the cellulose of said pulp to a low degree, of at least about 0.009 and not more than about 0.07, said pulp being maintained at about ambient temperature until said low degree of substitution is obtained in said pulp, and subsequently refining said pulp by beating.

5. The method of making improved cellulose pulp for the manufacture of paper of increased fold endurance and tensile strength, said method comprising the steps of preparing dried cellulose pulp, treating said pulp in situ by immersing said pulp in a substantially anhydrous environment comprising an anhydrous reagent comprising a mixture of anhydrous dimethyl sulfoxide and anhydrous monochloroacetic acid, said monochloroacetic acid being present in a concentration of about 4 percent, by weight of said dimethyl sulfoxide, sufficient to effect carboxymethylation of said cellulose of said pulp to a low degree of substitution, of between about 0.03 and 0.05, said reagent being present in a volume at least equal to that of said pulp, said immersion being carried out at about ambient temperature until said low degree of substitution is obtained in said pulp, and subsequently refining said pulp by beating.

6. The method of making improved cellulose pulp for the manufacture of paper of increased fold endurance and tensile strength, said method comprising the steps of preparing dried cellulose pulp, treating said pulp in situ by immersing said pulp in an at least substantially anhydrous environment comprising an at least substantially anhydrous reagent comprising a mixture of dimethyl sulfoxide and a compound selected from the group consisting of monochloroacetic, monoiodoacetic, monobromoacetic, monochloropropionic and monochlorobutyric acids, said compound being present in an amount sufficient to bring about carboxyalkylation of the cellulose of said pulp to a low degree of substitution, less than 0.08, said pulp being maintained in said reagent until said low degree of substitution is obtained, substantially separating said reagent and said pulp, and neutralizing said separated pulp with a base under at least substantially anhydrous conditions, and subsequently refining said pulp by beating.

7. The method of making improved cellulose pulp for the manufacture of paper of increased fold endurance and tensile strength, said method comprising the steps of preparing dried cellulose pulp, treating said pulp in situ by immersing said pulp in an at least substantially anhydrous environment comprising an at least substantially anhydrous reagent comprising a mixture of dimethyl sulfoxide and a compound selected from the group consisting of monochloroacetic, monoiodoacetic, monobromoacetic, monochloropropionic and monochlorobutyric acids and mixtures thereof, said compound being present in a concentration of at least about 2 percent, by weight of said dimethyl sulfoxide, and in an amount sufficient to bring about carboxyalkylation of the cellulose of said pulp to a low degree of substitution, less than 0.08 and more than about 0.009, said immersion being carried out for a time sufficient to obtain said low degree of substitution in said pulp, substantially separating said reagent and said pulp, and neutralizing said pulp with a base under at least substantially anhydrous conditions, and subsequently refining said pulp by beating.

8. The method of making improved cellulose pulp for the manufacture of paper of increased fold endurance and tensile strength, said method comprising the steps of preparing dried cellulose pulp, treating said pulp in situ in an at least substantially anhydrous environment by immersing said pulp in an at least substantially anhydrous reagent comprising a mixture of dimethyl sulfoxide and a monochloroacetic acid, said reagent being present in an amount of at least about one part by volume per part of pulp and said acid being present in a concentration of between about 2 percent and about 4 percent by weight of said dimethyl sulfoxide, the amount of said acid being sufficient to bring about the substitution of hydrophilic groups for hydroxyl groups in the cellulose of said pulp to a low degree, less than 0.07 and more than about 0.009, substantially separating said reagent and said pulp, overneutralizing said pulp with a water-soluble base at a substantially anhydrous condition, the excess amount of said base being at least about 0.3 percent, by weight of the total amount of base, neutralizing said excess base, washing said pulp to remove soluble salts formed therein, and refining said pulp by beating.

9. The method of making improved cellulose pulps for the manufacture of paper of increased fold endurance and tensile strength, said method comprising the steps of preparing dried cellulose pulp, treating said pulp in situ in a substantially anhydrous environment by immersing said pulp in an anhydrous reagent comprising a mixture of dimethyl sulfoxide and a monochloroacetic acid, said reagent being present in an amount of about two parts by volume to one part of said pulp, said acid being present in said reagent in a concentration of between about 2 percent and about 4 percent, by weight of said dimethyl sulfoxide, sufficient to bring about carboxyalkylation to substitute hydrophilic groups for hydroxyl groups in the cellulose of said pulp to a low degree, of at least about 0.03 and 0.05, said pulp being maintained at about ambient temperature until said low degree of substitution is obtained in said pulp, and subsequently refining said pulp by beating.

10. The method of making improved cellulose pulp for the manufacture of paper of increased fold endurance and tensile strength, said method comprising the steps of preparing dried cellulose pulp, treating said pulp in situ in a substantially anhydrous environment by immersing said pulp in an anhydrous reagent comprising a mixture of dimethyl sulfoxide and a monochloroacetic acid, said reagent being present in an amount of about two parts by volume to one part of said pulp, said acid being present in said reagent in a concentration of between about 2 percent and about 4 percent, by weight of said dimethyl sulfoxide, sufficient to bring about carboxyalkylation to substitute hydrophilic groups for hydroxyl groups in the cellulose of said pulp to a low degree, of at least about 0.03 and 0.05, said pulp being maintained at about ambient temperature until said low degree of substitution is obtained in said pulp, substantially separating said reagent and said pulp, and neutralizing said separated pulp with an anhydrous solution comprising dimethyl sulfoxide and a water-soluble base, the excess amount of said base being between about 0.3 and 1.0 percent, by weight of the total amount of base, neutralizing said base and washing said pulp to free said pulp of water-soluble salts, treating said pulp with an aqueous solution of sodium bicarbonate to convert the carboxymethylation compounds formed in the cellulose of said pulp.
pulp to their sodium salts, and subsequently refining said pulp by beating.

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