Aug. 13, 1974 N. S. THOMPSON ET AL 3,829,357

OXIDATIVE MANUFACTURE OF PULP WITH CHLORINE DIOXIDE

Original Filed Nov. 20, 1968

3 Sheets-Sheet 1

FIG. 2

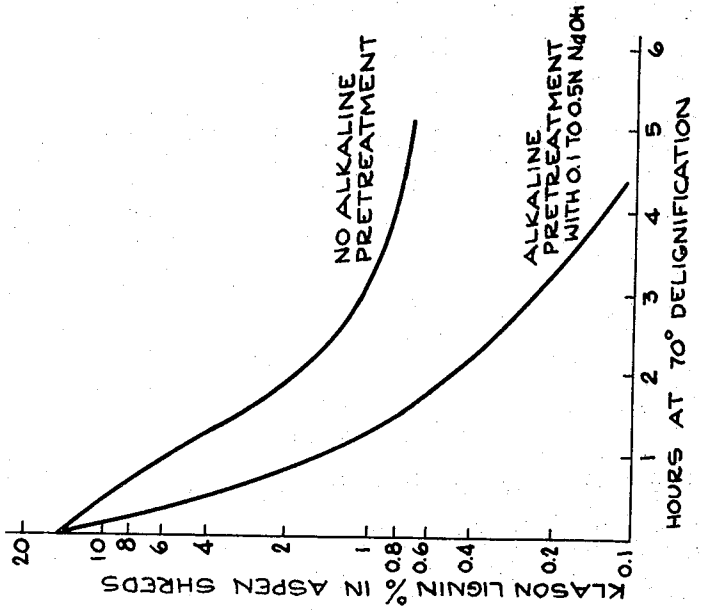
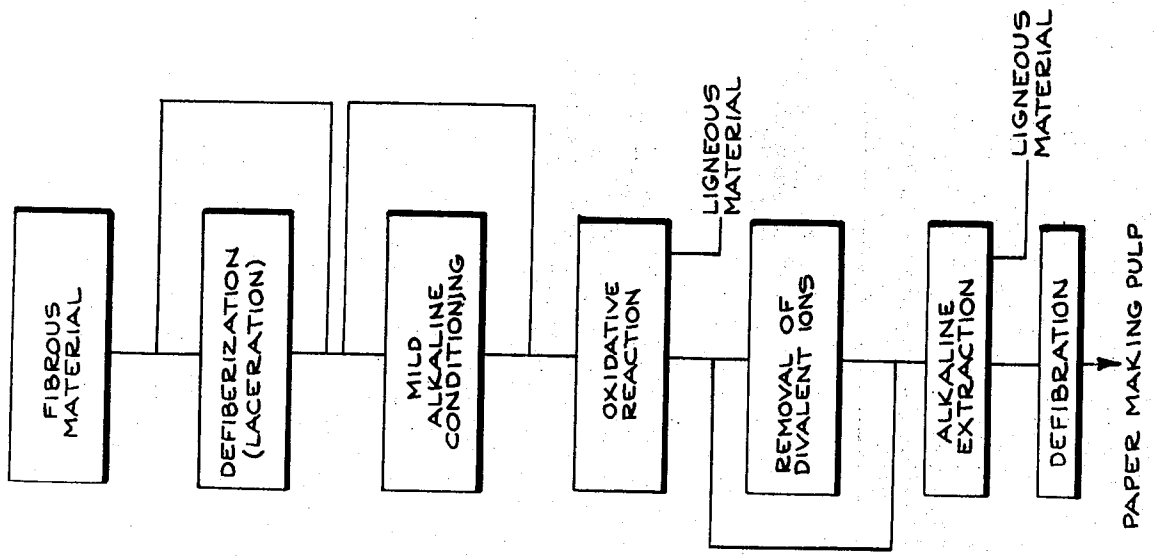


FIG. 1



INVENTORS
NORMAN S. THOMPSON
GORDON A. NICHOLLS
SHU-TANG-HAN

Anderson, Luedeka, Fitch, Even & Tabin
ATTYS.

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3 Sheets-Sheet 2

FIG.2a

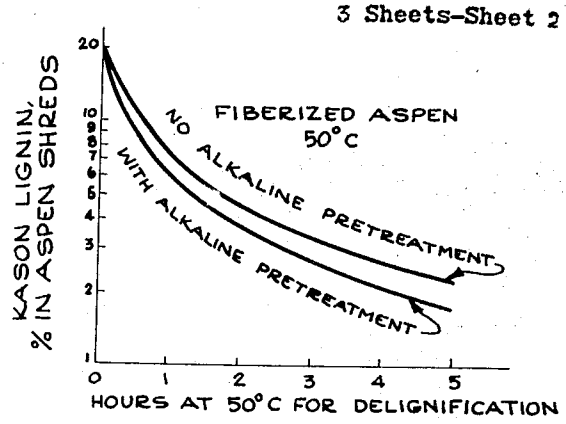


FIG.3

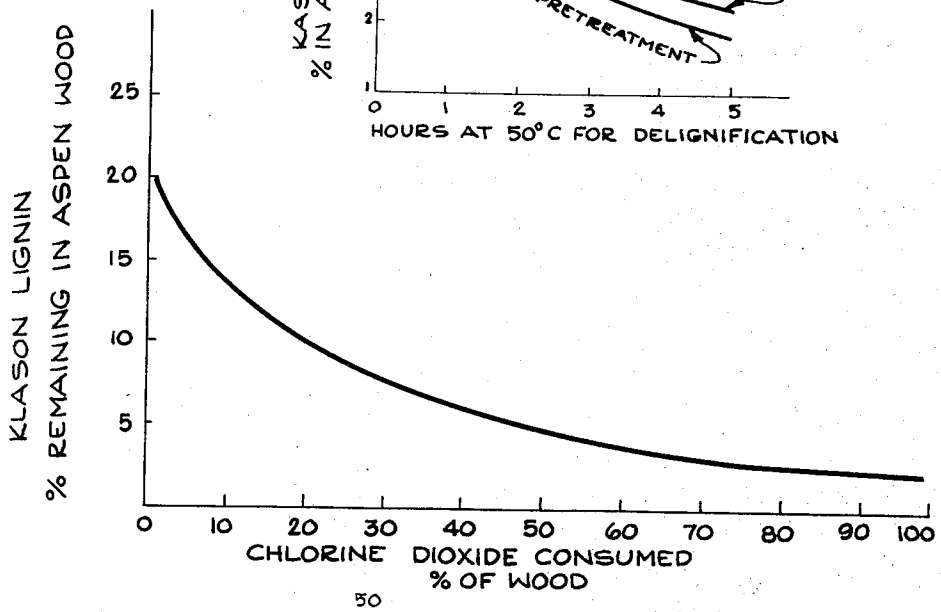
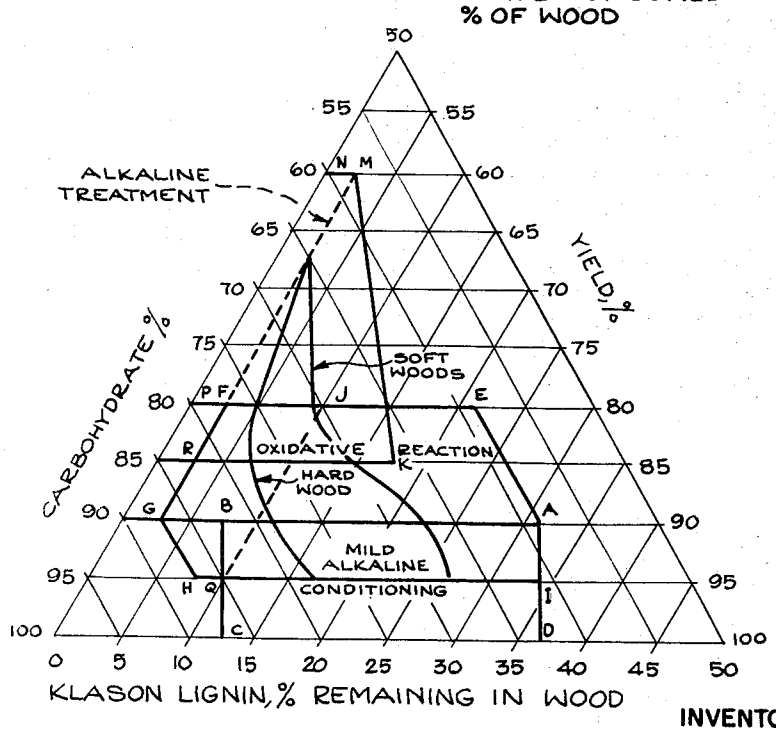


FIG.4



INVENTORS
NORMAN S. THOMPSON
GORDON A. NICHOLLS
SHU-TANG-HAN

Anderson, Luedeka, Fitch, Even & Tabin
ATTYS.

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OXIDATIVE MANUFACTURE OF PULP WITH CHLORINE DIOXIDE

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3 Sheets-Sheet 3

FIG.5a

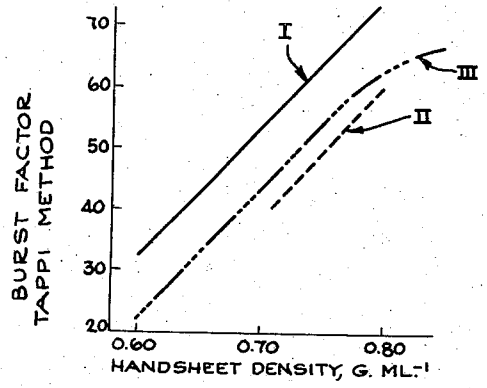


FIG.5b

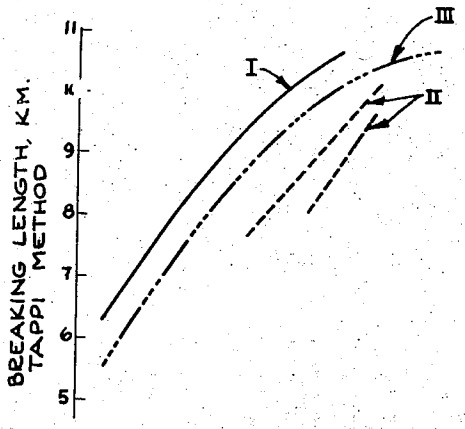


FIG.5c

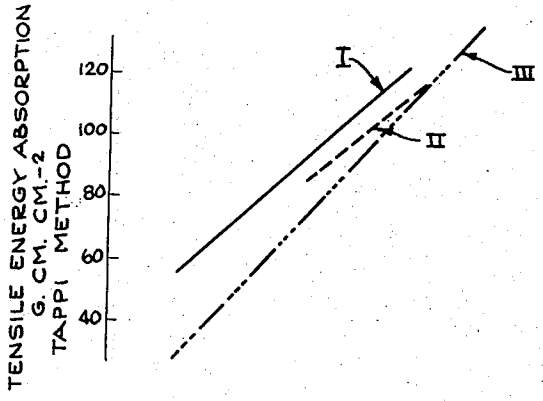


FIG.5d

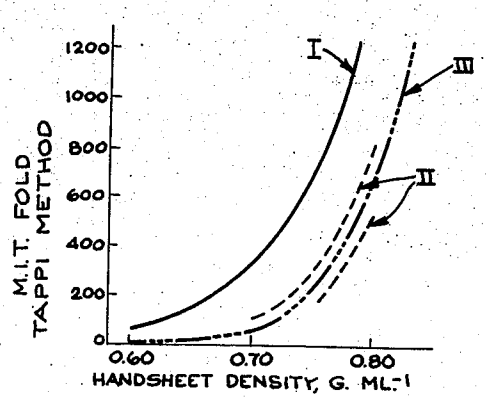
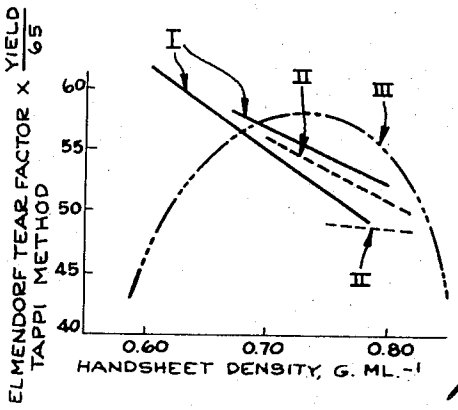


FIG.6



INVENTORS
NORMAN S. THOMPSON
GORDON A. NICHOLLS
SHU-TANG-HAN

Anderson, Luedeka, Fitch, Even & Tabin
ATTYS.

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3,829,357

OXIDATIVE MANUFACTURE OF PULP WITH CHLORINE DIOXIDE

Norman S. Thompson, Gordon A. Nicholls, and Shu-Tang Han, Appleton, Wis., assignors to The Institute of Paper Chemistry, Appleton, Wis.

Continuation of abandoned application Ser. No. 777,241, Nov. 20, 1968. This application Feb. 26, 1971, Ser. No. 119,383

Int. Cl. D21c 1/02, 3/18

U.S. Cl. 162—23 7 Claims

ABSTRACT OF THE DISCLOSURE

A process for producing papermaking pulp by first preconditioning the initial wood materials by lacerating the materials at a temperature above the thermal softening point of the lignin therein into fiber bundles, and second delignifying the lacerated material. The delignification includes digesting the materials with an oxidative chemical such as chlorine dioxide, peracids, ozone, or noble gas oxides, extraction of some of the lignin by alkaline treatment, and optional further defibration via mechanical or chemical treatment. The preferred oxidative chemical is chlorine dioxide, and the oxidative treatment is terminated when the residual lignin content of the wood material, measured as Klason lignin, is above 50% of the original Klason lignin content.

This application is a continuation of Ser. No. 777,241, filed Nov. 20, 1968, now abandoned.

This invention relates generally to a method for recovering cellulosic fibers from fibrous materials containing carbohydrates and lignin and to the products provided by such method. More specifically, the invention is directed to a pulping process for the selective removal of lignin with conservation of carbohydrates in the fibrous material without substantial loss in yield of carbohydrates, and to a pulp product and by-product recovered from such a process.

