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PROCESS OF TREATING LIGNOCELLULOSIC MATERIAL WITH ORGANOMERCAPTAN**William E. Fisher, Waterville, and Shibley A. Hider, Toledo, Ohio, assignors to Owens-Illinois, Inc., a corporation of Ohio**

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20 Claims

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ABSTRACT OF THE DISCLOSURE

Methods of treating lignocellulosic material for the removal of lignin therefrom in a single phase, the steps including (A) digesting said material with a treating liquor containing an organomercaptan such as thioglycolic acid in an amount corresponding to at least about 2 weight percent based on the weight of the oven-dried lignocellulosic material, the treating liquor also containing alkali equivalent to at least about 2% effective alkali calculated as Na_2O , or at least 4 weight percent total alkali calculated as Na_2O , the ratio of treating liquor to oven-dried lignocellulosic material and the time and temperature of digesting such as to cause the organomercaptan to react with the lignin and concurrently to extract therefrom the resulting mercaptan-reacted lignin in a single stage to obtain a digested material that is amenable to refining to a pulp; and (B) removing the excess liquor from the treated material of step A.

This invention relates broadly to a process of treating lignocellulosic material. More particularly it is concerned with a one-stage treatment or digestion of lignocellulosic material with a treating or cooking liquor comprising an organic thio compound, especially an organomercaptan, e.g., thioglycolic acid (TGA), $\text{HS}-\text{CH}_2-\text{COOH}$. A single organomercaptan or a plurality of different organomercaptans may be employed; or, one or more organomercaptans may be used in conjunction with one or more inorganic treating agents including, for example, sodium sulfhydrylate (sodium hydrosulfide, NaSH), sodium sulfide, sodium polysulfide, Na_2S_x , sodium borohydride, NaBH_4 , and the like.

It was known prior to the present invention to digest or cook wood, specifically spruce sawdust, with an organomercaptan, more particularly TGA. See, for example, Ingeniörs Vetenskaps Akademien, Proceedings No. 103, 75 pp. (1930), "The Mercaptans of Pine Wood," by Bror Holmberg. Holmberg's procedure was to treat, for instance, spruce sawdust with a solution containing TGA and hydrochloric acid.

In our copending application Ser. No. 605,978, filed concurrently herewith and assigned to the same assignee as the present invention, we have disclosed and claimed a two-stage treatment of lignocellulosic material with a treating liquor containing an agent reactive with the lignocellulosic material and which is comprised of a specified minimum amount of an organomercaptan. In this method the treating liquor has an initial pH not exceeding 12.0, and the time and temperature of the treatment of the lignocellulosic material with this treating liquor is sufficient to convert the said lignocellulose material to a treated material containing mercaptan-reacted lignin. After removing the excess liquor from the treated material resulting from this first-stage treatment, a second-stage treatment is applied whereby the organomercaptan-reacted lignin retained by the digested lignocellulosic material is extracted by contacting the residue with an extractive amidogen compound, e.g., an alkanolamine, aniline, urea, and the like.

The present invention differs from the known prior art and from our aforementioned copending application in that a one-stage treatment is applied to the lignocellulosic material, using a treating liquor of the kind broadly described in the first paragraph of the specification.

The invention is based on our discovery that a digestion or cooking of wood (lignocellulosic material) with a treating liquor comprising an organomercaptan, thereby to react the said mercaptan with the lignin in the wood and obtain a solid product amenable to refining to a pulp with good paper-making characteristics, can be effected in a single stage by carrying out the digestion in a particular way that includes the hereafter-described highly alkaline conditions. The highly alkaline conditions of the treating liquor (initially and, usually, only of slightly lesser alkalinity at the end of the digestion period) are such that there is present in the treating liquor at least 2 weight percent effective alkali calculated as Na_2O , or at least 4 weight percent total alkali also calculated as Na_2O . These minimum weight-percent values are based on the weight of the oven-dried (O.D.) lignocellulosic material.

The terms "effective alkali" and "total alkali" as used herein have the meanings commonly employed in the pulping and paper-making art. As used in this art, effective alkali for sulfate pulping means NaOH plus one-half of any Na_2S ; while total alkali includes Na_2CO_3 and one-half of any Na_2SO_3 in addition to all of the NaOH and Na_2S that may be present (reference: TAPPI-1203). In all cases, the amount of the said alkali (i.e., effective alkali or total alkali), the ratio of treating liquor to O.D. lignocellulosic material, and the time, temperature, and pressure of digestion are such as to cause the said organomercaptan to react with the lignin in the said lignocellulosic material and concurrently to extract therefrom the resulting mercaptan-reacted lignin so that there is obtained in a single-stage a digested, solid, cellulose-containing material that is amenable to refining to a pulp, more particularly a paper-making pulp. (Parenthetically it may here be stated that the term "active alkali" which is mentioned later herein differs from "effective alkali," as these terms are commonly used in the pulping and paper-making art, in that it includes NaOH plus all Na_2S that may be present instead of only one-half of any Na_2S ; see the aforementioned reference TAPPI-1203.)

The amount of effective alkali in the treating liquor may range, for instance, from 2 to about 250 or more weight percent, calculated as Na_2O , and based on the weight of the O.D. wood (lignocellulosic material) at l/w (liquor-to-wood) ratios of 1.5:1 to 20:1; but ordinarily is substantially above 6 weight percent (e.g., from 6.5, 7, or 8 to about 65 or 75 weight percent), calculated and on the same weight basis just mentioned, at l/w ratios of 2:1 to 9:1. The amount of total alkali in the treating liquor may range, for example, from 4 to about 400 or more weight percent at l/w ratios of 1.5:1 to 20:1; but ordinarily is substantially above 7 weight percent (e.g., from 8 or 10 to about 120 or 130 or more weight percent at l/w ratios of 2:1 to 9:1. These percentages, like that of the weight percent of effective alkali, are calculated as Na_2O and are based on the weight of the lignocellulosic material.

Surprisingly and unobviously, the technique of cooking a lignocellulosic material with a highly alkaline treating liquor containing an organomercaptan is more specific in delignification and provides higher yields of pulps of good papermaking characteristics than is obtainable by the Kraft process; the resulting pulps, especially under selected conditions, can be made into brighter papers; and a lignin is recoverable that is different in characteristics from Kraft-process lignin.

A primary advantage in using an organomercaptan as component of a treating liquor that contains alkali is that the organomercaptan not only reacts with the lignin in the lignocellulosic material (making it more soluble in the alkaline liquor) but also functions as a pH control by reason of buffering action of its —SH groups. For these reasons, the use of such treating liquors for pulp-bleaching wood and the like decreases the loss of carbohydrate material that normally results from degradation by alkali during delignification and thereby provides higher pulp yields.

In practicing the present invention, any wood or other lignocellulosic material, or mixtures thereof in any proportions, may be cooked or digested with an organomercaptan, with or without first removing the extractives by treating the lignocellulosic material in sub-divided form (e.g., in the form of sawdust, and/or shavings, wafers, or chips) with an organic solvent capable of extracting the water-soluble components of the material. Such lignocellulosic materials include softwoods, hardwoods, and fibrous annual plants. Examples of softwoods are balsam fir, eastern hemlock, jack pine, eastern white pine, red pine, black spruce, red spruce, white spruce, tamarack, and cypress. Example of hardwoods are black gum, quaking aspen, mixing tomahawk, American beech, paper birch, yellow birch, eastern cottonwood, sugar maple, silver maple, yellow poplar, black cherry, and white oak. Examples of fibrous annual plants are bagasse, hemp, and jute. Mixtures of woods or other lignocellulosic materials of different origins may be used if desired, e.g., mixtures of different softwoods, or of different hardwoods, or of one or more softwoods and one or more hardwoods.

Illustrative examples of organomercaptans that may be used to obtain a digested wood containing mercaptan-treated lignin are those embraced by the general formula



wherein R represents a divalent radical, more particularly a divalent hydrocarbon radical, Y represents a monovalent substituent bonded directly to R, and n represents a numeral ranging from 0 up to the combining power (i.e., a value that will completely satisfy all valences) of the divalent radical represented by R.

Illustrative examples of divalent radicals represented by R in Formula I are divalent hydrocarbon radicals and, more particularly, divalent aliphatic, e.g., ethylene, propylene (trimethylene), butylene, isobutylene, pentylene, isopentylene, decylene, etc., including divalent cycloaliphatic, e.g., cyclopentylene, cyclohexylene, cycloheptylene, etc.; divalent aromatic, e.g., phenylene, naphthylene, etc.; divalent aliphatic-substituted aromatic, e.g., 2,4-tolylene, ethyl-2,5-phenylene, isopropyl-3,3,4-phenylene, 1-butyl-2,4-naphthylene, etc.; divalent aromatic-substituted aliphatic, e.g., phenylethylene, phenylpropylene, naphthylisobutylene, xylylene, etc.; and radicals that may be classed either as divalent aromatic-substituted aliphatic or divalent aliphatic-substituted aromatic, e.g., 4,α-tolylene, 3,β-phenyleneethyl, 4,α-xylylene, 2,γ-phenylenebutyl, etc. Thus R may represent a divalent hydrocarbon radical represented by the general formula



where Ar represents an arylene radical and R' represents an alkylene radical. Preferably the divalent hydrocarbon radical represented by R contains not more than 10 carbon atoms, more particularly from 1 to 8 carbon atoms.

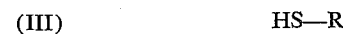
It is not essential that the divalent radical represented by R be composed solely of carbon and hydrogen atoms. For example, the chain of carbon atoms, whether straight-chain aliphatic or carbocyclic, may be interrupted in the chain by other atoms, e.g., by oxygen and/or sulfur and/or nitrogen atoms bonded directly to carbon atoms of the chain.

Illustrative examples of substituents represented by Y in Formula I are functional groups such as —OH; —CN; —SH; —COOH; —COOR', wherein R' is a monovalent hydrocarbon radical corresponding to the divalent hydrocarbon radicals represented by R in Formula II; —COOM, wherein M is a salt-forming cation, e.g., —NH₄, or Na, K, Li, or other alkali metal, a salt-forming amine such as mono-, di-, or tri-(hydrocarbon-substituted) or -(hydroxy-hydrocarbon-substituted) amine, or other salt-forming cation, and especially those which yield water-soluble salts when present in the particular thio compound. Or, Y may be a radical represented by



wherein R'' and R''' are members of the group consisting of hydrogen and monovalent hydrocarbon radicals corresponding to the divalent hydrocarbon radicals represented by R in Formula I.

It will be understood, of course, by those skilled in the art that when n in Formula I represents zero (0), then there are no radicals represented by Y in the formula, which latter then becomes



wherein R represents a monovalent radical, more particularly a monovalent hydrocarbon radical corresponding to the divalent hydrocarbon radicals represented by R in Formula I. Illustrative examples of mercapto compounds embraced by Formula III are the alkyl (including cycloalkyl) aralkyl, aryl, and alkaryl mercaptans, more particularly those which contain from 1 through 10 carbon atoms and especially those having not more than about 8 carbon atoms.

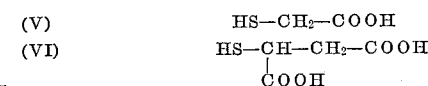
The relatively low water-solubility of the unsubstituted hydrocarbyl mercaptans embraced by Formula III make them much less suitable for use than substituted hydrocarbyl mercaptans having one or more polar or solvating substituent groups. However, if water-solubility of the mercapto reactant is unimportant, e.g., when it is to be used in undiluted state, or in solution in an organic solvent (e.g., ethanol) or in a mixture of water and an organic solvent in which mixture the unsubstituted hydrocarbyl mercapto is adequately soluble, then a mercapto within the scope of Formula III may be employed as a treating agent.

Particularly useful in practicing the present invention are organomercaptans represented by the general formula

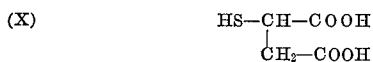
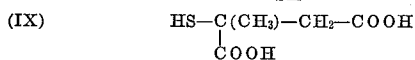
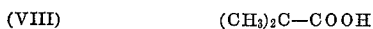


wherein Z represents an alkylene (including cycloalkylene) radical containing from 1 through 10, and preferably from 1 through about 8, carbon atoms; R represents a member of the group consisting of (a) hydrogen, (b) alkyl radicals containing not more than about 10 carbon atoms and preferably a lower alkyl radical (e.g., an alkyl radical containing from 1 through about 6 carbon atoms); and (c) a salt-forming cation, examples of which have been given hereinbefore with reference to M in the grouping —COOM which may be a substituent represented by Y in Formula I; and n represents an integer from 1 up to that of the combining power of the alkylene radical represented by Z. The alkylene radical represented by Z may be straight-chain, branched-chain, or cyclic as in, for example, cyclopentyl, cyclohexyl, and the like.