As used herein the term "fibrous material" is defined as any naturally occurring material which contains carbohydrate and cellulose constituents in the form of fibers and, in addition, which contains lignin, the materials being substantially in their natural condition and in an amount substantially equivalent to the amount in the naturally occurring material. The term includes wood, ground wood and wood chips, newsprint, bast, and flex. However, as used herein the term "fibrous material" does not include materials such as cotton, rags, and linters which do not contain lignin nor does it include chemical pulps from which most of the lignin has been removed from the raw material used to make the pulp. Wherever the term wood or wood product is used, it is intended that other fibrous materials, as herein defined, may also be used. The term "lignin" as used herein includes native lignin and modified lignin. The term "native lignin" refers to those materials which exist in wood or other fibrous materials in nature. The formula for native lignin has not been fully established but various structural components have been suggested, see for example, *The Chemistry of Lignin*, Irwin A. Pearl (1967). The term "modified lignin" refers to that lignin which has been chemically modified from the native form but which is still retained in the fibrous mateiral. Modified lignin includes material detected as acetone soluble lignin, Klason lignin and acid soluble lignin.

As used herein the term "papermaking pulp" or "pulp" is defined as the fiber product obtained from fibrous material after removal of lignin, and after separation into individual fibers and/or fiber bundles. Pulp includes, in addition to the pure cellulose present in the fibrous material, hemicelluloses and other naturally occurring carbohydrates, and is the basic raw material in the manufacture of paper. Pulp, however, is to be distinguished from the paper stock or "furnish" from which a paper web is formed.

It is known that wood, including hard wood and soft wood, generally comprises the following:

(a) Carbohydrate materials (60–80):

	Percent
Cellulose	40–55
Hemicellulose	15–25

(b) Non-carbohydrate materials (20–40):

Lignin	15–35
Extractives	3–10

Various chemical processes have existed for many years for the treatment of fibrous material to recover the cellulosic materials in the form of a papermaking pulp for use in papermaking processes.

The known chemical treating processes, referred to as "pulping" processes, utilize (a) sulfite chemicals under acid or near-neutral conditions, in processes known as sulfite, bi-sulfite, and neutral sulfite processes; (b) sulfate chemicals, under alkaline conditions, in a process known as the sulfate or kraft process; and (c) caustic chemicals, under alkaline conditions, in a process known as the soda process. In all of these processes the lignin is converted to soluble or removable compounds and is separated in the pulping liquor. In the sulfite process, the lignin is convterted into lignosulfonates and in the soda and kraft processes, it is converted into soluble alkali lignin. It is important to note that in each case, the aromatic rings of the lignin structure appear to remain intact.

It is also important to note that in the various known commercial processes for treating fibrous materials by chemical action, generally more carbohydrates than lignin are removed by the pulping chemicals. As a result, when most of the lignin is removed from the fibrous material, a yield of only about 50 percent by weight of the fibrous material is obtained. Such a result is obviously wasteful and is desirably avoided. Furthermore, these known commercial processes effect changes in the form of the carbohydrate material in the fibrous material.

In the sulfite process, the carbohydrate materials tend to be hydrolyzed to sugars and this is especially the case in respect to the hemicelluloses. In the kraft and soda processes, the carbohydrate materials tend to be broken down into simple acids and acetyl groups are removed from the hemicelluloses. Because of these treatments, sulfite pulps provide paper which tends to be soft and weak, and kraft or soda pulps provide paper which tends to be strong but hard.

The known chemical pulping processes are generally carried out at high temperatures in an aqueous solution, with resulting high pressures, in order to remove lignin at commercially attractive rates. This not only requires higher equipment costs with associated maintenance and safety problems, but, perhaps, more significantly, heat and pressure effect accelerated degradation of cellulose and hemicellulose resulting in yield losses and carbohydrate degradation. In the sulfite processes, the fibers are weakened. In the kraft process, the degradation of cellulose is less severe, but the hemicelluloses tend to be lost from the pulp and are removed with the pulping liquor. Also, the by-products of these chemical pulping processes must be appropriately handled.

The commercial chemical pulping processes also cause the production of color bodies in the pulp and this is particularly the case in the sulfate process. As a result, extensive bleaching is often necessary to remove color bodies which may result in further degradation of the pulp.

An objective of the pulping processes outlined above is to separate the individual cellulosic fibers from the gross wood structure and from the lignin without damage to the fibers and with minimum loss of carbohydrates. It is particularly desirable to separate the fibers with minimum breaking of the fibers into short lengths. To accomplish this objective, it is desirable to cause the separation of the fibers in the middle lamella region which is between the cellulosic walls of adjacent fibers. It is generally taken for granted that almost one-half of the lignin of wood and other fibrous materials is in the middle lamella region. It is also generally understood that the material in the middle lamella region is comparable in strength to that in other zones of the structure, and attempts to separate the cells into individual fibers without first removing all or most of the lignin from the middle lamella region results in frequent rupture of the fibers.

The known chemical pulping processes set forth before effect partial or substantially complete removal of the lignin from the middle lamella region to permit the fibers to be separated from each other without significant fiber damage such as shortening of fiber length. However, as pointed out, these processes accomplish this result at a sacrifice of yield and significant changes in the form of carbohydrate material in the fibrous material. While limited chemical treatment may be used, as in the semi-chemical pulping process to improve yields, such limited treatment sacrifices carbohydrates and can cause significant changes in the material form of the carbohydrate material, does not remove substantially all of the lignin and does not provide pulp of good color stability and characteristics for many purposes. At higher yields with semi-chemical processes, e.g. yields above about 75 percent, it is not commercially feasible to bleach the pulp with multi-stage processes using chlorine, chlorine dioxide and like chemicals.

In the forgoing chemical processes, more carbohydrate is removed than lignin. This is inherent in such processes and results in reduction in yield as well as loss of some fiber properties.

It has been known that wood and other fibrous materials may be treated with oxidizing chemicals to selectively remove lignin and provide a substantially lignin-free material which has been identified by The Institute of Paper Chemistry at Appleton, Wis., as "holopulp." The holopulp contains celluloses, and, in addition, other carbohydrate materials, particularly the hemicelluloses. However, the known oxidative pulping processes for selectively removing lignin have not been practical for commercial operation and have been generally uneconomical because of extensive treatment times and excessive chemical consumption. Excessive consumption of oxidative chemicals causes a corresponding increase in oxidation of the native carbohydrates. Furthermore, the previously known oxidative pulping processes have not provided a pulp which has most desired properties for papermaking and which can be employed in the manufacture of diverse paper products.

It is, of course, well known to use chlorine, chlorine dioxide and like chemicals to bleach pulp resulting from the various pulping processes. However, such oxidizing chemicals, when used for bleaching, are applied to a material which has already undergone significant treatment, has had a substantial change in native carbohydrates, or has had significant fiber modification. As indicated, such pulping processes result in substantial yield loss before bleaching.

The kraft process, one of the major chemical pulping processes results in the formation of volatile, malodorous sulfur compounds. This is a particular disadvantage of this commercially significant process.

The previously known pulping processes provide pulps which are refined with varying degrees of difficulty and, in some cases, refining causes high power requirements. The various chemical pulping processes heretofore known do not realize the potential strength of the individual fibers. In other words, these earlier chemical pulping processes resulted in substantial weakening of the natural strength of the individual fibers.

The chemical pulping processes mentioned have not permitted the provision of varying paper making properties within the parameters of the process. For example, the earlier known pulping processes do not permit adjustment of the hydrodynamic properties of the pulp produced in the process.

It is a principal object of the present invention to provide a pulping process for recovering high yields of papermaking pulp from fibrous materials as hereinbefore defined. It is a further object of the invention to provide a papermaking pulp in high yields having good versatility and which may be employed in the manufacture of diverse paper products. It is an additional object to provide a pulping process for recovering pulp from fibrous material at low temperature and pressures which provides increased yield of high quality pulp without the necessity of bleaching and high power refining. A still further object is to provide a pulping process for selectively removing lignin from fibrous raw material with economic and safe plant facilities. It is a still further object to provide a pulping process which provides minimum environmental pollution. Another object is the provision of a process for treating fibrous materials which results in fibers having strengths approaching the natural strength of the fiber. A still additional object of this invention is to provide a process which can be adjusted to influence hydrodynamic properties of the pulp. Furthermore, an object of this invention is to provide new pulps having desired paper and papermaking properties. Additionally, an object of this invention is to provide novel by-products of fibrous materials, particularly new ligneous products.

These and other objects of the invention will be readily understood from the following detailed description and from the drawings in which:

FIG. 1 is a schematic flow diagram of pulping processes in accordance with the invention.

FIG. 2 is a graph illustrating the effect of mild alkaline pretreatment on delignification where the axis of ordinates is Klason lignin in aspen shreds plotted on a log scale and the axis of abscissas is time in hours at 70° C.

FIG. 2(*a*) is a graph illustrating the effect of alkaline pretreatment on lacerated aspen at 50° C., the axes being the same as in FIG. 2

FIG. 3 is a graph illustrating consumption of chlorine dioxide where the axis of ordinates is the Klason lignin remaining in aspen wood and the axis of abscissas is chlorine dioxide consumed, expressed as a percent of the wood.

FIG. 4 is a triangular graph illustrating the relationship of Klason lignin remaining in the wood, carbohydrates remaining in the wood, and yield in practicing a pulping process in accordance with the invention.

FIGS. 5(*a*) through 5(*d*) show comparisons between pulps prepared in accord with the invention and unbleached kraft pulp, various hand sheet properties being shown as a function of hand sheet density measured as grams per milliliter.

FIG. 5(*a*) shows the relationship between hand sheet density and the burst factor.

FIG. 5(*b*) shows the relationship between the hand sheet density and the breaking length measured in kilometers.

FIG. 5(*c*) shows the relationship between hand sheet density and tensile energy absorption measured as gram-centimeters per square centimeter.

FIG. 5(*d*) shows the relationship between hand sheet density and M.I.T. fold.

FIG. 6 shows the relationship between hand sheet density and the Elmendorf tear factor corrected for an equal fiber count at 65 percent yield. The graph shows a major difference between the pulp of the invention and unbleached kraft paper.

Very generally, the invention is directed to a method of providing papermaking pulp in high yield from fibrous materials as hereinbefore defined which includes preconditioning the fibrous material to effect an initial partial separation of the fibrous material into fiber bundles and to disrupt the packing of the cell structures of the fibrous materials without causing significant reduction in fiber strength. This is an important feature of the invention.

The preconditioned fibrous material is subjected to selective delignification in a process which includes (a) digesting the preconditioned fibrous material with an oxidative pulping chemical selected from chlorine dioxide; peracids of the formula

$$RC(=O)OOH$$

where R is hydrogen, methyl or ethyl; ozone; and noble gas oxides; (b) removing or complexing divalent cations in the fibrous material at a pH below about 5, (c) extracting lignin materials from the fibrous material and (d) defiberizing in the presence of a monovalent alkaline material which is present in sufficient amounts to convert the acidic components to soluble salts and this is usually accomplished by establishing an initial pH of at least about 10, or alternatively, defiberizing by mechanical means.

It is contemplated that the oxidative pulping chemical may be in an aqueous solution or may be gaseous. The extraction and removal of divalent cations from the fibrous material is inherent when the pH of the fibrous material is below about 5 during digestion with the oxidative pulping chemical. However, if the pH of the fibrous material is above about 6 during digestion with the oxidative pulping chemical, a separate acidic extraction at a pH below about 5 is necessary if chemical conditions are used for defibration. It is important that divalent cations not be present for effective defibration by alkaline treatment.

The digestion of the preconditioned fibrous material with the oxidative pulping chemical may be carried out in a single stage or in multiple stages and each such digestion stage may be followed by the removal of divalent cations and one or more alkaline extractions. Multiple stage digestion with the oxidative pulping chemical generally results in lower consumption of the chemical per pound of pulp produced.

After extraction, the pulp may be further conditioned with chlorine, chlorine dioxide and like chemicals which can improve the hydrodynamic properties of the pulp as well as bleach the pulp to higher brightness. The papermaking pulp product obtained from the process of the invention has a yield of above 60 percent by weight and has a defibration point, as defined hereinafter, above about 65. (Percentages herein are weight percent on an oven dry basis.) The individual fibers in the pulp have a zero span tensile strength of greater than about 85 percent of that inherent in the fibers in the fibrous material.

For purposes of determining the zero span tensile strength, the pulp is made into a hand sheet. It is important that the pulp and hand sheet be substantially free of fiber bundles which, if present, indicate a lower zero span tensile strength. The above indicated strength of the pulp is based upon hand sheets having substantially all of the fiber bundles separated into individual fibers and if this is not accomplished apparent lower zero span tensile strength values are obtained.

Chemical pulping processes result in reductions in zero span tensile strength of the fibers from the fibrous material in excess of about 30 percent. Thus, the oxidative treatment in the process described herein results in substantial improvement in the preservation of fiber strength.

(The inherent strength of the fibers is determined by delignifying chips of fibrous material with excess sodium chlorite to remove all Klason lignin and by fiberizing the fiber bundles to provide individual fibers. The fibers are then made into a hand sheet and zero span tensile strength is determined.)

The pulp derived from aspen wood, before beating, has an unbeaten freeness of at least 350 as measured by the Canadian Freeness Test. This freeness is to be compared with holocellulose derived from aspen woods in high yields which have Canadian Freeness values significantly lower, e.g. 200. In addition to being lower in freeness, the holocellulose is much more sensitive to beating than the pulp provided herein.

Further, remaining ligneous material present in the pulp may be readily removed therefrom at low temperatures without drastic chemical modification and/or deterioration of carbohydrate in the pulp.

The pulp of the invention may be refined with low power requirements, i.e. mild beating. The pulp is much more readily bleached by chlorine, chlorine dioxide and like chemicals than pulps having comparable yields.

As before noted, the invention is applicable to groundwood pulp, the preparing of which may cause some fiber weakening. However, the invention does not result in more than about 15 percent reduction of zero span tensile strength of fibers in the initial fibrous material.

The invention is also applicable to fibrous material which has been given mild chemical treatment provided that such treatment does not result in yields of less than about 80 percent and does not result in more than 15 percent reduction in zero span tensile strength.

The selective delignification provides new ligneous materials which have distinct chemical properties. The ligneous materials include a fraction which is obtained from the oxidative reaction and a fraction which is obtained from the alkaline extraction operation. In the preferred practice of the invention, a major fraction of the ligneous material will be obtained from the alkaline extraction operation and the native lignin, while modified during the oxidative reaction, will remain with the pulp. This is a unique feature of the process. These ligneous materials differ considerably from those obtained from chemical pulp and also from those obtained during the preparation of holocellulose. The ligneous materials are free from sulfur compounds which are present in the ligneous materials resulting from the kraft and sulfite processes and the ligneous materials when the oxidant contains chlorine contain combined chlorine compounds which are not present in liquors provided from chemical pulping processes mentioned hereinbefore. The ligneous material from the oxidative reaction is water soluble, whereas the ligneous material from the alkaline extraction is not soluble in water although it is soluble in alkaline solutions.

It has been found that the alkaline conditioning step in combination with the oxidative reaction and alkaline extraction can be varied to provide pulps of differing properties, such as freeness, wet compressibility, opacity, and sheet density. Previously known processes for preparing holocellulose have not employed the mild alkaline conditioning of fibrous material as herein defined in combination with oxidative reaction.

Furthermore, previously known processes for preparing holocellulose have not attempted to control the oxidative reaction to retain substantial amounts of water insoluble ligneous materials with the pulp nor have they provided alkaline extraction to selectively remove such ligneous materials.

Prior to digesting the fibrous material with the oxidative pulping chemical, it has been found to be desirable to subject the fibrous material to a preconditioning treatment. The purpose of the preconditioning treatment, which includes an initial "laceration" of the fibrous material, and also may, if desired, include mild alkaline conditioning of the lacerated fibrous material, is to subject the fibrous material, e.g., wood, to an initial treatment to reduce the gross wood structure to fiber bundles and to preferentially expose the lignin rich middle lamella region for subsequent oxidative delignification without breaking of the fibers. As used herein, the term "laceration" is de-

fined as a step which reduces the bulk density of the fibrous material substantially more than wood grinding operations used in the paper industry, and does not reduce the zero span tensile strength more than 10 percent while providing a yield of fibers of at least about 95 percent in the form in which they exist in the fibrous material.

Ideally, it would be desirable to reduce the fibrous material to individual fibers prior to delignification, if this could be accomplished without breaking of the fibers and without causing undesirable changes in the components of the fibers. Attempts have been made heretofore to defiber wood without chemical delignification as, for example, in the groundwood process, in the thermomechanical process, and in the semimechanical process. In these processess, however the wood is subjected to drastic mechanical forces which is accompanied either by substantial destruction of the wood cells, shortening of the fibers, and/or undesirable chemical changes. Pulps obtained from these processes are not suitable for many papermaking applications.

The mechanical separation of the wood into fiber bundles, which is effected by laceration, is to be distinguished from heretofore known mechanical, thermomechanical, and semimechanical processes. The fibrous material, after preconditioning in accord with this invention, is not suitable for use as a pulp without further chemical and/or mechanical treatment. The preconditioned fibrous material is primarily fractured in the middle lamella region to expose the lignin and this is to be distinguished from groundwood processes which seek to expose cellulose and leave the lignin relatively unexposed thereby avoiding fracture in the middle lamella region. The preconditioned fibrous product can have a predominance of shives which are undesirable in papermaking pulp.

Laceration of the wood may be carried out in diverse manners so long as care is taken to ensure that the wood is preferentially separated into fiber bundles, or ideally, individual fibers with a minimum of fiber damage and the lignin rich middle lamella region is sufficiently exposed for subsequent reaction with the oxidative pulping chemical during delignification. The wood raw materials may be in the form of wood chips, as conventionally obtained from the wood chipper in usual pulping processes. Typically wood chips from hard woods have an average size of about ⅝ inch by 1 inch by ⅛ inch. In the case of soft woods, the chips will normally be somewhat longer and thicker.

When the wood raw material is in chip form, laceration may be effected by subjecting the chips to mild defiberization while maintaining the chips at about the thermal softening point of the lignin content of the wood, e.g., between about 100° C. and about 120° C. To effect such softening there must be sufficient moisture present to plasticize the lignin and minimize fiber damage during fiberization. The moisture level should be above about 100 percent of dry weight of the chips. The time at temperature should be limited so as to minimize chemical change. Under the indicated conditions, there is very limited degradation of carbohydrate materials. Mechanical defiberization of the wood under such conditions has been found to provide a lacerated wood fiber product predominantly containing fiber bundles which have separated in the middle lamella region without substantial shortening or weakening of the fibers.

The laceration of wood chips at the thermal softening point of the lignin may be accomplished by application of mechanical forces as by grinding, exploding or defiberization. Grinding tends to shorten and split the fibers, and explosion techniques, effected by heating wood chips at pressures up to 1000 p.s.i.g. followed by rapid discharge to ambient conditions, tend to cause excessive hydrolysis of carbohydrates and undesirable changes in lignin. Accordingly, the preferred form of laceration is defiberization, which can accomplish the desired separation of the wood structure into fiber bundles without significant fiber damage, carbohydrate degradation, and/or changes in lignin.

A preferred laceration method includes (a) impregnating wood chips with moisture to a level of between about 50 percent and about 75 percent by weight, (b) heating the impregnated chips to a temperature of between about 100° C. and about 120° C., for example, with steam, to soften the lignin materials, and (c) defiberization. The fiberized wood fiber product will be lacerated as hereinbefore described.

The laceration of the wood is desirably carried out under conditions which retain maximum quantities of the original wood constituents in the fibers, and which provide minimum fiber damage. In this connection, heating of the impregnated wood chips is preferably carried out rapidly, for example, between at a time about one minute and about ten minutes, and the length of heating is inversly proportional to the temperature in order to minimize hydrolysis of carbohydrates. Further, in order to prevent excessive fiber damage, defiberization is desirably carried out at wood moisture contents in excess of 50 percent by weight.

It has been determined that a desirable defiberization of the moistened and heated wood chips may be accomplished in a double disc Bauer mill, available from the Bauer Brothers Manufacturing Company. Good results have been obtained with a plate clearance in the Bauer mill of between 0.020 and 0.035 inches, preferably between about 0.025 and 0.030 inches. It is also contemplated that defiberization may be carried out in other forms of apparatus such as the Asplund defibrator.

The degree of treatment to effect laceration of the fibrous material is related to the particular form of raw material. When the raw material for the process of the invention is wood or wood chips, it is apparent that more severe treatment is required than when the raw material is newsprint, ground wood pulp or a fibrous material resulting from mild chemical treatment, i.e., some previous operation. In such instances treatment to effect laceration may be provided by minor mechanical action.

As indicated, the preconditioning step of the process may include mild alkaline conditioning following laceration. When the wood is lacerated, as described herein by defiberization at the thermal softening point of the lignin, it has been found that it is not necessary to subject the lacerated wood fiber product to a mild alkaline conditioning. In most instances, however, the lacerated wood fiber product is subjected to mild alkaline conditioning to provide desired characteristics in the pulp. The mild alkaline conditioning is to be distinguished from the caustic soda process which effects pulping by the use of alkali with substantial reduction in yield and weakening of fiber strength and is to be further distinguished from the cold caustic process which effects substantial swelling of the cellulosic material and weakening of the outer secondary wall or transition lamella without removing the lignin to any great degree.

It has been determined that alkaline conditioning of the lacerated fibrous material prior to selective delignification can have a significant effect upon the degree of separation of the fibrous material into individual fibers during and subsequent to selective delignification, and further, it has a marked effect on interfiber bonding. In this connection, photomicrographs of alkaline conditioned fibrous material after selective delignification show a marked improvement in the separation of the individual fibers in the region of the middle lamella, and substantially less lignin content, as measured by the Graff C stain. Furthermore, mild alkaline conditioning of the lacerated wood fiber prior to selective delignification can result in a substantially increased rate of Klason lignin removal in the oxidative reaction which may be of importance in commercial operation. The

change in the rate of Klason lignin removal in the oxidative reaction which is obtained by alkaline conditioning can be illustrated as in FIGS. 2 and 2(*a*) where Klason lignin remaining in the fibrous material is plotted versus the time of oxidative reaction with and without alkaline conditioning.

The mild alkaline conditioning appears to effect more uniform selective delignification and also to function in the ultimate properties of the pulp. In this connection, mild alkaline conditioning appears to reduce screen rejects, hereinafter described, and thereby improves the nature of the pulp. Some effects of mild alkaline conditioning upon the properties of the pulp are illustrated in FIGS. 5(*a*) to 5(*d*) and FIG. 6. In these figures, the curves designated I represent hand sheets prepared from pulps which were not subjected to mild alkaline conditioning, whereas the curves designated II represent hand sheets prepared from pulps which were subjected to mild alkaline conditioning.

However, it has been found that the mild alkaline conditioning is less important when the oxidative reaction is carried out to lesser degrees. Under milder conditions of the oxidative reaction, the mild alkaline conditioning may be eliminated.

The mild alkaline conditioning is effected by soaking the lacerated fibrous material in an aqueous sodium hydroxide solution. The solution has a concentration equivalent to between 0 and about .5 N and preferably between .05 N and .15 N. Enough solution should be present to provide sodium hydroxide at a weight level, on a dry wood basis of 0 to 6 percent and, for hard wood it is desirably between 1.5 percent and 3 percent, with larger amounts of sodium hydroxide generally being used for soft woods. The consistency of the stock during mild alkaline conditioning is desirably about 6 percent, but it can be as high as 20 percent. The mild alkaline conditioning is effected at a temperature between about 40° C. and about 80° C., but is preferably carried out at about 60° C. The time for mild alkaline conditioning can vary from 0 to 2 hours but it is desirably carried out in 10 minutes to 60 minutes. These conditions for effecting mild alkaline conditioning are to be distinguished from the conditions utilized for the cold soda process and for the soda process, the conditions for which effect undesired changes in the fibrous material, as pointed out hereinbefore.

Equivalent amounts of other monovalent water soluble alkaline materials can be used for the mild alkaline conditioning for example, ammonia, potassium hydroxide, sodium carbonate, sodium bicarbonate, sodium sulfite, sodium alcoholates, sodium bisulfite and short chain alkyl amines having from one to five carbon atoms may also be employed as the alkaline material. It has been determined that the alkaline material should be monovalent. Alkaline materials which provide divalent ions in solution have been found to interfere with subsequent steps in the process. The alkaline conditioning may be carried out in either aqueous or nonaqueous systems, the aqueous systems being preferred.

It is not fully understood precisely what occurs during mild alkaline conditioning of the lacerated fibrous material. It is known that there is some extraction of carbohydrates and lignin during mild alkaline conditioning, and there may be some modification of lignin. There may be some hydrolysis of the lignin-carbohydrate bonds resulting in observable differences in the middle lamella region. It also appears that there may be some swelling of the individual fibers and fiber bundles but it is difficult to ascertain whether this swelling is an internal swelling or an external swelling, or whether swelling is significant in relation to removal of lignin in the subsequent selective delignification.

In any event, the alkaline conditioning of the lacerated fibrous material should be controlled so as to provide a maximum yield of papermaking pulp from the process and to minimize the amount of oxidative pulping chemicals required during selective delignification. Generally, it has been found that the mild alkaline conditioning should be controlled so that the yield from the alkaline conditioning step is at least about 90 percent of the lacerated fibrous material. Preferably, the alkaline conditioning is controlled so that a yield of at least about 95 percent by weight of the lacerated wood fibers is provided. Such mild alkaline conditioning is to be distinguished from the more extensive treatment given fibrous material in the soda process. It will be understood that in the case of some exceptional woods, larger amounts of materials may be removed by the mild alkaline conditioning.

Having reference to FIG. 4, the mild alkaline conditioning provides a preconditioned fibrous material having a composition and yield which lies within the region bounded by A, B, C, and D. The mild alkaline conditioning does not effect significant delignification, but can extract carbohydrates. Accordingly, the mild alkaline conditioning is necessarily limited to provide high yields of pulp.

The preconditioned fibrous material which is obtained from the above described laceration step, with or without mild alkaline conditioning, is in the form of that resulting from laceration. In other words, the mild alkaline conditioning does not change the appearance in terms of the physical form of the fibrous material although there may be some difference in color. The preconditioned fibrous material is distinguishable from heretofore known fibrous products commercially prepared for mechanical and chemical pulping processes. Examination of the preconditioned fibrous material under a microscope indicates that the gross wood structure has been separated predominantly in the middle lamella region.

The preconditioned fibrous material is then subjected to the oxidative reaction. Delignification, i.e., the separation of lignin from the fibrous material, in the conventional chemical pulping processes occurs in a single processing step in which the lignin reacts with the pulping chemicals and is solubilized in the pulping liquors. As is more fully disclosed below, in the oxidative reaction in selective delignification described herein, the steps of lignin reaction and lignin removal occur in two interrelated steps. In the first step, the lignin is reacted with an oxidative pulping chemical. This reaction can produce some degraded lignins which are soluble in the liquor, and also produces modified lignins which are insoluble in the liquor and water, and are retained as a part of the fibrous material. In the selective delignification process, the modified lignins, and more particularly the acetone soluble lignins, are solubilized by the alkaline extraction. Thus, as used herein, the term delignification includes the removal of lignin during the oxidative reaction and during alkaline extraction.

The oxidative reaction and alkaline extraction effect selective delignification which, as used herein, means that more lignin is removed than carbohydrate materials. Referring to FIG. 4, there are shown representative curves illustrating hard wood and soft wood treatments. It will be noted that the curves all lie to the left of a perpendicular line which can be drawn from the base line which indicates, in each instance, that more lignin is removed than carbohydrate material. Points along this perpendicular line represent equal removal of carbohydrates and lignin. Generally, in the chemical pulping processes of the prior art, greater amounts of carbohydrates are removed than lignin which means that a curve for such processes on FIG. 4 would be to the right of the perpendicular line drawn from the relevant base point.

The selective delignification, i.e., oxidative reaction and alkaline extraction, which occurs in the described process proceeds by a reaction mechanism different than that which occurs in the conventional chemical pulping processes mentioned above. In this connection, the oxidative reaction and alkaline extraction can effect fiber

liberation without substantial loss of carbohydrate materials which losses are effected at the high temperatures and reacting conditions of the chemical pulping processes.

A conventional method of determining residual lignin after chemical pulping is the Klason (TAPPI Method No. T 222 m–54). As seen in FIG. 3, as the amount of Klason lignin approaches low values, consumption of chlorine dioxide increases rapidly in comparison to the reduction in Klason lignin content. Investigation into the rapid increase in chlorine dioxide consumption lead to the discovery that the oxidative reaction resulted in the formation of modified lignins of unkown chemical structure which are not detectable as in usual Klason lignin, but which are insoluble in the oxidative reaction liquor and are retained in the fibrous material. It was further determined that modified lignins are capable of continued reaction with chlorine dioxide resulting in needless consumption of oxidative pulping chemicals when the Klason lignin content was reduced below about 10 percent by weight. As shown in FIG. 4, the Klason lignin remaining in the wood can be reduced during the oxidative reaction to about 2.5 percent by oxidative treatment but such reduction requires excessive amounts of oxidative chemicals.