More specific examples of mercapto compounds embraced by Formula IV are monocarboxylic and polycarboxylic acids such as those having the formulas

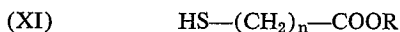


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the ammonium, alkali-metal (sodium, potassium, lithium, etc.) and other water-soluble salts of the aforementioned mono- and di-carboxylic acids; and the cyclohexyl and cyclohexyl esters, as well as the methyl, ethyl, and propyl through pentyl (normal or isomeric alkyl) esters of the aforesaid acids. In the case of the salts and esters of the dicarboxylic acids, one may use either the mono- or di-salt, or a mixture thereof, or a mono- or diester, or a mixture thereof.

As the organomercaptan reactant we prefer to use thio acids, or salts or esters thereof represented by the general formula

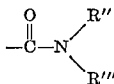


wherein n represents an integer from 1 to 6, inclusive, more particularly from 1 to 4, inclusive, and R has the same meaning as given above with reference to Formula IV. Thus, compounds embraced by Formula XI may be the thio acid itself or a salt (especially a water-soluble salt) or an ester of such an acid. Of these compounds thioglycolic acid and the water-soluble salts and the lower alkyl esters thereof are the more preferred sub-group. Mixtures of acids and/or salts and/or esters embraced by Formula XI may be used if desired.

Instead of using organomercaptan compounds that are within the scope of Formula XI, one may employ those wherein the COOR group in that formula has been replaced by other hydrolyzable or solvating groups such as $-\text{OH}$, $-\text{CN}$, $-\text{SH}$,



and



wherein R'' and R''' in the last two groups are hydrogen or a monovalent hydrocarbon radical corresponding to one of the divalent hydrocarbon radicals represented by R in Formula I.

TREATMENT OF LIGNOCELLULOSIC MATERIAL WITH AN ORGANOMERCAPTAN

The treatment of wood or other lignocellulosic material with an organomercaptan is described in, for example, the aforementioned Holmberg publication. Other methods of treating wood and other lignocellulosic materials with an organomercaptan are described in, for instance, the copending application of Carl A. Johnson, Ser. No. 606,024, filed concurrently herewith and assigned to the same assignee as the present invention.

In practicing the instant invention, the digestion with the treating liquor (white liquor) may be effected, as previously has been mentioned, with or without first removing the extractives including tall oil. Advantageously, the extractives are first removed by pre-extracting the wood or other lignocellulosic material with an organic solvent, preferably isopropanol, n-butanol, or other high-boiling organic solvent. If a hot fluid medium, e.g., steam, is used to remove the aforesaid organic solvent, it is desirable that the wood in subdivided (e.g., chip) form remain in swollen state before digestion in the cooking

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liquor in order to facilitate diffusion of the liquor into the chips and thorough impregnation of the latter.

Chemical treatment with the organomercepto compound may be effected at a temperature within the range of, for instance, from about 100° to about 250° C., more particularly from about 120° to about 210° C., and preferably at a temperature of 150° - 190° C. (The foregoing temperatures refer to the peak or maximum temperature after the cook has been raised to said temperature.) The time of digesting or cooking the lignocellulosic material at the maximum temperature varies, for example, from a few minutes (e.g., 3-5 minutes) to 6 hours or more.

The time period and the reaction temperature depend upon such influencing factors, as for instance, the type, amount, and concentration of the organomercepto compound in the treating liquor, the type and degree of division of the lignocellulosic material being treated, the type and size of digester used, the degree of reaction desired, and other influencing factors. In all cases the cooking times and temperatures are correlated so that the wood or other lignocellulosic material is digested and the lignin concurrently extracted to an extent such that it is unnecessary to apply a second-stage or extract (lignin-extraction) treatment to the single-stage extracted wood or the like. Generally the desired degree of digestion is effected by cooking the lignocellulosic material in the treating liquor for from about $\frac{1}{4}$ to about 3 hours at a maximum temperature of from about 140° or 150° C. to about 190° C., e.g., for from about $\frac{1}{2}$ hour to about 1 or $1\frac{1}{2}$ hours at a temperature of approximately 170° C. $\pm 10^\circ$ C.

The digestion of the lignocellulosic material may be effected under atmospheric, subatmospheric or superatmospheric pressure, or under any combination of these pressure conditions as desired, or as conditions may require. For example, if desired, vacuum may be applied initially to the system in order to facilitate diffusion of the treating liquor into the lignocellulosic material in chip or other subdivided form. In lieu of or in addition to such initial vacuum impregnation or treatment, the subdivided lignocellulosic material may be "soaked" at atmospheric pressure and at ambient or an elevated temperature for a short or a long time interval, followed by digestion in an autoclave under autogenous, superatmospheric pressure. Digestion in an autoclave at a temperature within the aforementioned temperature ranges is a satisfactory technique. The existing pressure at a particular temperature is then primarily dependent upon the vapor pressures of the volatile components of the treating liquor at that temperature.

The proportion of organic thio treating agent, e.g., TGA, with respect to oven-dried (O.D.) lignocellulosic material may be within the range of, for example, from about 1:1 (i.e., about 50% by weight of each to about 2:100 to 2.5:100 (i.e., 2.5% by weight of the organomerceptan reactant based on the weight of the O.D. lignocellulosic material). The upper limit of the organomerceptan component is not critical, but because of its relatively high cost it is economically desirable to use not more of it in the cooking liquor than is required to effect the desired result. Hence there are economic advantages in restricting the upper limit of the amount of organomerceptan to not more than about 50%, more particularly to not more than about 30 or 35%, by weight of the O.D. lignocellulosic material. Advantageously, TGA or equivalent (in its effectiveness as a reactant) organomerceptan is employed in an amount corresponding to from about 5 to about 20 or 25 weight percent based on the weight of the O.D. lignocellulosic material.

The amount of TGA or equivalent organomerceptan employed is preferably about the same as or near to the equivalent amount of the effective alkali in order to obtain the maximum benefit of carbohydrate protection during the digestion period. (For example, when the treating liquor contains 16% effective alkali and the liquor-to-

wood ratio is 4.5/1, i.e., a ratio of treating liquor to O.D. lignocellulosic material corresponding to 45 ml. of the former for each 10 grams of the latter, then the liquor contains an excess of 0.516 mole NaOH per 100 g. wood; and the equivalent amount of TGA would be 47.5 g. per 100 g. wood.) When larger amounts of TGA or equivalent organomeraptan are employed, less severe cooking conditions are, in general, required; and the maximum benefit of pH control and protection of the carbohydrate component of the lignocellulosic material is secured.

The substantially pure organic thio compound, or a crude form thereof such as is obtained commercially in its preparation, or mixtures of organic thio compounds may be employed as the reactive agent or component of the treating liquor. Minor amounts (less than 50% by weight) of inorganic thio reactants, e.g., sodium sulfhydrylate, sodium sulfide, sodium polysulfide, etc., may be used in the form of an admixture with the organic thio compound.