The oxidative reaction is carried out to provide values of yield, carbohydrate and Klason lignin within the area defined by points E, F, G, H, I and A in FIG. 4. Preferably, the oxidative reaction is practiced to provide such values within the area defined by points E, J, Q, I, and A in FIG. 4. With soft woods, the Klason lignin values resulting from the oxidative reaction without needless consumption of oxidative pulping chemicals may be above about 15 percent.

In order to determine the amount of modified lignins in the oxidative reaction pulp, a determination is made by extracting the oxidative reaction pulp with sodium hydroxide, and (a) measuring the Klason lignin (i) and acid soluble lignin (ii) in the residual pulp from the extraction and (b) measuring the acetone soluble lignin (iii) in the aqueous sodium hydroxide used for extraction. The acetone soluble lignin is measured by acidifying the sodium hydroxide extraction lignin with acid to a pH of about 2 which causes the hemicelluloses to reprecipitate. After separation of the hemicellulose, the acidified solution is dried and the dry material resulting is extracted with acetone. Then the acetone is evaporated off to leave the acetone soluble lignin (iii). It has been found that the modified lignin fractions (i), (ii) and (iii) may exceed the Klason lignin found in the oxidative reaction pulp. Thus, it has been found that the oxidative reaction modifies the native lignin to substantial degree even though the Klason lignin of the oxidative reaction pulp is at a relatively high level.

The amount of modified lignin present after reaction with the oxidant varies depending upon the extent of the oxidative reaction. Generally, between about 14 percent and about 18 percent of modified lignins will be present when the Klason lignin content is between about 6 and about 16 percent. As discussed hereinafter, it is desirable to remove some of the modified lignins from the pulp. The ligneous material removed in the alkaline extraction step contains less chlorine but higher methoxyl groups than the ligneous material removed with the liquor from the oxidative reaction.

The discovery that reaction of lignin with an oxidative chemical produces significant amounts of modified lignins which are insoluble in the oxidative reaction liquor, but which are soluble under alkaline conditions is significant in determining optimum conditions in the selective delignification process. In order to minimize the amount of oxidative pulping chemical consumed during the oxidative reaction, it is desirable to terminate the oxidative reaction at the time that the residual lignin content, measured as Klason lignin, is above about 50 percent of the Klason lignin content in the fibrous material. As discussed hereinafter, when the selective delignification process includes multiple oxidative reactions with intermediate alkaline extractions to remove modified lignins, it is desirable to terminate the initial oxidative reaction at higher levels of Klason lignin.

In order to obtain high yields of pulp and economy of oxidative pulping chemicals, it is desirable to terminate the oxidative reaction before the pulp yield is reduced below about 80 percent, by weight. It has been found that if the oxidative reaction is unduly extended there is unnecessary degradation of the lignin and removal of the degraded products in the spent liquor. This degradation occurs when there is high chlorination of the lignin. Extended oxidative reaction periods also result in excessive consumption of oxidative pulping chemicals.

The oxidative pulping chemicals which are employed in the process may be any suitable chemical which, during the oxidative reaction, provides oxidation by electron transfer. This may be typified by the following equation:

$$4H^+ + ClO_2 + 5e \rightarrow Cl^- + 4H_2O$$

Such compounds are to be distinguished from compounds which merely yield oxygen in solution. A preferred oxidant is chlorine dioxide, and this term, as used herein, is intended to include compounds which yield chlorine dioxide in aqueous solution, such as sodium chlorite and sodium chlorate. Other examples of oxidants which provide oxidation by electron transfer upon dissolution in water include peracids of the formula



where R is hydrogen, methyl, or ethyl, e.g., performic acid, peracetic acid and perpropionic acid. Ozone may also be employed as the oxidant as well as noble gas oxides of the formula XO where X is an inert gas, e.g., argon, xenon, krypton. Oxidants which do not yield a nascent oxygen, for example, oxygen gas and hydrogen peroxide, do not provide good results in the process.

In the oxidative reaction, oxidation occurs but when chlorine compounds are employed there is also substitution of chlorine in the lignin. Accordingly, it has been found that the oxidative pulping chemical can include chlorine without harming the efficiency of the oxidative pulping chemical. In this connection, mixtures of chlorine and chlorine dioxide in weight ratio of 15:85 have been as effective for selective delignification as 100 percent chlorine dioxide chemical. However, somewhat larger amounts of the mixture need to be added to provide the oxidative chemical equivalent of chlorine dioxide. From a commercial point of view, the discovery of the ability to use the mixture is very significant because of the fact that commercial manufacture of chlorine dioxide in large amounts at favorable cost results in a mixture of chlorine and chlorine dioxide.

Reaction between the oxidative pulping chemical and lignin is desirably controlled to consume a minimum amount of chemical in the oxidative reaction. The solubility of a number of oxidative pulping chemicals is limited and desirably saturated solutions of such oxidative pulping chemicals are utilized. However, it is desirable to carry out the oxidative reaction with dilute liquors to effect control. Generally, the oxidative pulping chemical concentration in the liquor, expressed as chlorine dioxide, should be between about 5 percent and about 20 percent chlorine dioxide by weight of the preconditioned fibrous material, dry basis. Preferably, less than about 15 percent by weight is employed and under optimum conditions between about 5 percent and about 10 percent by weight of chlorine dioxide provides good results. Accordingly, to effect higher treatment of the fibrous material, the amount of liquor used in treating the fibrous material should be increased. Thus, if the fibrous material is to be given three times the amount of treatment, three times as much liquor needs to be employed.

The time of the oxidative reaction may vary depending upon the amount of the oxidative pulping chemical. Generally, the reaction will be completed to the desired extent in the liquid phase after a period of between about one hour and about ten hours, usually between about two hours and about six hours when the oxidative pulping chemicals are in the form of an aqueous solution.

The temperature of the oxidative reaction in liquid phase is desirably maintained below about 70° C. when chlorine dioxide is used. At temperatures above 70° C., the solubility of chlorine dioxide in water is sufficiently low that extended reaction times and handling problems are encountered. Good results are obtained at temperatures between about ambient temperature (25° C.) and about 60° C. When an oxidative pulping chemical other than chlorine dioxide is employed, higher temperatures may be used since solubility of the oxidant may not be a problem. The temperature is desirably maintained at as low a temperature as possible while providing sufficient rapidity of reaction but should be below the boiling point at the pressure condition utilized for treatment.

The oxidative reaction in the liquid phase may be carried out at a pH between about 1 and about 9. When chlorine dioxide is employed, the pH is desirably maintained below pH 7 and good results are obtained by initiating the reaction at a pH slightly less than 7. As the reaction proceeds, the pH is lowered slowly and a final pH in the vicinity of 4 results when a buffer is used. Without a buffer, lower pH values result. When sodium chlorite is employed as the oxidative pulping chemical, an initial pH of about 5 is usually desirable and, after the oxidative reaction, the pH is in the vicinity of 3 to 5 when a buffer is used. Adjustment of the pH can be accomplished by the addition of suitable alkali or acid.

It has been discovered that the oxidative reaction can be practiced under gaseous conditions with very rapid reactions, which reactions can be carried out at low temperatures and more quickly than liquid phase reactions. In this connection, reaction times of 5 to 30 minutes at temperatures from ambient temperature to 50° C. are effective the time being generally inversely proportional to the temperature.

For gaseous treatment, the preconditioned fibrous material should contain moisture and the moisture in the fibrous material should be between about 25 percent and about 70 percent. If the moisture is too low, the reaction does not proceed with rapidity and if the moisture is too high, free moisture can interfere with effective handling of the fibrous material. Excellent results are achieved with moisture contents of about 50 percent.

As before indicated, selective delignification primarily comprises two steps, one step involving the oxidative reaction and the second step involving the alkaline treatment of the product from the oxidative reaction step. The alkaline treatment effects some extraction and, heretofore, there has been reference to alkaline extraction after the oxidative reaction. As used herein, alkaline extraction and alkaline treatment are used interchangeably. However, the alkaline treatment provides, in addition to extraction, considerable versatility to the process and variations in the alkaline treatment provide very significant differences in the character of the pulp resulting from the alkaline treatment. In FIG. 4, the alkaline treatment results in pulp generally having values falling within the area defined by the letters K, M, N, P, F, and R. Preferably the values of the pulp fall within the area defined by the letters K, M and R so that the pulp after alkaline treatment comprises a significant amount of Klason lignin in the pulp and, accordingly, not all of the lignin is extracted by the alkaline treatment.

In addition to the removal of some materials from the material resulting from the oxidative reaction, the alkaline treatment, if carried out for more extended periods of time, effects changes in the carbohydrates. Such changes appear to affect the papermaking properties of the fibers and for some papers it would be desirable to avoid extensive alkaline treatment. However, the carbohydrates differ less from the native carbohydrates in the fibrous material after the alkaline treatment than the carbohydrates in chemical pulps.

It should be noted that the material from the oxidative reaction not only differs from chemical pulp in the character of the carbohydrates which are present, but also in the character of the ligneous materials which are present. It has been found that the alkaline treatment will rapidly remove some carbohydrate material, and some of the ligneous material which appears to primarily be the acetone soluble modified lignin. It has been found that the degree of removal of the desired ligneous material is a function of both time and temperature, with higher amounts of ligneous material being removed at elevated temperatures in a shorter times. In this connection, removal of ligneous material can be effected in 10 minutes at 60° C. If the pulp from the alkaline treatment is to be subjected to further chemical treatment, such as bleaching conditions, the alkaline treatment is desirably limited. In this connection, the limited treatment will involve temperatures between about 40° C. and 70° C. with times from about 5 minutes to about 120 minutes. However, longer times can be used for pulps not subjected to additional chemical treatment.

As before pointed out, the carbohydrate materials in the material from the oxidative reaction are significantly changed after about one hour of alakine treatment and are still further changed after about 4 hours of such treatment. The nature of these changes is not fully understood, but nevertheless such changes can be desirable for certain papermaking pulps. In general, these changes effect lower pulp freeness, higher density sheets and lower opacity, especially when the pulp from the alkaline treatment is subjected to further chemical treatment.

A unique feature of the process is the ability to change pulp properties by control of the alkaline treatment. We have discovered that desired pulp properties can be obtained by leaving certain modified lignins in the pulp. This is new to the art and is contrary to the practice in making holocellulose pulp.

It has further been found that the alkaline treatment and the mild alkaline conditioning can be inter-related to effect desired pulp characteristics. This concept of the inter-relationship of mild alkaline conditioning and alkaline treatment after an intermediate step of the oxidative reaction has not been heretofore known.

It has been determined that it is essential that the alkaline treatment to be carried out in the substantial absence of divalent cations which appears to interfere with defiberization by the alkaline treatment and, thus, adversely affect the properties of the pulp. Examples of such divalent cations, naturally occurring in wood, are calcium and magnesium. The divalent cations are soluble under acidic conditions, and if the oxidative reaction is carried out at a pH below about 7, as when chlorine dioxide is used, the divalent cations will solubilized and removed in the liquor. However, if the oxidative reaction is carried out under alkaline conditions, the divalent cations will not have been solubilized in the pulping liquor. In such instances it is necessary to treat the pulp from the oxidative reaction under acidic conditions prior to alkaline treatment unless mechanical defibration is used in place of the defiberization by alkaline treatment.

The alkaline treatment may be carried out with any of the monovalent alkaline materials mentioned herein as, for example, sodium, potassium and ammonium hydroxides, carbonates, bisulfites, etc. It has been found that an amount of alkaline material equivalent to between about 4 and about 20 percent sodium hydroxide, and preferably less than about 15 percent sodium hydroxide, by weight of the fibrous materials, provides good alkaline treatment.

There is a rapid decrease in yield which occurs during the initial portion of the alkaline treatment, the losses in yield coming about due to solubilization of the modified lignins with some loss of carbohydrates. If the alkaline treatment is continued for extended times, the carbohydrate materials are changed and if the alkali concentration is too high and/or the temperature is too high, yield losses result. The alkaline treatment should be terminated before the yield falls below about 60 percent by weight of the fibrous material, and preferably before the yield falls below about 65 percent by weight.

In addition to the desirability of terminating the alkaline treatment before there is excessive yield loss, it has also been determined that it is desirable to continue the alkaline treatment until the yield, based on the weight of the fibrous material, is below about 85 percent by weight. Yields above 85 percent, by weight, may be possible but do not appear feasible in mill operations. The oxidative reaction so conditions the material that the alkaline treatment rapidly reduces the yield to at least about 85 percent. At higher yields, some additional operation is desirably used to separate fibers. This operation is referred to in FIG. 1 as defibration and may be effected by chemical and/or mechanical means.

In addition to extraction of modified lignin, as above indicated, the alkaline treatment may provide chemical defibration. Chemical defibration can occur during the terminal portions of the alkaline treatment, after solubilization of modified lignin. The desirable chemical defibration effect may be illustrated by comparing an alkaline treated pulp (without mechanical defibration) having a yield of about 80 percent, which contains excessive screen rejects, with an alkaline treated pulp having a yield of about 70 percent, which contains substantially less than about 3 percent by weight of the pulp of screen rejects on a .006 inch cut screen.

Accordingly, when alkaline treatment provides adequate defibration, the process is capable of providing a papermaking pulp which does not require further defibration and a separate defibration step is not necessary, as indicated in FIG. 1. Furthermore, such pulp can be provided at yields substantially in excess of yields which are generally obtainable with conventional chemical pulping processes. It should be noted that the pulps obtained after alkali treatment are not "bleached pulps" and may require bleaching for some purposes.

One method of characterizing a chemical pulping process is in terms of a "defibration point" of the pulp. The defibration point is the yield in percent at which there is not more than about 2 percent rejects on a cut screen of a pulp which has not been subjected to significant mechanical forces.

The size of the cuts in the screen will differ for different fibrous materials. For hard woods and northern soft woods a screen with .009 or .010 inch wide cuts will usually be used. Different fiber morphology indicates the a screen with 0.12 inch wide cuts will usually be used. Different fiber morphology indicates the utilization of different screens to those skilled in the art.

A conventional sulfate pulp has a defibration point at about 50. A papermaking pulp obtained from the disclosed process has a defibration point of above about 65, representing about a 30 percent increase in yield of pulp having low screen rejects from the disclosed process as compared to a sulfate pulping process.