Water is preferably used as the liquid reaction medium of the mercaptan cooking liquor. However, other inert solvents or mixtures of inert solvents may be employed if desired.

The effective alkali concentration of the treating liquor is preferably adjusted by the addition of sodium or other alkali-metal hydroxide, or with other alkaline substances (singly or a plurality thereof), e.g., hydroxides of "alkaline-earth metals" within which term are herein included not only calcium, strontium and barium but also magnesium.

The ratio of the treating liquor to the O.D. lignocellulosic material may be considerably varied but usually the ratio corresponds to from about 25 or 30 to about 90 or 100 ml. of the former for each 10 grams of the latter, more particularly from about 30 to about 60 ml. of the former for each 10 grams of the latter. Good results have been obtained using a so-called "liquor-to-wood" ratio of 4.5 to 1; that is, a ratio corresponding to 45 ml. of treating liquor for each 10 grams of wood (lignocellulosic material).

The type of reaction vessel required for the cook depends upon such influencing factors as, for example, the conditions of the cook, the properties of the organomeraptan reactant, and the vapor pressure and alkalinity of the cooking liquor.

In carrying out the treatment of the lignocellulosic material with the organomeraptan compound, the lignocellulosic material, in a suitably subdivided form, is saturated and/or covered with, or suspended in, a liquor containing the organomeraptan compound alone or admixed with inorganic thio reactants or other chemicals, examples of which previously have been given. It is then cooked or digested for a period of time and at a temperature and pressure which depend upon such influencing factors as have been mentioned hereinbefore.

At the end of the cooking period, the alkaline spent liquor (black liquor), and which contains the mercaptan reacted lignin and hemicellulose, is preferably recovered, e.g., by draining from the treated wood or the like in chip or other sub-divided form. The chips are thoroughly washed, e.g., with hot water, to remove any spent liquor containing mercaptan-reacted lignin and unreacted mercaptan (including organomeraptan) compound.

The lignin may be recovered from the spent liquor by precipitation with carbon dioxide or a mineral acid, e.g., hydrochloric, sulfuric, nitric, etc. The lignin that precipitates is filtered off. The filtrate contains unreacted mercaptan compound. This filtrate may then be concentrated, for example by removal of the solvent (H₂O); or by the addition of "make-up" chemicals including, for example, effective alkali, organomeraptan compound and, also, of inorganic thio reactant material if the latter was a component of the fresh treating liquor. This concentrated liquor may be recycled in the process.

Dialysis also may be employed to separate the lignin from the spent liquor. Or, the liquor containing the dissolved lignin may be passed through an anion-exchange resin in free-base form thereby selectively to adsorb on the resin anionic materials contained in the liquor while the lignin in purified form passes through the resin for subsequent evaporation of the eluate and recovery of lignin. This latter technique is more fully described and broadly and specifically claimed in the pending application of William H. Greive and Karel F. Sporek, Ser. No. 418,872, filed Dec. 16, 1964, now abandoned and assigned to the same assignee as the present invention. The lignin-free liquor resulting from treatment of the lignin-containing spent liquor with anion-exchange resin may then be recycled in the process after adding any necessary make-up chemicals.

Instead of allowing the unreacted organomeraptan compound to remain in the lignin-free spent liquor and reusing it directly, after adding "make-up" organomeraptan (plus other chemicals if necessary), the unreacted organomeraptan compound may be recovered from the lignin-free liquor by distillation or by further concentrating it if necessary, and then extracting the residue with a solvent for the unreacted organomeraptan, e.g., alcohol, ether or other organic solvent in which the particular organomeraptan is known to be soluble.

A typical overall process for the treatment of lignocellulosic material, e.g., wood in chip form, in accordance with this invention is outlined below:

(1) Pre-extract the wood for the removal of organic-solvent soluble extractives such as tall oil and the like. (Optional.)

(2) Immerse the chips (in swollen state if step 1 has been used) in the aqueous organomeraptan-containing treating liquor adjusted to, by weight, above 2% (more particularly above 4%) effective alkali or above 4% (more particularly 6.5% and above) total alkali, calculated as Na₂O, and based on the O.D. weight of the lignocellulosic material.

(3) Digest the chips for from a few minutes to 6 hours (preferably from ¼ to 3 hours) at 100°–250° C. (preferably at 150°–190° C.) maximum temperature to obtain pulp.

(4) Remove the organomeraptan-reacted lignin from the spent digestion liquor.

(5) Reuse the remaining lignin-free liquor, after adding such make-up chemicals as may be necessary, for treating additional wood or other lignocellulosic material.

The above-mentioned overall process may be carried out continuously, semi-continuously or by batch technique. The process is especially adapted for use in a continuous, rapid, vapor-phase digestion or pulping operation. Such a vapor-phase procedure has the advantages of both minimizing the time of cooking and the amount of chemicals required in the treating liquor, thereby providing distinct economic advantages. Thus, the pre-extracted chips (swollen with water, isopropanol and/or other organic solvent used in the pre-extraction), and while still hot, may be so impregnated with the highly alkaline organomeraptan-containing treating or white liquor that the amount of liquor absorbed by the chips is sufficient for pulping. The excess liquor is then drained from the chips, and the chips are rapidly brought to the maximum temperature of digestion (e.g., 150°–190° C.) by contact with high-pressure steam.

The washed, digested, subdivided lignocellulosic material, or crude pulp, regardless of whether it has been produced by a continuous or semi-continuous method or by a batch technique, is mechanically defibrated in the presence of water if it has not already been effectively defibrated to a suitable pulp. The resulting pulp is then usually screened to remove the residual liquor and to provide a more uniform pulp. Further washing of the pulp may be effected if deemed necessary in view of the particular

contemplated end use. Bleaching and/or drying steps are likewise optional depending upon the end use.

If bleaching is to be effected, it is usually done before drying the pulp. Prior to a bleaching step the pulp may be washed with a dilute aqueous solution of an inorganic acid, e.g., a 5% aqueous HCl solution, thereby to provide a more complete and efficient bleaching action than when bleaching is effected in the absence of such a dilute acid wash. The pulp, with or without further treatment as may be required for the particular end use, is then suitable for utilization in making any desired cellulosic product including, for example, paper and related products, cellulose acetate, cellulose xanthate, regenerated cellulose, etc.

In order that those skilled in the art may better understand how the present invention can be carried into effect, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight unless otherwise stated.

EXAMPLE 1

This example illustrates the pulping of a softwood, specifically isopropanol-extracted Southern pinewood, using a treating liquor comprised of (a) a relatively low concentration of an organomercaptan, specifically TGA, which was converted to sodium thioglycolate (NaTGA) in the treating liquor, and (b) a high content of effective (and active) alkali. A soda cook at the same effective and active alkali concentration is made under the same cooking conditions for purpose of comparison.