Of course, increased yields above 50 percent for sulfate pulp and above 65 percent for a pulp product in accordance with the disclosed process may be obtained by application of suitable mechanical forces to the pulp. However, increased yields due to such mechanical forces are greater when the pulp is produced in accordance with the disclosed process than with previously known chemical pulping processes.

It has been determined that a preferred process includes multiple oxidative reactions with the oxidative pulping chemical, with an alkaline treatment following an oxidative reaction. Such a multi-stage process has been found to provide a desirable papermaking pulp with less consumption of the oxidative pulping chemical.

In the event that the alkaline treatment does not effect the desired defibration, the pulp may be subjected to defibration by mechnical forces and/or by further chemical treatment. The further chemical treatment may involve the use of bleaching conditions. Thus, bleaching of the pulp may effect two functions, i.e., bleaching and defibration.

It is significant to note that the pulp from the alkaline treatment is not a bleached pulp and it may be necessary to bleach this pulp. In this connection, the G.E. brightness of the pulp resulting from the alkaline treatment is not expected to exceed 60.

For various purposes, it is desirable to increase the G.E. brightness, and therefore, bleaching may be required. A significant advantage of the pulp prepared in accord with the foregoing is that bleaching may be effected without substantial loss of yield. Thus, a high yield pulp has been provided which bleaches without significant yield loss and this distinguishes this pulp from previously known high yield pulps which have substantial yield losses when bleached with chlorine, chlorine dioxide and like chemicals.

Having described our invention in general but in sufficient detail for those skilled in the art, specific examples are set forth below.

EXAMPLE I

Aspen chips are prepared in the usual manner from aspen wood logs. The chips are approximately dimensioned ⅝ x 1 x ⅛ inch. The wood has about 42 percent moisture and comprises about 25 percent lignin including about 18 percent Klason lignin, about 5 percent acetone soluble lignin and about 2 percent acid soluble lignin, about 74 percent carbohydrates and about 3 percent of wood extractives, based upon oven dry woods.

The chips are introduced into a pressure vessel and steamed for 2 minutes at 15 p.s.i.g., i.e. pounds per square inch by gauge. The pressure is released and the steam treatment is repeated. The chips are then immersed in cold water for 30 minutes under a hydraulic pressure of 100 p.s.i., i.e. pounds per square inch. The chips are uniformly impregnated with moisture and comprise about 66 percent moisture. At this moisture level, the chips hold the moisture while at higher moisture levels, water tends to be free in the chips.

The moisture impregnated chips are then treated to soften the lignin without significant loss of yield or overheating of the wood. In this connection, the chips are held in the pressure vessel under steam pressure of 80 p.s.i.g. for 3 minutes. The steam pressure is then released and the chips are ready for mechanical defiberization. The chips, without undue loss of heat, are fed into a refiner.

A Bauer No. 185 double disc Pulper is used. The discs are each 36 inches in diameter and are driven at 1185 r.p.m. by two 100 horsepower motors. The Pulper has B 957 plates.

The heated chips are fed into the Pulper at a slow rate and the lowest feed rate is used for the Pulper. A Reeves drive is employed on a spiked roll driven at the rate of 3 r.p.m., the lowest feed rate designated No. 1 on the drive.

The defiberized chips from the Pulper have a moisture of 57 percent, having lost moisture as steam, and are defiberized by the Pulper with minimum fiber damage and maxium fiber separation in the middle lamella region.

The fiberized chips are subjected to Bauer-McNett Classification with the following results:

Screen:	Percent
On 6 mesh	11.8.
On 12 mesh	22.4.
On 35 mesh	35.8.
On 65 mesh	9.4.
Through 65 mesh	20.6 (by difference).

The fiberized chips from the Pulper are very light and fluffy so that it is difficult to measure the bulk density because the fiberized chips tends to compact in making the measurement. However, when air dried chips (6 percent moisture) are compared to air dried fiberized chips, which have been lightly compacted in depths up to about 24 centimeters, the fiberized chips have a bulk density of from about one-fourth (¼) to one-ninth (⅑) of the bulk density of the chips.

The fibers in the defiberized chips, when compared to fibers in the initial chips are not significantly weakened, and in this connection, the zero span tensile strength of the fibers in the defiberized chips are more than 95 percent of the zero span tensile of fibers in the chips. Zero span tensile strength is measured in accord with TAPPI Standard Method T 231 SM–60 on 50 gram per square meter hand sheets (oven dry basis).

The yield loss is minimal in the defiberizing operation and the defiberized chips are used unscreened. Microscopic studies concerning the defiberized chips discloses that the fibers are primarily separated in the region of the middle lamella without any extensive breaking of fibers. from about one-fourth (¼) to one-ninth (⅑) of the bulk

The foregoing material, referred to herein as "defiberized chips," will be used as a base material in this and various other of the Examples hereinafter. The defiberized chips may be further preconditioned by mild alkaline conditioning, to be illustrated in later Examples, or they may be selectively delignified without the mild alkaline treatment.

The defiberized chips are selectively delignified by first subjecting the defiberized chips to an oxidative reaction using aqueous chlorine dioxide, followed by alkaline treatment with sodium hydroxide.

The defiberized chips are placed in a ten gallon polyethylene carboy, with the fiberized chips being slurried at a 6 percent consistency. Sodium hydroxide is used to a level of 3½ percent as a buffering agent and about one-half of the sodium hydroxide is added to the slurry of fiberized chips and the other one-half is added to the aqueous chlorine dioxide solution to provide a resultant solution having a pH of 6.0–6.5. The amount of chlorine dioxide in the reaction mixture is 9.0 percent based upon the weight of fiberized chips (oven dry basis).

The reaction mixture in the carboy is brought to about 35° C. in about 45 minutes by immersion of the carboy in a constant temperature bath and by shaking from time to time. After exhaustion of the chlorine dioxide which requires about 5 hours at 25° C.–35° C., the pH is 2.6. The treated defiberized chips are collected in a nylon bag lined centrifuge and, following removal of the liquor, the material is washed with tap water by reslurrying the material in the nylon bag. The wash water is removed and the washing treatment is repeated about 3 times. The material drains readily and the yield is 94.9 percent based upon the chips.

The material from the oxidative reaction is then subjected to alkaline treatment and, in order to effect this treatment, the defiberized material is placed in a high density polyethylene bag as a slurry which has a consistency of 8 percent and which contains 6 percent sodium hydroxide based upon the weight of defiberized chips, oven dried basis. The alkaline treatment is carried out at a temperature of about 60° C., and in one instance the treatment is accomplished in 10 minutes and in another instance the treatment is accomplished in 120 minutes. The final pH in the first instance is 10.9 with a yield of 81.5 percent and in the second instance the final pH is 9.3 with a yield of 77.1 percent.

The pulp from the shorter alkaline treatment has Klason lignin in an amount of 7.8 percent and acid soluble lignin in an amount of 3.5 percent. The pulp from the longer alkaline treatment has Klason lignin in an amount of 7.0 percent and acid soluble lignin in an amount of 3.2 percent.

Another portion of the material from the oxidative reaction is subjected to somewhat different alkaline treatments, and in this connection, the treatments in the respective times are made with slurries containing 9 percent sodium hydroxide. The alkaline treatments are done in 10 minutes and 120 minutes as above described. At the end of 10 minutes treatment, the pH is 11.9 with a yield of 72.3 percent and at the end of 120 minutes the pH is 11.7 with a yield of 67.7 percent. The pulp from the shorter alkaline treatment has Klason lignin in an amount of 5.3 percent and acid soluble lignin in an amounut of 2.3 percent. The pulp from the longer alkaline treatment has Klason lignin in an amount of 3.8 percent and acid soluble lignin in an amount of 1.7 percent.

The alkaline treated material is, in each instance, poured into a fritted glass funnel and thoroughly washed with tap water at a temperature of 60° C. and then with cold tap water.

The pulps from the various alkaline treatments are then defibrated and bleached with hypochlorite by placing the pulps in standard polyethylene bags. The defibration and bleaching are carried out with hypochlorite having 4.5 percent average chlorine based on the material with the pulps at 12 percent consistency and at a temperature of 40° C. The results of different defibration and bleaching treatments are set forth in the table below, pulp 1 being pulp which is subjected to 6 percent sodium hydroxide for 10 minutes, pulp 2 being pulp subjected to 6 percent sodium hydroxide for 120 minutes, pulp 3 being pulp subjected to 9 percent sodium hydroxide for 10 minutes, and pulp 4 being pulp subjected to 9 percent sodium hydroxide for 120 minutes.

TABLE A

Pulp	1	2	3	4
Time (minutes)	150	170	180	235
pH (final)	8.2	8.2	7.9	7.9
Yield (percent)	76.8	71.6	68.2	66.2
Rejects (percent)	17.6	16.9	9.0	4.4
G.E. brightenss	69.0	70.5	74.0	77.5
Canadian Freeness, ml	690	640	580	460
Klason plus acid soluble lignin	8.1	6.8	4.5	3.0

The G.E. brightness is determined according to TAPPI Standard Method T 218 m–59 and the Canadian Freeness (TAPPI Standard Method T 227 m–58) is determined after the pulp has been circulated in a Valley Beater for 5 minutes with no bed plate load. The brightness and freeness are determined after screening of the pulp.

The pulp is screened on a flat bed, .006 inch cut screen, with the accepts being collected on a muslin covered wash box and the rejects being taken from the top of the screen. The accepts are dewatered in nylon bag lined centrifuge and are held for evaluation.

In order to evaluate the above pulps after the respective treatments, the pulps are beaten to varying degrees in a Valley Beater in accordance with TAPPI Standard Method T 200 ts–66 to provide pulps of different freenesses and with different hand sheet densities. Hand sheets are prepared according to TAPPI Standard Method T 205 m–58.

A determination of the burst factor is made by a TAPPI Standard Method T 220 m–60 and the results are shown in FIG. 5(*a*) of the drawings by the line designated I.

The breaking length is determined on an Instron machine by TAPPI Standard Method T 220 m–60 with a

test span of 4 inches, a test piece width of one inch and a cross head speed of one inch per minute and the results are shown in FIG. 5(*b*) of the drawings by the curve designated I.

The hand sheets are further evaluated for tensile energy absorption by TAPPI Standard Method T 494 su–64 and the results are shown in FIG. 5(*c*) of the drawings by the line designated I. The tests are under the same conditions mentioned for the use of the Instron machine in determining the breaking length.

In addition, the hand sheets are evaluated for MIT fold in accord with a TAPPI Standard Method T 220 m–60 and the results are shown in FIG. 5(*d*) of the drawings by the curve designated by I.

The hand sheets are further evaluated in respect of the Elmendorf tear factor by TAPPI Standard Method T 220 m–60 which are corrected to a yield of 65 percent. Results of this evaluation are shown by the two lines designated by I in FIG. 6. These lines indicate some difference between the times of alkaline treatment. The longer line represents the effect of a shorter time of alkaline treatment and the other line represents a longer time of alkaline treatment.

It will be noted that the pulps of this Example contain a measurable amount of lignin materials. Thus, the pulps are not wholly free of lignin materials and, in this respect, they differ from holocellulose pulps. As will be seen below in Table C, the presence of increasing lignin materials improves certain properties such as breaking length and Z-tensile.

It will be seen that the pulps of this Example are varied in characteristics and the degree of alkaline treatment is significant in the pulp which is provided. It should also be noted that the materials provided in the Example give products which are in accord with FIG. 4 of the drawings. The drawings show comparison of the pulps of this Example with a kraft pulp prepared in accord with a standard procedure which is shown in FIGS. 5(*a*) to 5(*d*) inclusive, and FIG. 6. The tests on the hand sheets made from unbleached kraft pulp are indicated by the lines or curves designated III. The hand sheets are prepared from pulps beaten as herein specified.

Aspen chips are used for the kraft pulp which is prepared in a vertical batch stainless steel digester having a capacity of about 2 cubic feet. The digester is fitted with a pump and heat exchanger for external heating of the liquor.

The kraft pulp is prepared by a standard procedure having the following characteristics with the indicated yield and rejects:

TABLE B

Liquor/wood	4.0
Active alkali, percent Na_2O	19.4
Sulfidity, percent	30.0
Blowdown to 80 p.s.i. min.	5
Kappa No.	11.2
Max. temp., ° C.	174
Time to 174°, min.	90
Time at 174°, min.	120
Unscreened yield, percent	50.5
Rejects, percent	0.2

It will be seen that the pulps of this Example are comparable to kraft pulp in many respects although the pulp is different. The pulp of this Example is a unique pulp and the control of the alkaline treatment can provide pulps of differing characteristics.

In order to more clearly demonstrate the unique pulp characteristics when compared to kraft pulp, the following comparison of Pulp 1, Pulp 2 and Pulp 3 is made to kraft pulp.

TABLE C

Pulp	1	2	3	Kraft
Density of hand sheet, g./cc.	0.59	0.59	0.59	9.59
Canadian Freeness, ml.	430	490	560	620
Beating [1] time, min.	22	11	0	0
Opacity, percent, TAPPI T 425 m-60	75	74	74	
Breaking length, km.	7.4	7.0	6.1	5.4
Stretch, percent, TAPPI T 220 m-60	1.8	2.0	2.0	1.1
Tens. energy, abs., g. cm./cm^2	55	55	55	26
Tens. stiffness,[2] kg./cm	480	470	460	580
Burst factor	34	36	31	20
Tear factor (Elmendorf)	49	54	59	57
Tear factor×yield/65	58	59	62	44
Zero-span breaking length, km.	16	16	[4] 14	20
Zero-span breaking length×yield/65	19	18	15	16
Z-tensile,[3] kg./cm.^{2}	10.5	9.5	9.0	
M.I.T. fold	66	60	55	3

[1] Beating in Valley beater with bed plate load of 5.5 kilograms for kraft and 2.0 kilograms for other pulps.
[2] Calculated from the slope of the load/elongation curve of the tensile energy absorption tests.
[3] Made on 120 g./m.^{2} handsheets. TAPPI Volume 60, No. 8, page 393, (1967).
[4] Estimated.

The liquor from the oxidative reaction provides lignin which is believed to be new and which has not been provided by heretofore known processes.

The liquor from the alkaline treatment also provides lignins which are believed to be novel and which have unique applications.

EXAMPLE II

Pulps are prepared in accord with this Example by taking defiberized chips prepared in accord with Example I and subjecting them to mild alkaline conditioning before selective delignification.

The mild alkaline conditioning is effected by placing the defiberized chips in polyethylene bags and slurrying them to a 6 percent consistency with 3 percent sodium hydroxide being present based upon the weight of defiberized chips. The alkaline conditioning is effected at 50° C. in about one hour. The final pH is 10.5. This conditioning effects very little removal of carbohydrates and/or change in the native carbohydrates.

After alkaline conditioning the defiberized chips are filtered in a fritted glass funnel and washed with tap water at about 50° C. and then with cold tap water. The free water is removed without difficulty from the treated material by suction. The yield from the alkaline conditioning is 94.6 percent. The material after alkaline conditioning is then ready for the oxidative reaction of the selective delignification step.

The oxidative reaction is carried out in accord with Example I except that the consistency is 5 percent instead of 6 percent and the time of the reaction is about 4½ hours. The final pH is 3.0 and the yield is 89.2 percent.

The material from the oxidative reaction is subjected to alkaline treatment in accord with Example I with 6 percent sodium hydroxide, based upon the weight of the defiberized chips, and with effecting treatment in 10 minutes and in 120 minutes. With the 10 minutes treatment, the final pH is 11.6 and the yield is 71.5 percent. The Klason lignin plus acid soluble lignin amounted to 5.2 percent. With the 120 minutes treatment, the final pH is 11.4 and the yield is 67.6 percent. The Klason lignin plus acid soluble lignin amounted to 3.7 percent.

It will be noted that each pulp, overall, is treated with 9 percent sodium hydroxide and this is to be compared with Pulps 3 and 4 of Example I which are also treated with 9 percent sodium hydroxide but the treatment is effected wholly in the alkaline treatment without alkaline conditioning.

The material from alkaline treatment is defibrated and bleached. In this connection, the material from the shorter time alkaline treatment is divided into two parts, as is the material from the longer alkaline treatment in providing pulps identified below as Pulp 5, Pulp 6, Pulp 7, and Pulp 8. The materials are treated with hypochlorite as in Example I at different levels, indicated below, the material in each case being at a consistency of 12 percent on a

defiberized chip basis and at a temperature of 40° C. The other conditions and results are set forth below.

TABLE D

Pulp	5	6	7	8
OCl⁻, percent av. Cl_2	1.5	4.5	1.5	4.5
Time (minutes)	75	245	110	7,270
pH (final)	9.8	7.7	9.9	7.9
Yield (percent)	69.9	67.1	65.8	63.1
Rejects (percent)	3.1	0.9	1.3	0.3
G.E. brightness	66.0	75.5	71.0	78.0
Canadian Freeness, ml	550	490	470	405
Klason plus acid soluble lignins		2.2		1.4

The pulps are beaten and made into hand sheets as described in connection with Example I and the effect of the treatment on the burst factor is shown in FIG. 5(*a*) by the line designated II.

The effect of the treatment on breaking length of the fibers is shown in FIG. 5(*b*) by the two lines designated II. The upper line shows the effect of the shorter time of alkaline treatment and the lower line shows the effect of the longer time of alkaline treatment.

FIG. 5(*c*) discloses, in the line designated II, the relationship to tensile energy absorption.

FIG. 5(*d*) discloses two curves designated II and the relation to MIT fold. The upper curve indicates the shorter time of alkaline treatment and the lower curve designates the longer time of alkaline treatment. It is interesting to note in FIG. 5(*d*) that the two curves fall on opposite sides for the curve for the unbleached kraft pulp designated by III.

FIG. 6 shows the relationship of pulps, by the lines designated II, to the Elmendorf tear factor corrected to 65 percent yield. The upper curve is in respect to the pulp which was the shorter alkaline treatment time and the lower curve is in respect to the pulp which has the longer alkaline treatment. It will also be noted that in FIG. 6 the two curves designated II are within the kraft pulp curve designated III and have a wholly different characteristic.

It should be pointed out that the pulps of this Example II provide differing characteristics and characteristics which are also different from the pulps of Example I. It will be recalled that the pulps of Example I were not subjected to mild alkaline conditioning prior to the oxidative reaction and it should be noted that this conditioning has an effect upon the pulp.

In order to compare pulps of Example I with pulps of this Example II and kraft pulp, the following tables are set forth and to which apply the footnotes 1, 2, and 3 as in Table C.

TABLE E

Pulp	5	1	2	3	4	Kraft
Density, g./cc	0.69	0.69	0.69	0.69	0.69	0.69
C.F., ml	460	180	220	360	400	470
Beating time, min	0	45	28	9	0	10
Opacity, percent	70	71	69	68	69	
Stretch, percent	2.3	2.2	2.3	2.3	2.6	2.0
Tens. stiffness, kg./cm.	482	570	560	550	530	625
Tear factor (Elmen.)	58	43	46	53	57	74
In-plane tear, g. cm./cm	42	36	39	44	48	
Zero-span breaking length, km.	15	18	18	17	16	21
Zero-span breaking length× yield/65	16	21	20	18	17	16
Z-tensile, kg./cm.²	14	18.5	19	18	18	

TABLE F

Pulp	5	6	7	8	3	4	Kraft
Density, g./cc	0.75	0.75	0.75	0.75	0.75	0.75	0.75
C.F., ml	286	340	340		230	290	370
Beating time, min	18	6.5	4		16	6	17
Opacity, percent	66	68	69	71	64	65	
Stretch, percent	2.8	2.8	3.0	3.0	2.6	2.7	2.5
Tens. stiffness, kg./cm.	541	518	495	500	600	590	645
Tear factor (Elmen.)	52	53	52		49	53	74
In-plane tear, g. cm./cm.	44	42	47	43	42	46	
Zero-span breaking length, km.	18	17	17	16	19	19	20
Zero-span breaking length× yield/65	19	17	17	16	20	19	16
Z-tensile, kg./cm.²	24.5	24	20.5	(22)	25	24	

TABLE G

Pulp	6	7	8	3	4	Kraft
Density, g./cc	0.80	0.80	0.80	0.80	0.80	0.80
C.F., ml	200	200	247	130	160	280
Beating time, min	18	14	7.5	21	10	25
Opacity, percent	61	64	66	58	59	
Stretch, percent	2.8	3.2	3.1	2.8	2.7	2.9
Tens. stiffness, g. cm./cm.²	576	547	550	640	630	660
Tear factor (Elmen.)	48	55	48	46	51	69
In-plane tear, g. cm./cm	40	45	39	41	44	
Zero-span breaking length, km.	18	19	16	20	(20)	20
Zero-span breaking length× yield/65	19	19	16			16
Z-tensile, kg./cm.²	34	30	31.5	33	32	

The hypochlorite treatment of this Example II effects defibration and permits the use of milder alkaline treatment. Thus, the hypochlorite treatment not only effects bleaching but, in addition, effects defiberation.

The defibration point of Pulps 5, 6, 7 and 8 are each above 65 as indicated by Table D with reference to the screen rejects.

EXAMPLE III

In accord with this Example the defiberized chips are treated with chlorite rather than chlorine dioxide in the oxidative reaction.

The defiberized chips of Example I are given alkaline conditioning in two cases, (b) and (c) below, and in one case are not given any alkaline conditioning, (a) below. The conditioning is effected at a consistency of 6.0 percent at ambient temperature in about one hour.

The defiberized chips have the following lignin analysis:

TABLE H

Klason lignin	22.2
Modified lignin	25.0
(i) Klason	17.9
(ii) Acid soluble	1.9
(iii) Acetone soluble	5.2

The conditions for the defiberized chips to produce the materials (a), (b), and (c) are set forth below:

TABLE I

	(a)	(b)	(c)
Sodium hydroxide, percent	0	3.0	6.0
pH at 5 minutes	7.3	12.2	12.7
pH at 60 minutes	7.3	9.5	9.4

The oxidative reaction is carried out on each of the materials at a consistency of 6 percent with the use of sodium chlorite in an amount of 100 percent of the weight of the defiberized chips. The reactions are carried out at a temperature of 50° C. and the pH is adjusted to 4.5 with acetic acid. The results of the treatment with chlorite for the respective pulps are set forth below:

TABLE J

	(a)	(b)	(c)
Time (hours)	1	1	1
pH (final)	4.9	4.9	5.0
Klason lignin	7.3	6.4	5.9
Yield, percent	94.0	89.5	86.5
Modified lignin, percent	19.2	19.9	14.0
(i) Klason	2.6	2.8	1.1
(ii) Acid soluble	1.7	1.5	1.5
(iii) Acetone soluble	14.8	15.6	11.4

The material from the oxidative reaction is then given alkaline treatment at a consistency of about 8.0 percent at about 50° C. in about one hour. The conditions and

results of the treatment for pulps (a), (b), and (c) are set forth below:

TABLE K

	(a)	(b)	(c)
Sodium hydroxide, percent	9.0	6.0	3.0
pH (final)	12.2	12.3	12.3
Yield, percent	72.0	71.0	74.0
Klason lignin, percent	1.7	1.6	2.1
Modified lignin	4.1	5.2	6.4
Acetone soluble	1.2	2.0	2.0
Klason	1.6	1.6	2.7
Acid soluble	1.3	1.6	1.8

It will be seen, in accord with this Example, that the oxidative reaction may be practiced with the use of chlorite as the oxidative pulping chemical.

It will be noted from this Example that only about one-fourth of the modified lignin is removed from the defiberized chips by the oxidative reaction. It should also be noted that the oxidative reaction increases the amount of acetone soluble lignins as much as three times. Thus, the oxidative reaction has a positive effect upon the lignin without substantial removal of modified lignins and this discovery permits much more economical use of oxidative pulping chemicals. It will be further noted that the alkaline treatment effects preferential removal of the acetone soluble lignins and permits retention of Klason (i) and acid soluble lignins (ii) which, as above indicated, can improve certain characteristics of the pulp.

EXAMPLE IV

It is quite advantageous to utilize an aqueous mixture of chlorine and chlorine dioxide because of the fact that in the commercial manufacture of chlorine dioxide it is more economical to include some chlorine with chlorine dioxide than to provide pure chlorine dioxide. A particular advantage of this process is its ability to utilize the mixture of chlorine and chlorine dioxide.

It has also been found advantageous to carry out the process in a step-wise manner by effecting the oxidative reaction in two or more steps. This Example illustrates the step-wise treatment of defiberized chips with a mixture of chlorine and chlorine dioxide and with chlorine dioxide.

Defiberized chips are prepared in accordance with Example I and are subjected to an oxidative reaction at a temperature of 25–35° C. at a consistency of a 5 percent in about 3½ hours. The reaction is buffered with sodium hydroxide at a level of 2.25 percent. Using a mixture of chlorine and chlorine dioxide in an amount of .88 percent chlorine and 4.97 percent chlorine dioxide, based upon the weight of defiberized chips, a yield of 99.1 percent is achieved and the product has a Klason lignin of 17.0 percent and an acid soluble lignin of 6.9 percent. With chlorine dioxide alone being used at a level of 5.3 percent, based upon the weight of defiberized chips, a yield of 99.4 percent is obtained and the product has a Klason lignin of 16.3 percent and an acid soluble lignin of 6.8 percent. The products of each oxidative reaction are then given alkaline treatment at a consistency of 8 percent with sodium hydroxide being present at a level of 6 percent. In both cases the alkaline treatment is given for 40 minutes at a temperature of 60° C. The final pH of the material from the treatment of chlorine plus chlorine dioxide is 9.8 percent. The yields are 82.1 percent and 81.8 percent, respectively. The Klason lignin is 10.8 percent in each case and the acid soluble lignin in the material from the treatment of chlorine plus chlorine dioxide is 3.3 percent and in the case of chlorine dioxide it is 3.7 percent.

The alkaline treated materials are again subjected to an oxidative reaction in accord with the following table:

	Cl—ClO_2	ClO_2
Consistency, percent	5.0	5.0
Time (hours)	5.0	4.75
Buffer (sodium hydroxide)	.75	.75
Chlorine-chlorine dioxide, percent	.45-2.53	
Chlorine dioxide, percent		2.7
Yield, percent	79.9	78.2
Klason lignin, percent	7.6	7.2
Acid soluble lignin, percent	3.8	4.2

Following the oxidative reaction, the materials are again given an alkaline treatment in accord with the following table:

	Cl—ClO_2	ClO_2
Consistency	8.0	8.0
Sodium hydroxide, percent	3.0	3.0
Time (minutes)	120	120
Temperature, ° C	60	60
pH (final)	10.4	11.0
Yield, percent	65.7	66.1
Klason lignin plus acid soluble lignin, percent	3.2	3.2

It will thus be seen that the treatment with the mixture of chlorine and chlorine dioxide is substantially equivalent to the treatment with chlorine dioxide. This is of substantial commercial significance to the practice of this process.

EXAMPLE V

It has been found that a very fast oxidative reaction can be carried out through the use of a gaseous oxidative pulping chemical to provide a pulp which, upon bleaching, provides high brightness. The liquid reactions for providing the oxidative reaction, as seen in the previous Examples, take several hours, whereas an oxidative reaction with gas can be effected in less than one-half hour. The defiberized chips may be subjected to alkaline conditioning prior to the oxidative reaction but highly satisfactory results have been achieved without the alkaline conditioning.

In accord with this Example, defiberized chips of Example I are adjusted to a moisture content of about 50 percent and treated with gaseous chlorine dioxide in a continuous reaction. The oxidative reaction is carried out in a single pass with concurrent flow of gas in the reactor. If the defiberized chips have too high or too low moisture contents, the reaction is not as effectively carried out.

The reactor consists of a glass tube which is 5 feet long and which has 6 inches inside diameter. A T, having an inside diameter of 6 inches, is located at each end of the tube so that the total length of the reactor is somewhat over 8 feet. At the inlet end of the reactor, the T is turned up to receive the defiberized chips, while at the other end of the reactor, the T is turned down to discharge the treated material. The length from the inlet to the outlet is about 7 feet. The reactor is inclined at a slight angle from the horizontal so as to provide a one foot drop for every 10 feet of length. Inside the reactor there is provided a motor driven scraper which travels back and forth through an arc of about 300°. The scraper functions to lift the defiberized chips from the bottom of the tube sufficiently high so that the fiberized chips fall off the scraper. This action of the scraper combines with the inclination of the reactor and causes the defiberized chips to move from the inlet end to the outlet end with a positive flow.

Chlorine dioxide gas is introduced adjacent the inlet end and removed from the reactor adjacent the outlet end.