The apparatus and general procedure for making these cooks are as follows:

For each cook a 400.0 g. charge (based on the O.D. weight) of air-dried Southern pine chips from which the isopropanol-soluble extractives previously have been removed, and a total of 1800 ml. of aqueous liquor containing the chemicals set forth in Table I-A in an amount based on the weight of the charge of O.D. wood chips, are charged into a stationary digester. The mixture, which is at a liquor-to-wood ratio of 4.5 to 1, is heated to 170° C. with a steady rise of temperature from 100° C. to 170° C. over a period of 43-47 minutes. It is maintained at 170° C. under the pressure generated by the mixture for 39 minutes. The mixture is then cooled to approximately 100° C. over a period of about 1 hour, after which the charge is removed from the digester and drained through a screen to separate the solid residue from the spent liquor. This residue is soaked and washed with hot water, defibrated and then given a final washing.

The wet cellulosic pulp obtained as described above is dried to 20-30% solids, then made into 8" x 8", 26 lb./MSF basis weight hand sheets for testing in the following manner: At least three aliquots of the experimental pulp, in an amount based on the O.D. weight of the wet pulp, are refined with water at 1% consistency for varying periods of time in a Mead Laboratory Refiner (manufactured by the Bauer Bros. Company, Springfield, Ohio). The degree to which each pulp aliquot is refined, as determined by measuring the drainage rate of the pulp in a "Slowness Tester" (manufactured by Williams Apparatus Company, Watertown, N.Y.), is controlled as much as possible so as to provide three or more refining points bracketing 55 seconds Williams Slowness. Each of the refined pulp slurries is diluted to 0.5% consistency and

uniformly mixed prior to making the handsheets. The sheets are formed in an 8" x 8" Williams sheets mold from aliquots of the pulp slurry that are measured volumetrically for producing 26 lb./MSF sheets. The pulp consistency on forming the sheets is adjusted to 0.05% by further dilution of the pulp aliquot in the mold. The seven or more sheets (wet webs) formed from each batch of pulp slurry are couched from the wire of the mold onto standard 12" x 12" TAPPI blotters, then stacked between blotters with six blotters separating the sheets. The stack is then pressed for 5 minutes at 150 p.s.i.g. pressure on a Williams press (manufactured by Williams Apparatus Company). The pressed sheets, retained on the couch blotters, are dried at 260°-280° F. on a steam-heated Noble and Wood drier, with the sheet contacting the drum for approximately 2 minutes. After removing the blotters, the dried sheets are conditioned at 50% relative humidity and 75° F. for a minimum of 24 hours before testing.

More detailed information on the operating conditions and the results is given in Table I-A. In all three cooks the liquor-to-wood ratio was 4.5 to 1, and the cooking time was 39 minutes at the maximum temperature of 170° C. The value for the pulp characteristic listed as "Lignin" is the result obtained when the pulp is tested for acid-insoluble lignin using the apparatus and procedure set forth in TAPPI Standard Test Method T222 m-54. The "Williams Slowness" test, which measures the rate in seconds per liter at which one liter of pulp at 0.3% consistency drains at 20° C. in the Williams Slowness instrument, is used in the manner previously described in order to measure the degree to which the pulp was refined in the Mead refiner. The time in seconds for refining the pulp in the Mead refiner to 55 seconds Williams Slowness, as determined from the three or four refinings made, is listed in the column of Table I-A headed "Mead Refine Time."

The results of tests on papers (handsheets) made from the pulps produced as described in Table I-A are given in Table I-B. The values for the paper characteristics listed under the columns headed "Tensile," "Mullen," "Tear," "Ring Crush" and "Brightness" are the results obtained when the respective handsheets are tested using apparatus and procedures set forth where indicated below:

"Density," TAPPI Standard: T411 m-44
 "Basis Weight," TAPPI Standard: T410 os-61
 "Tensile," TAPPI Standard: T404 os-61
 "Tear," TAPPI Standard: T414 ts-64
 "Mullen," TAPPI Standard: T403 ts-63
 "Ring Crush," TAPPI Standard: T472 m-51
 "Brightness," TAPPI Standard: T452 m-58

The only exceptions from the above-identified test methods are that only 5 sheets, each 49 square inches in area, are used in the "Density" and "Basis Weight" tests.

The tabulated values are adjusted for 26 lb./MSF basis weight paper and for pulp refined to 55 seconds Williams Slowness. The values in Tables I, II, III, IV and VI are determined from the results of tests on four sets of handsheets made from each test pulp as described above. The values in Table V are from 3 sets of handsheets.

Tables I-A and I-B follow.

TABLE I-A

Soda and TGA Cooks of Southern Pinewood at 16% Effective Alkali¹

Cook No.	Chem./100 g. Wood	Cooking Conditions		Pulp Data		
		pH Range	Yield (Percent)	Pulp Lignin (Percent)	Pulp Carbohydrate (Percent of Initial O.D. wood)	
1-a	20.7 g. NaOH, 5.0 g. Na ₂ CO ₃	13.5 to 13.3	62.7	24.4	47.4	
1-b	9.8 g. NaTGA, ² (7.9 g. TGA), 20.7 g. NaOH, 5.0 g. Na ₂ CO ₃	13.5 to 13.2	60.3	19.9	48.3	
1-c	9.8 g. NaTGA, ² (7.9 g. TGA), 20.7 g. NaOH, 0.5 g. Na ₂ CO ₃	13.5 to 13.0	60.3	19.5	48.5	

¹ Calculated as Na₂O and based on the O.D. weight of the wood.

² NaTGA=Sodium Thioglycolate.

TABLE I-B
Tests on 26 lb./MSF Papers Made from Pulps of Cooks of Table I-A

Papers From Cook No.	Mead Refine Time (Sec.)	Williams Slowness (Sec.)	Density (p.c.f.)	Dry Tensile (lbs./in.)	Tear (g./16 sh.)	Mullen (p.s.i.)	Ring Crush (lbs.)	Brightness (percent)
1-a-----	193	55.0	27.8	39.5	147	71	51.5	19.7
1-b-----	171	55.0	30.3	46.2	177	83	68.0	19.2
1-c-----	186	55.0	30.6	45.4	184	87	67.0	18.8

The results given in Tables I-A and I-B demonstrate the effect that a relatively low charge of TGA (converted to NaTGA in the cooking liquor as in all other examples herein wherein the charge included TGA) has in the pulping of a softwood, specifically Southern pine, in a single stage with the liquor at a high (specifically 16% as Na₂O based on the O.D. wood) effective alkali content. The lower lignin and higher residual carbohydrate content of the pulps obtained from the TGA cooks (i.e., Cooks 1-b and 1-c) compared to that of the pulp from the caustic soda cook, viz., Cook 1-a, which was carried out under comparable cooking conditions and with the same concentration of effective alkali, show the improved selectively and faster rate of delignification that are provided when an organomercaptan reactant is included in the alkaline treating liquor.