9.3 percent chlorine dioxide, based upon the weight of the defiberized chips, is consumed from the glass flow into the reactor and the gas exits at a temperature of 40–45° C. The time of treatment is about 15 minutes, average time, in the reactor. There is no substantial yield loss in the reactor. The final pH is estimated to be about .05.

After the oxidative reaction, the defiberized chips are given an alkaline treatment, at a consistency of about 8 percent, with 9 percent sodium hydroxide being used, based upon the oven dry weight of defiberized chips. The alkaline treatment is effected at 60° C. in 60 minutes. The yield is 68 percent with screen rejects at a level of 4 percent. The Klason lignin plus acid soluble lignin in the product is 5.7 percent and when the pulp is made into hand sheets it has a G.E. brightness of 44. The pulp has a Canadian Freeness, after circulation in a Valley Beater for 5 minutes with no bed place load, of 505 and a defibration point in excess of 65. This pulp is referred to below in Table K as Pulp 9.

The pulp from the alkaline treatment is bleached with hypochlorite at a level of 2.5 percent expressed on an available chlorine basis, which basis applies to other Examples herein, with some sodium hydroxide being added to maintain a pH above about 10. Bleaching is carried out at a consistency of 8 percent and at a temperature of 40° C. in 3 hours. The final pH of the bleaching solution is 10.6 and the yield of bleached pulp is 64 percent. The bleached pulp contains 2.7 percent of Klason lignin and acid soluble lignin. This bleached pulp is referred to below in Table L as Pulp 10. When made into hand sheets, the G.E. brightness of Pulp 10 is 80 which is a high brightness. The pulp has a Canadian Freeness of 405, after 5 minutes of circulation in a Valley Beater with no bed plate load.

TABLE K.—UNBLEACHED PULP 9

Beating time, min	0	3	12	22	36
Canadian Freeness, ml	505	460	385	305	195
Density, g./cc	0.625	0.663	0.722	0.763	0.794
Opacity, percent	74	74	73	69	63
Breaking length, m	6.3	7.7	9.9	10.9	12.1
Burst factor	27	37	50	58	67
Tear factor (Elmendorf)	71	66	64	58	53
Zero-span breaking length, km	15	17	19	19	19

TABLE L.—BLEACHED PULP 10

Beating time, min	0	2	9	15	22
Canadian Freeness, ml	405	370	305	245	185
Density, g./cc	0.713	0.741	0.770	0.789	0.815
Opacity, percent	69	66	64	60	56
Breaking length, km	8.8	9.7	10.7	11.2	11.7
Burst factor	45	50	62	66	68
Tear factor (Elmendorf)	69	66	62	58	55
Zero-span breaking length, km	18.0	18.7	20.0	20.3	19.0

The gas phase oxidative reaction leads to handsheet properties from Pulp 10 which, when compared with those properties for Pulp 4, indicates a higher tear factor, while providing other properties generally like those provided by liquid phase oxidative reactors.

The material obtained from the alkaline treatment contained a new and unusual ligneous material which can be developed for various purposes.

EXAMPLE VI

In accord with this Example, the defiberized chips are first given alkaline conditioning and are then subjected to selective delignification by an oxidative reaction with gas and alkaline treatment.

Defiberized chips, prepared in accord with Example I, are mixed with 3.2 percent of sodium hydroxide at a temperature of 60° C. for one hour and at a consistency of about 8 percent. There is a yield loss of about 5 percent in this alkaline conditioning.

The defiberized chips are then recovered and introduced into the reactor described in the previous Example at a moisture content of about 50 percent. The gas treatment is effected in two stages. In the first stage, chlorine dioxide is utilized at a level of 6.1 percent and in the second stage chlorine dioxide is utilized at a level of 1.7 percent to provide a total chlorine dioxide use of 7.8 percent. The gas exits from the reactor during each stage at 25–36° C. The time of treatment of defiberized chips during each stage was about 15 minutes, average. The final pH after the oxidative reaction is less than 1.

The defiberized chips are then subjected to alkaline treatment at a consistency of about 8 percent with 6.2 percent sodium hydroxide being utilized. The alkaline treatment is effected at 50° C. in about one hour. The yield is 73 percent. The Klason lignin plus acid soluble lignin totals 9.7 percent and the pulp, when made into hand sheets has a G.E. brightness of 30. The pulp has a Canadian Freeness of 555 after 5 minutes treatment in a Valley Beater with no bed plate load.

The following table indicates handsheet data for the pulp of this Example which is designated Pulp 11.

TABLE M.—PULP 11

Beating time, min	0	10	20	27	42
Canadian freeness	555	475	365	305	210
Density, g./cc	0.576	0.626	0.699	0.728	0.768
Opacity, percent	78	79	77	76	70
Breaking length, km	4.5	6.2	8.5	9.1	10.1
Burst factor	19	27	39	46	52
Tear factor (Elmendorf)	64	55	50	50	45
Zero-span breaking length, km	12.6	14.6	16.1	16.9	17.1

EXAMPLE VII

In order to clearly understand the effect of the alkaline conditioning, oxidative reaction and alkaline treatment, this Example is made and defiberized chips are prepared in accord with Example I. The lignin and carbohydrate materials in the chips are set forth in Table N.

TABLE N

Defiberized Chips

Klason lignin, percent	24.5
Modified lignin, percent	25.0
(i) Klason	17.9
(ii) Acid soluble	1.9
(iii) Acetone soluble	5.2
Carbohydrates, percent	75

The defiberized chips are subjected to alkaline conditioning in accord with the conditions set forth below in Table O.

TABLE O

Sodium hydroxide, percent	3.0
Temperature, ° C.	50
Final pH	10.5
Consistency, percent	6.0
Time, min.	60
Yield, percent	96.4

The lignin composition of the defiberized chips after alkaline conditioning is set forth below in Table P.

TABLE P

Klason lignin, percent	21.0
Modified lignin, percent	22.8
(i) Klason	18.3
(ii) Acid soluble	1.5
(iii) Acetone soluble	3.0

The alkaline conditioned defiberized chips are then subjected to the oxidative reaction and the conditions of this reaction are set forth below in Table Q.

TABLE Q

Chlorine dioxide, percent	9.0
Initial temp., ° C.	25
Temp. from 0.75 hr.	35
Time, hr.	4.5
Yield, percent	90.7
Sodium hydroxide, percent	3.5
Consistency, percent	5.0
Final pH	3.0

The analysis of the material from the oxidative reaction, in respect to lignins and carbohydrates, is set forth below in Table R.

TABLE R

Klason lignin, percent	11.8
Modified lignin, percent	19.6
(i) Klason	4.4
(ii) Acid soluble	1.4
(iii) Acetone soluble	13.8
Carbohydrates, percent	72

The material from the oxidative reaction is then given alkaline treatment which effects both defibration and extraction, with 6 percent sodium hydroxide in a stock of 8 percent consistency at a temperature of 50° C. The stock is subjected to alkaline treatment for three different times, as indicated below in Table S. The alkaline treatment results in three pulps designated Pulp 12, Pulp 13 and Pulp 14. The conditions for preparing of these stocks is set forth below in Table S.

TABLE S

Pulp	12	13	14
Time, min	10	60	240
Final pH	11.8	11.7	11.6
Yield, percent	73.0	69.0	67.6
Rejects, percent	7.0	2.8	2.2

Pulp 13 is analyzed for lignins and carbohydrates and this analysis is set forth below in Table T.

TABLE T

Klason lignin, percent	3.3
Modified lignin, percent	6.1
(i) Klason	2.9
(ii) Acid soluble	1.0
(iii) Acetone soluble	2.2
Carbohydrates, percent	60

The carbohydrates, as shown in FIG. 4, and as indicated by the above analyses includes polysaccharides, polyuronic acids and acetyl groups. The polysaccharides can be determined by sugar analysis in accord with one of the following methods:

(1) Gas chromatography, essentially as described by P.C. Crowell and B. B. Burnett, Anal. Chem., *39*, No. 1:121–4 (1967)

(2) Paper chromatography, as described by J. F. Saeman, W. E. Moore, R. L. Mitchell and M. A. Miller, Tappi, *37*:336 (1954)

(3) Ion exchange chromatography, as described by R. B. Kesler, Anal. Chem., *39*, No. 12:1416–22 (1967).

Polyuronides are determined by Institute of Paper Chemistry method 25 and acetyl content is determined by the method of R. Whistler and A. Jeanes, Ind. Eng. Chem., Anal. Ed., *15*, No. 5:317 (1943).

It will be noted, in the foregoing, that each of the Pulps 12, 13 and 14 have a defibration point in excess of 65 indicating that the alkaline treatment has effectively separated fibers.

The Pulps 12, 13 and 14 are made into hand sheets and the data for the hand sheets is set forth below in Table U.

TABLE U

Canadian Freeness/beating time, min.: [a]				
Pulp:				
12	560/0	460/6	350/20	210/38
13	565/0	465/6	345/20	205/38
14	515/0	440/6	325/20	205/25
Density, g./cc.:				
Pulp:				
12	0.585	0.633	0.691	0.749
13	0.625	0.673	0.721	0.790
14	0.628	0.691	0.747	0.756
Opacity, percent:				
Pulp:				
12	82	83	81	78
13	81	80	78	72
14	80	80	78	76
king length, km::				
BreaPulp:				
12	4.8	6.3	8.2	9.2
13	5.3	7.0	8.7	9.2
14	5.9	7.4	9.1	9.2
Burst factor:				
Pulp:				
12	21	29	40	48
13	23	34	45	53
14	27	36	49	53
Tear Factor (Elmendorf):				
Pulp:				
12	62	61	57	51
13	65	62	56	51
14	64	59	56	54
Zero-span breaking length, km.:				
Pulp:				
12	12.4	15.4	16.0	17.6
13	13.2	15.7	16.9	18.1
14	14.6	16.1	17.5	17.7

[a] Two kg. weight on Valley beater.

The G.E. brightness is determined in respect of Pulp 13 to show that the pulp is unbleached: The G.E. brightness of Pulp 13 is 50.

It will be observed from the foregoing data that more lignin is removed from defiberized chips than carbohydrates. Thus, the pulps are selectively delignified. It will also be noted that the oxidative reaction substantially increases the amount of acetone soluble lignin and that the acetone soluble lignin substantially remains with the material resulting from the oxidative reaction. At the same time, it should be noted that the alkaline treatment removes a larger portion of the acetone soluble lignin than the other lignins and leaves a significant amount of Klason lignin and acid soluble lignin in the pulp. These are unique features of the process and pulp.

It will also be noted that the characteristics of the pulp after the respective treatments fall within the indicated areas set forth in FIG. 4.

EXAMPLE VIII

This Example will demonstrate the effect of mechanical defibration in the process and, in this Example, the oxidative reaction is effected step-wise, as is the alkaline treatment.

Defiberized chips are obtained in accord with Example I and this material is subjected to an oxidative reaction without prior alkaline conditioning. The defiberized chips are made into a stock having a consistency of 1.1 percent and are treated with chlorine dioxide at a level of 6 percent. The oxidative reaction continues for 22 hours at a temperature of 16–21° C. The final pH is 3.6 and some sodium hydroxide is used during the reaction to obtain the final pH. The yield at the end of the reaction is 92.7.

The material from the first step of the oxidative reaction is given an alkaline treatment, the consistency being at a level of 7 percent and 40 percent sodium hydroxide being used. The alkaline treatment is carried out over a period of one hour at 50° C. and the final pH is 8.8. The yield of material is 84.1 percent.

The oxidative reaction is then continued at a consistency of 3.0 percent and with chlorine dioxide at a level of 3.0 percent. 0.16 percent sodium hydroxide is used to buffer the reaction which is continued for 20 hours at a temperature of 25° C. The final pH is 4.2 and the yield is 79.7 percent. The Klason lignin in the material is 4.7 percent. The modified lignin amounts to 15.3 percent com-

prising (i) Klason lignin at 3.3 percent, (ii) acid soluble lignin at 3.8 percent and (iii) acetone soluble lignin at 8.2 percent.

Material from the second stage of the oxidative reaction is refined at a 25 percent consistency for one minute in a PFI mill with an applied load of 3.4 kilograms at about 25° C. The pulp within the main housing of the mill is screened on a .006 inch cut flat screen to give an accepts yield of about 99 percent of the material put into the mill. The pulp is designated as Pulp 15 in Table V.

Other material from the second stage of the oxidative reaction is given further alkaline treatment at a consistency of 75 percent with 2.0 percent sodium hydroxide. This alkaline treatment continues for one hour at 50° C. and has a final pH of 9.8. The yield is 70.6 percent and the Klason lignin is 3.6 percent. The modified lignin amounts to 8.5 percent comprising (i) Klason lignin at 2.6 percent, (ii) acid soluble lignin at 3.0 percent and (iii) acetone soluble lignin at 2.9 percent. The pulp from this second alkaline treatment is placed in the PFI mill and treated as before described. This pulp is designated as Pulp 16 in Table V.

Pulps 15 and 16, when made into hand sheets have the following characteristics:

TABLE V

Pulp	15	16
Canadian Freeness, ml	660	460
Density, g./cc	0.48	0.69
Opacity, percent	82	73
Breaking length, km	3.4	8.6
Burst factor	12	48
Tear factor (Elmendorf)	34	57
Zero-span breaking length, km	13	17
G.E. brightness	60	60

It will be seen that the materials can be defibrated by mechanical means and that alkaline treatment effects changes in the pulp properties. For example, the freeness is changed and the wet compressibility is changed as indicated by the significant difference in hand sheet density following similar mechanical treatment. There is also a significant difference in breaking length and in tear factor. This alkaline treatment is to be distinguished therefore, from alkaline extractions used in bleaching processes for chemical pulps which do not particularly affect these hydrodynamic and hand sheet properties.

EXAMPLE IX

In accord with this Example, the process is applied to "old news" which is newspaper available as an article of commerce and which primarily comprises ground wood pulp from soft woods. The old news is first slushed by placing it in a Waring Blendor for one minute at 5 percent consistency and at 50° C. The water is then drained from the material and it is then preprocessed to reduce the ink and sizing at 5 percent consistency by adding 2 percent sodium hydroxide along with .5 percent Igepal, which is a wetting agent. After 30 minutes, the stock is screened on a .010 inch cut flat screen and washed. The pulp is dewatered on a sidehill screen which has a 48 mesh wire screen. The yield is 63 percent of the weight of the old news. 16 percent passes through the wire and is reclaimed on muslin. 21 percent of the old news is lost. The recovered 63 percent to be the fibrous material as herein defined.