From the data given in Table I-B it will be noted that the papers made from the pulps of Cooks 1-b and 1-c wherein TGA in the form of a sodium salt thereof was a component of the treating liquor, showed greatly increased strength characteristics as compared with the

paper made from the pulp of soda Cook 1-a. Furthermore, the former papers approached that of high-strength kraft paper in Mullen, tensile, tear and ring crush values.

EXAMPLE 2

This example illustrates the preparation of pulps in one-stage from Southern pinewood with the alkaline liquor comprised of higher concentrations of organomercaptan, specifically TGA as sodium thioglycolate, than was used in Example 1. The effective alkali concentration of the liquor, the temperature of digestion, the apparatus used and the general procedure are the same as described in Example 1. The time of digestion is varied from 39 to 58 minutes. As in Example 1, the temperature of digestion is 170° C. and the liquor-to-wood ratio is 4.5 to 1.

More detailed information on the cooking conditions and on the results obtained are given in Tables II-A and III-A. The results of tests on handsheets made from pulps produced as described in Tables II-A and III-A are given in Tables II-B and III-B.

Tables II-A, II-B, III-A and III-B follow.

TABLE II-A
TGA Cooks of Southern Pinewood at 16% Effective Alkali¹—Variation of TGA Charge

Cook No.	Cooking Conditions			Pulp Data			
	Chem./100 g. Wood	pH Range	Time (min.)	Yield (percent)	Pulp Lignin (percent)	Pulp Carbohydrate (percent of Initial O.D. Wood)	
2-a-----	18.6 g. NaTGA, (15.0 g. TGA), 20.7 g. NaOH.....	13.4 to 13.0..	39	63.0	20.8	49.9	
2-b-----	24.8 g. NaTGA, (20.0 g. TGA), 20.7 g. NaOH.....	13.4 to 12.6..	39	63.7	21.0	50.3	
2-c-----	43.4 g. NaTGA, (35.0 g. TGA), 20.7 g. NaOH.....	13.1 to 10.6..	39	64.9	19.9	52.0	
2-d-----	61.9 g. NaTGA, (50.0 g. TGA), 20.7 g. NaOH.....	11.3 to 10.3..	39	62.4	16.2	52.3	
2-e-----	123.9 g. NaTGA, (100.0 g. TGA), 20.7 g. NaOH.....	9.8 to 9.7....	39	57.9	10.7	51.7	

¹ See Footnote to Table I-A.

TABLE II-B
Tests on 26 lb./MSF Papers Made from Pulps of Cooks of Table II-A

Papers From Cook No.	Mead Refine Time (Sec.)	Williams Slowness (Sec.)	Density (p.c.f.)	Dry Tensile (lbs./in.)	Tear (g./16 sh.)	Mullen (p.s.i.)	Ring Crush (lbs.)	Brightness (percent)
2-a-----	169	55.0	32.0	44.2	172	85	54.7	17.5
2-b-----	181	55.0	28.7	44.0	176	85	67.0	16.4
2-c-----	161	55.0	32.4	51.0	174	88	62.8	17.1
2-d-----	133	55.0	32.8	52.6	178	98	69.0	18.4
2-e-----	142	55.0	35.1	51.2	174	112	69.4	21.1

TABLE III-A
TGA Cooks of Southern Pinewood at 16% Effective Alkali¹—Variation of TGA Charge

Cook No.	Cooking Conditions			Pulp Data			
	Chem./100 g. Wood	pH Range	Time (min.)	Yield (percent)	Pulp Lignin (percent)	Pulp Carbohydrate (Percent of Initial O.D. Wood)	
3-a-----	123.9 g. NaTGA, (100.0 g. TGA), 20.7 g. NaOH.....	9.8 to 9.7....	39	57.9	10.7	51.7	
3-b-----	123.9 g. NaTGA, (100.0 g. TGA), 20.7 g. NaOH.....	9.8 to 9.6....	58	57.7	8.8	52.6	

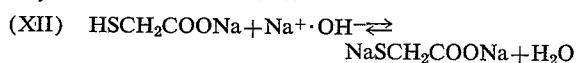
¹ See Footnote to Table I-A.

TABLE III-B
Tests on 26 lb./MSF Papers Made from Pulps of Cooks of Table III-A

Papers From Cook No.	Mead Refine Time (Sec.)	Williams Slowness (Sec.)	Density (p.c.f.)	Dry Tensile (lbs./in.)	Tear (g./16 sh.)	Mullen (p.s.i.)	Ring Crush (lbs.)	Brightness (percent)
3-a-----	142	55.0	35.1	51.2	174	112	69.4	21.1
3-b-----	118	55.0	36.4	55.0	185	105	70.2	20.2

The data in Tables II-A, II-B, III-A, and III-B demonstrate the pulping, and show the improvements that result in one-stage alkaline pulping, of isopropanol-extracted Southern pinewood with an alkaline treating liquor containing organomercaptan at a increased level above that employed in Example I. The effective alkali content of the liquors is maintained the same in both Examples I and 2 at 16 weight percent calculated as Na₂O and based on the weight of the O.D. lignocellulosic material.

The pH data in Tables II-A and III-A show the effect that the mercapto groups of TGA (sodium thioglycolate in the liquor) have in reducing and controlling the hydroxyl ion concentration of the alkaline pulping liquor. The differences in the pH levels of the initial cooking liquors provide evidence that, as the TGA charge is increased (with comparable increases in the amount of sodium thioglycolate in the individual cooks), more of the hydroxyl ions originating from the effective alkali (NaOH) are "tied-up" by the equilibrium reaction that may be illustrated as follows:



As pulping proceeds the hydroxyl ions that are consumed are replenished by the resultant shift of the equilibrium in the above-described reaction. The hydroxyl ion control (i.e., pH control), which is thereby provided during the cook, is shown most pronouncedly by the low level and small change of the liquor pH in Cook Nos. 2-d and 2-e in Table II-A, and in Cook Nos. 3-a (2-d repeated) and 3-b of Table III-A in which the molecular amounts of the TGA charge (present in the liquor as sodium thioglycolate) exceed that of the effective alkali (NaOH).

The pulping advantages provided by TGA (sodium thioglycolate in the liquor), as a result of its influence in controlling the hydroxyl ion concentration of the cooking liquor and due to its reactivity with the wood lignin, are shown by the pulp and paper data given in these tables.

The data on the pulps of the cooks reported in Tables II-A and II-B, which cooks were carried out under the same conditions of cooking time, temperature, and level of effective alkali, show that as the amount of organomercaptan is increased (as in Cook Nos. 2-b through 2-e), delignification is more complete, i.e., there is less lignin left in the pulp; at the same time the carbohydrate yield (i.e., the amount of residual carbohydrate in the pulp) is advantageously increased. This gain in the carbohydrate yield provides evidence that the organomercaptan, as a result of its control of the hydroxyl ion concentration of the cooking liquor, is effective in decreasing the alkaline degradation and resultant loss of carbohydrate material that ordinarily occurs in highly alkaline pulping processes.

The results presented in Table III-A provide additional evidence of the aforementioned effect. Cook Nos. 3-a and 3-b shown in this table differ from each other only in the time (39 minutes vs. 58 minutes) of digestion at the maximum digestion temperature of 170° C. The data show that delignification continues as the cooking time is extended. Surprisingly and unobviously, however, there is no further loss of carbohydrate material and the high yield of pulp is substantially maintained (57.9% pulp yield for the 39-minute cook vs. 57.7% yield for the 58-minute cook).

The pronounced improvements attained by the presence in the treating liquor of thioglycolic acid in the form of its alkali-metal, specifically sodium, salt will be readily apparent from a comparison of the pulp and paper data for the organomercaptan cooks shown in Tables II-A and II-B with the corresponding soda Cook No. 1-a presented in Tables I-A and I-B. All these cooks were carried out under the same conditions of time, temperature, and level of effective alkali.

It will be noted that the residual carbohydrate content of the pulps was increased from 47.4 weight percent of the initial O.D. wood in the case of the soda Cook No. 1-a to as high as 52.3 weight percent (Cook No. 2-d) of the initial O.D. wood as a result of including an organomercaptan in the cooking liquor. It will further be noted that the lignin content of the pulps was decreased from 24.4% for soda Cook No. 1-a to 10.7% in the case of Cook No. 2-e that contained an organomercaptan in the cooking liquor. As has been indicated hereinbefore, this is because of the accelerated rate of delignification that occurs when an organomercaptan, specifically thioglycolate in the form of its sodium salt, is a component of the treating liquor.

In addition to, and as a result of, the aforementioned improvements from a delignification standpoint of the method of this invention, a comparison of the test data given in Tables II-A and II-B with that for the soda cook given in Tables I-A and I-B shows that other beneficial and unobvious results are attained by including an organomercaptan in the treating liquor.

Thus, it will be noted that at pulp yields both comparable to and higher than the yield (62.7%) obtained in soda Cook No. 1-a, e.g., at the 62.4-64.9% pulp yields from organomercaptan Cook Nos. 2-a, 2-b, 2-c, and 2-d, the pulps from the last-mentioned cooks contain much less lignin, specifically as low as 16.2% in the case of Cook No. 2-d as compared with the 24.4% lignin content of the soda pulp from Cook No. 1-a. Furthermore, the papers made from the pulps wherein the treating liquor contained an organomercaptan had far superior strength characteristics as compared with the paper made from the soda pulp, more particularly (at the same comparable and higher yields) 44.0-52.6 vs. 39.5 tensile; 172-178 vs. 147 tear; 85-98 vs. 71 Mullen, and 54.7-69 vs. 51.5 ring crush.

The data in Tables II-A, II-B, III-A, and III-B also show that pulps produced by the method of this invention can be obtained in higher yields than by the Kraft process and yet can be made into papers having strength characteristics which, except for tear values, are comparable to those of papers made from Kraft pulp. Evidence of this fact is found in the aforementioned tables, especially the data given with regard to the pulps (and papers made therefrom) of Cooks 2-d, 2-e, 3-a (2-e), and 3-b; and a comparison of that data with corresponding data for laboratory Kraft cooks, more particularly Cook Nos. 6a, 6-b, and 6-c as given in Tables VI and VI-B that are presented later herein and which cooks were made at the same active alkali concentration as the cooks of Tables I, II and III. A comparative examination of the data shows that the method of this invention provides pulps at yields of 57.7% to 62.4% (Cook Nos. 2-d, 3-a, and 3-b) from which can be made papers having Mullen, tensile, and ring crush properties comparable to that of paper made from Kraft pulp in a yield of 55.9% Cook No. (6-a). Also, papers made from the organomercaptan pulps (referring particularly to the papers made from the pulps of Cook Nos. 2-c, 2-d, 3-a, and 3-b) are better in Mullen, tensile, and ring crush properties (i.e., have higher strength values) than those papers made from the Kraft pulps (Table VI-A and VI-B) at comparable pulp yields.

Evidence that the process of this invention is more selective in delignification than is kraft pulping is also provided by the results from the above-identified cooks. This is shown by the fact that the pulps from the organomercaptan cooks (i.e., cooks wherein an organomercaptan, specifically TGA in the form of a sodium salt thereof, was a component of the treating liquor) contain less residual lignin and more carbohydrate material, at a given pulp yield, than do the Kraft pulps.

In addition, more rapid delignification than by kraft pulping under the same cooking conditions of time, tem-

perature, and level of active alkali is obtainable by the method of the present invention. Evidence of this fact is found in the low (10.7%) lignin content of the organomercaptan pulp from Cook No. 2-*e* as compared with the substantially higher value of 13.4% lignin content of the kraft pulp from Cook No. 6-*a*.

EXAMPLE 3

This example illustrates the pulping of isopropanol-extracted pinewood with treating liquors comprised of various concentrations of an organomercaptan as in Example 2 but at a lower concentration of effective alkali, more particularly 8 weight percent, calculated as Na₂O, and based on the weight of the O.D. pinewood, instead of 16 weight percent effective alkali (on this same basis) as was employed in Examples 1 and 2.

The apparatus and general procedure are the same as described in Example 1. The digestion time is varied from 39 to 80 minutes at the same maximum temperature of digestion, viz, 170° C., and the same liquor-to-wood ratio of 4.5 to 1 as that employed in Examples 1 and 2.

More detailed information on the cooking conditions is given in Table IV-A. The properties of the handsheets made from the pulps described in Table IV-A are given in Table IV-B.

Tables IV-A and IV-B follow.