The fibrous material prepared from old news is subjected to oxidative reaction in multiple steps. The fibrous material is first treated with 20 percent sodium chlorite solution which is acidified to pH 4. The reaction is carried out at a temperature of 50° C. at a consistency of 5 percent for 16 hours. The liquor is then removed and the material is water washed.

The resulting material is next subjected to alkaline treatment with 6.5 percent sodium hydroxide at a consistency of 8 percent and a temperature of 50° C. The alkaline treatment continues for 30 minutes, whereupon the material is drained and washed with water.

This material is then subjected to further oxidative reaction at 5 percent consistency and 50° C. for 16 hours with 2 percent chlorine dioxide. The material is drained and water washed.

The material is again reacted at 5 percent consistency and 50° C. for 24 hours with 2 percent chlorine dioxide. The material is drained and water washed.

The material is further subjected to oxidative reaction at a consistency of 5 percent and a temperature of 35° C. for 48 hours with 2 percent chlorine dioxide. The material is drained, washed with water and then washed with weak sulfurous acid to chemically reduce any residual chlorine dioxide. The material is again drained and given a final water wash.

The fibrous material is designated 17 in Table W, and the pulp is designated 18 in Table W, and are made into hand sheets and various characteristics compared.

TABLE W

	17	18
Canadian Freeness, ml	485	500
Density, g./cc	0.46	0.67
Opacity, percent	91.3	70.5
Breaking length, km	4.3	7.7
Tear factor (Elmendorf)	67	65
Zero-span breaking length, km	13	17
G.E. brightness	53	73
Yield	100	84

EXAMPLE X

In accord with this Example, peracetic acid is used as the oxidative pulping chemical.

Logs of Quaking Aspen are taken and debarked. The debarked logs are then chipped in a 38 inch Carthage chipper. Oversize chips, knots and the fraction which goes through a ¼ inch screen are removed.

The chips are fiberized in the Bauer pulper set forth in Example I. The chips are first steamed at 15 p.s.i.g. for 2 minutes and, after breaking the pressure, the chips are again steamed for 2 minutes at 15 p.s.i.g. After the steaming treatment, the chips are soaked in cold water for 30 minutes in a pressure vessel having a head pressure of 100 p.s.i.g. established by nitrogen gas. The water is drained from the chips which are then steamed at 80 p.s.i.g. for 3 minutes and fed into the Bauer pulper which has been preheated. The plate clearance is 0.25 inches and the Reeves drive setting is number 1. The electrical load during fiberization is 500 amps.

The defiberized chips are placed in plastic bags for the various reactions to be described. The reaction are carried out in plastic bags while immersed in a water bath for temperature control. The components of the mixture are preheated to the desired temperature before placing into the plastic bags. After the reactions, the materials are separated in a sintered glass funnel and washed with distilled water at about 25° C.

The defiberized chips are subjected to alkaline conditioning by reaction with 3 percent sodium hydroxide at a consistency of 6 percent. The alkaline conditioning is effected in 10 minutes at 60° C. The final pH is 10.6 and the yield is about 93 percent.

The alkaline conditioned defiberized chips are then reacted with 20 percent peracetic acid at a consistency of 6.5 percent. The peracetic acid is a mixture comprising 30–35 percent peracetic acid, 5–10 percent acetic acid and less than 1 percent hydrogen peroxide. The reaction with the peracetic acid is carried at about 60° C. in 300 minutes. (It was found that this extended treatment is not altogether necessary and that considerably shorter times may be used.) The final pH is 2.6 and the yield of resulting material is 85 percent. The material contains modified lignin in an amount of 14.7 percent and has a G.E. brightness of 44.

The material recovered form the peracetic acid reaction, i.e., oxidative reaction, is subjected to an alkaline treatment at a consistency of 10 percent and with 6 percent sodium hydroxide. The alkaline treatment is effected at 60° C. in 120 minutes with the final pH being 11.9 and the yield of pulp being 67 percent with a modified lignin content of 5.8 percent. The G.E. brightness of the pulp is 44.

The pulp is bleached with hypocholrite with an available chlorine level of 4.5 percent and with .25 percent sodium hydroxide. The consistency during bleaching is 10 percent and the temperature 40° C. The final pH is 8.7 and the hypochlorite is exhausted in 154 minutes. The bleached pulp has a yield of 62 percent and a G.E. brightness of 79.

It will be seen from the foregoing that peracetic acid can be used as an effective oxidative chemical.

EXAMPLE XI

Black spruce wood chips were prepared and immersed in water, the weight ratio of water to wood being 6.5. Over a period of ten days, five additions of sodium chlorite ($NaClO_2$) were made and the total weight ratio of sodium chlorite to wood was 1.0. The solution was maintained at a pH of about 4 so as to effect release of chlorine dioxide for effecting the oxidation. The temperature of the solution was maintained at between about 24 degrees C. and 28 degrees C.

The solution was withdrawn from the chips and they were then fiberized by treatment with .1 N sodium hydroxide. It was determined that the yield was 65 percent.

The pulp was tested by conventional methods and found to have the following physical characteristics, measured in metric units:

Burst factor	93.6
Tear factor (Elmendorf)	70.6
Breaking length, km.	12.4
Zero-span breaking length, km.	23.8
Z-direction tensile, kg./cm.^{2}	17.0

The pulp was analyzed and the following were found:

	Percent
Klason lignin	.3
Carbohydrate	85.2
Soluble residue [1]	14.5

[1] This comprises soluble lignin and uronic acid.

The pulp has a rather slimy feel and very large specific surface. While the chips may be subjected to an initial extraction with an alcohol-chloroform mixture, it was found that this was not necessary in the case of black spruce wood.

The pulp of Example XI provides a holopulp but the conditions for its preparation are not particularly commercially attractive. Furthermore, the feel of the pulp and the large surface area are undesirable.

EXAMPLE XII

Chips of black spruce wood were prepared and treated with sodium hydroxide. It was found that .1 N soduim hydroxide was not strong enough and sodium hydroxide of higher strength was required. In order to obtain desired impregnation of the chips with sodium hydroxide, the chips were evacuated and the sodium hydroxide was added to the evacuated chips. The conditions for the mild alkali treatment were, as follows:

Concentration of sodium hydroxide	.5 N
Maximum temperature ° C.	60–70
Impregnating condition, minutes:	
Vacuum impregnation	20
Time to temperature	30
Time at temperature	30
Time to cool to ambient temperature	60

After the sodium hydroxide treatment, the chips were immersed in a sodium chlorite solution and the pH adjusted to about 4 to effect release of chlorine dioxide. Complete delignification appeared to be effected after 3 days using a temperature of about 40 degrees C. The yield of pulp was 67 percent and the viscosity of the pulp was 31.7 centipoises.

The physical properties of the pulp, when compared to the pulp of Example XI were as follows, in metric units:

Example	XII	XI
Burst	57.4	88.3
Tear factor (Elmendorf)	99.5	65.4
Breaking length, km	9.0	13.6
Zero-span breaking length, km	18.4	22.2
Z-direction tensile, kg/cm.^{2}	3.4	19.4

It will be noted that the pretreatment with sodium hydroxide effected a substantial increase in tear strength, but that there was a reduction in other properties when compared with the pulp of Example XI.

EXAMPLE XIII

In order to provide more mild alkaline treatment, sodium carbonate was utilize for pretreatment. Black spruce wood chips were treated with vacuum and treated with .5 N sodium carbonate solution at room temperature for 18 hours. The chips were then delignified with a sodium chlorite solution having a pH of 4 to release chlorine dioxide. Complete delignification took 43 days and a pulp yield of 64.7 percent was achieved.

The pulp had the following physical properties when compared to a control:

Example	XIII	XI
Burst	79	88.3
Tear factor	111	65.4
Breaking length, km	7.6	13.6
Zero-span breaking length, km	19.2	22.2
Z-direction tensile, kg/cm.^{2}	2.3	19.4

The great increase in tear strength will be noticed and this increase is larger than was achieved by pretreatment with sodium hydroxide.

Beating of the pulp exhibited unusual hydrodynamic stability of the pretreated fibrous material when compared with the pulp of Example XI. The pulp from this Example was introduced into a Jokro Mill and beaten for the indicated times. The pulp was then evaluated and provided the following physical characteristics, when measured in metric units:

Time of beating, min	0	20	50	(1)
Freeness, cc., S.-R.	880	850	660	
Burst factor	79	143	146	88.3
Tear factor	111	70.4	56.5	65.4
Breaking length, km	7.3	12.1	9.7	13.6
Zero-span breaking length, km	19.2	20.0	19.6	22.2
Z-direction tensile, kg/cm.^{2}	2.3	8.1	18.0	19.4

[1] Example XI.

The increase in burst strength and the above referred to stability is to be noted.

EXAMPLE XIV

As a further Example of pretreatment of fibrous material, black spruce wood chips were placed in a pressure vessel and ammonia gas was introduced under a pressure of 10 p.s.i.g. until no more gas was consumed by the chips. The chips were allowed to stand for two hours at room temperature, whereupon the vessel was evacuated and free ammonia withdrawn from the chips. The chips were then selectively delignified over a period of seven days at room temperature in a sodium chloride solution at a pH of about 4. Additions of sodium chlorite were made to the solution as it was used up during chloriting. The chips were analyzed for acetyl and the percent acetyl was determined to be .59. The pulp from Example XI, which was not subjected to the pretreatment and which was chlorited for 10 days, had an acetyl con-

tent of 1.38 percent. The chips were then defibrated in .1 N sodium hydroxide.

A comparison of the pulp from this Example to the pulp from Example XI showed the following, measured in metric units:

Example	XIV	XI
Yield, percent	65	65
Burst	80.1	76
Tear factor	141	49
Breaking length, km	13.1	13.8
Zero-span breaking length, km	19.9	22.5
Z-direction tensile, kg/cm.^{2}	7.3	21.2
Klason lignin, percent	0.7	.3
Carbohydrates, percent	87.9	85.2
Filtration resistance, cm./gm	$.486\times10^8$	1.89×10^9
Specific surface, sq. cm./gm	7,660	15,260

From the foregoing, the substantial increase in tear strength will be noted as well as the relatively small specific surface. The large specific surface of the pulp from Example XI is typical of the holopulps which are not pretreated. The reduction of filtration resistance effected by the pretreatment will also be noted.

EXAMPLE XV

Various delignification conditions are set forth in respect to a number of fibrous materials in an article in Tappi, vol. 47, No. 3, pp. 157–162. In accord with this Example, the fibrous materials are given pretreatments in accord with prior Examples XII, XIII, and XIV. The resulting pulps are improved in physical characteristics.

In each of Examples XI to XIV, the conditions of the pretreatment or preconditioning are sufficient to swell the fibers in the fibrous material, but are limited so that less than 10 percent of the carbohydrate materials are removed. These pretreatment conditions can vary substantially, depending upon the fibrous materials being treated, the extent of defiberization, and other factors, but the swelling of the fibers may be important for preparing the fibrous material for selective delignification, and for limiting the loss of carbohydrates is important to provide high yields and desired pulps. As before indicated, the pretreatment effects a reduction in the specific surface of the fibers and improves the hydrodynamic behavior of the pulp when compared to previously known rolocellulose pulps. Preferably, the pretreatment should effect at least a 25 percent reduction in specific surface when compared to previously known oxidative pulps.

The conditions of pretreatment and selective delignification are chosen so as to provide a yield from raw fibrous material of at least 60 percent, and more desirably, at least 65 percent.

In the foregoing the percentages of materials used, except as otherwise indicated, are based upon the weight of the defiberized chips or fibrous material so that the percentages are on a constant basis throughout the process. However, the screen rejects or rejects, are based upon the weight of material which is supplied to the screen.

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

We claim:

1. A pulping process for wood material containing substantial amounts of lignin and carbohydrate materials, said process comprising the steps of (a) lacerating the wood material primarily in the middle lamella region into fiber bundles, said lacerating including the steps of (1) heating the wood material in the presence of moisture and heat to the thermal softening point of the lignin material and (2) defiberating the wood material into fiber bundles by lacteration of moisturized and heated wood material at a temperature above the thermal softening point of the lignin material; (b) selectively delignifying said lacerated wood material to remove more lignin material than carbohydrate material by (1) reacting the lignin with chlorine dioxide for a period between about one hour and about ten hours, the chlorine dioxide being present in dilute liquor at a level of between about five percent and about twenty percent by weight (dry basis)of the lacerated wood material and the liquor being at a temperature between about 25° C. and about 60° C. with a pH between about one and about seven, (2) terminating the reaction when the residual lignin content, measured as Klason lignin, is above about fifty percent of the lignin content, measured as Klason lignin, of the wood material, (3) alkaline treating the reacted material with monovalent alkaline material in an amonut equivalent to between about four percent and about twenty percent sodium hydroxide based on the weight of wood material and terminating alkaline treatment at a yield above about sixty percent based upon the wood material and (4) defibrating the resulting pulp.

2. A process in accordance with Claim 1 wherein the wood material is impregnated with moisture to a level between about fifty percent and about seventy-five percent and the wood material is heated to a temperature between about 100° C. and about 120° C. for a time between about one minute and about ten minutes to minimize degradation of materials.

3. A process in accordance with Claim 2 wherein defibration into fiber bundles is effected between relatively moving plates having a clearance between about .020 and about .035 inches.

4. A process in accordance with Claim 1 wherein the lacerated wood material, prior to selective delignification, is subjected to mild alkaline conditioning at a temperature between about 40° C. and about 60° C. for a time between about ten minutes and about two hours in a sodium hydroxide solution having a concentration between about .05 N and about .15 N and the solution being present to provide between about 1.5 percent and about six percent sodium hydroxide based on the wood material and to provide a consistency between about six percent and about twenty percent, the mild alkaline conditioning being terminated when the yield is above about ninety percent.

5. A process in accordance with Claim 1 wherein the reaction with chlorine dioxide is terminated at a yield above about eighty percent and the level of chlorine dioxide is between about five percent and about ten percent by weight (dry basis) of the lacerated wood material.

6. A process in accordance with Claim 1 wherein the chlorine dioxide is present in combination with chlorine.

7. A process in accordance with Claim 1 wherein selective delignification is effected on the lacerated wood material at a moisture level between about twenty-five percent and about seventy percent with gaseous chlorine dioxide at a temperature between about 25° C. and about 50° C. in a time between about five minutes and about thirty minutes.

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ROBERT L. LINDSAY, JR., Primary Examiner

R. H. TUSHON, Assistant Examiner

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