TABLE IV-A
TGA Cooks of Southern Pinewood at 8% Effective Alkali—Variation of TGA Charge

Cook No.	Cooking Conditions			Pulp Data		
	Chem./100 g. Wood	pH Range	Time (min.)	Yield (percent)	Pulp Lignin (percent)	Pulp Carbohydrate (Percent of Initial O.D. Wood)
4-a	31.0 g. NaTGA, (25.0 g. TGA), 10.3 g. NaOH	9.5 to 9.4	80	65.4	20.1	52.3
4-b	61.9 g. NaTGA, (50.0 g. TGA), 10.3 g. NaOH	9.5 to 9.2	39	66.6	18.4	54.3

¹ See Footnote to Table I-A.

TABLE IV-B
Tests on 26 lb./MSF Papers Made from Pulps of Cooks of Table IV-A

Papers From Cook No.	Mead Refine Time (Sec.)	Williams Slowness (Sec.)	Density (p.c.f.)	Dry Tensile (lbs./in.)	Tear (g./16 sh.)	Mullen (p.s.i.)	Ring Crush (lbs.)	Brightness (percent)
4-a	162	55.0	32.3	48.0	166	91	64.8	16.8
4-b	152	55.0	33.7	52.8	150	95	65.8	24.6

The results given in Tables IV-A and IV-B again show the effectiveness that an organomercaptan, specifically thioglycolic acid in the form of a sodium salt thereof, has (under the conditions used in practicing this invention) with respect to delignification, protection of the carbohydrate material during digestion and the obtainment of a high yield of pulp having good paper-making properties; and that such results are obtainable in the pulping of a softwood, specifically southern pinewood, using a treating liquor comprised of 8% effective alkali, calculated as Na₂O, and based on the weight of the O.D. wood.

The low and narrow pH range of the treating liquors during cooks show the control of the hydroxyl ion concentration (i.e., pH) provided by the mercapto groups of the organomercaptan. Evidence of the benefit of this control, in addition to that shown in Examples 1 and 2, is found in the high (i.e., 52.3–54.3%) carbohydrate yields from these cooks, viz., Cook Nos. 4-*a* 4-*b*, as compared with soda Cook No. 1-*a* in Table I-A (carbohydrate yield of 47.4%) and with kraft Cook No. 6-*c* in Table VI-A (carbohydrate yield of 51.1%). By comparison, the pulps from these kraft and soda cooks contain more lignin than do the organomercaptan pulps of this example (20.6% and 24.4% for the kraft and soda cooks, respectively, vs. 18.4–20.1%). As indicated hereinbefore, the higher yields of carbohydrate material are

desirable. It shows that less degradation of the cellulose has occurred during digestion.

The results also show that a high yield of pulp having a good quality is produced by the technique of this example. More particularly, the pulp and paper data show that from pulps obtained in yields of 65.4–66.6% there can be produced paper (handsheets) having better paper properties (except for tear strength) than can be made from kraft pulp at much lower yields; and with properties that approach those of papers made from high-strength kraft pulp.

Thus, by comparing the pulp yield of 66.6% (and data on paper made therefrom) of Cook No. 4-*b* in Tables IV-A and IV-B with corresponding data for kraft pulp yields of 60.8 and 64.3%, respectively (and data on paper made therefrom), of Cook Nos. 6-*b* and 6-*c* in Tables VI-A and VI-B, it will be noted that the paper made from the 66.6% yield of organomercaptan pulp is higher in tensile strength (52.8 vs. 42.5–44.3), Mullen (95 vs. 81–90), and ring crush (approx. 66 vs. 60–65).

Of particular significance is the fact that the addition of a sufficient amount of an organomercaptan to the treating liquor gives an unbleached pulp from which can be made a paper that is much brighter than can be made from a kraft pulp. This is shown by comparing the high 24.6% brightness of the paper prepared from the pulp of Cook No. 4-*b* of Table IV-B with that of the lower

17.8–18.8% brightness values of the kraft papers made from the pulps of Cook Nos. 6-*a*, 6-*b*, and 6-*c* that are given in Table IV-B. The higher brightness value for paper made from the organomercaptan pulp was obtained using a higher concentration of organomercaptan in the treating liquor than was employed in carrying out Cook No. 4-*a* shown in Tables IV-A and IV-B.

EXAMPLE 4

This example illustrates the pulping of isopropanol-extracted southern pinewood with a treating liquor comprised of (a) a major amount of an organomercaptan, specifically TGA in the form of a sodium salt thereof, and (b) a minor amount of sodium sulfhydrylate (NaSH). The active alkali content of the treating liquor is 11.3%. The effective alkali content of the cook containing both the organomercaptan and the sodium sulfhydrylate is 10.8%. A kraft-type cook with liquor comprised of a higher concentration of NaSH (as Na₂S) and the same active alkali concentration is provided for comparison. In both kraft cooks and cooks of the present invention, the NaSH is present in the treating liquor as NaSH or Na₂S. This latter kraft treating liquor has an effective alkali concentration of 10.3%. The apparatus and general procedure are the same as described in Example I. The time of digestion is 120 minutes at the maximum temperature of 150° C., and the liquor-to-wood ratio is 4.5 to 1.

More detailed information on the cooking conditions is given in Table V-A. The yields and properties of the pulps are also described in Table V-A while those of the handsheets made from the pulps are given in Table V-B.

Tables V-A and V-B follow.

ratory kraft cooks of isopropanol-extracted southern pine. These cooks are made for the purpose of comparing the properties of the pulps and of the handsheets made therefrom with the corresponding products of Examples 1, 2, and 3. Details of the pulping conditions for individual Cook Nos. 6-a, 6-b, and 6-c, and yields and properties

TABLE V-A
Kraft-Type and TGA plus NaSH Cooks of Southern Pinewood at 11.3% Active Alkali ¹

Cooking Conditions				Pulp Data		
Cook No.	Chem./100 g. Wood	Effective Alkali (Percent)	pH Range	Yield (Percent)	Pulp Lignin (Percent)	Pulp Carbohydrate (Percent of Initial O.D. Wood)
5-a	18.6 g. NaTGA, (15.0 g. TGA), 0.9 g. NaSH, 13.9 g. NaOH	10.8	12.4 to 11.0	66.6	21.4	52.3
5-b	2.5 g. Na ₂ S, (1.8 g. NaSH), 12.0 g. NaOH, 2.0 g. Na ₂ CO ₃	10.3	13.2 to 12.7	66.8	24.4	50.5

¹ Calculated as Na₂O and based on the O.D. weight of the wood.

TABLE V-B

Tests on 26 lb./MSF Papers Made from Pulps of Cooks of Table V-A

Papers From Cook No.	Mead Refine Time (Sec.)	Williams Slowness (Sec.)	Density (p.c.f.)	Dry Tensile (lbs./in.)	Tear (g./16 sh.)	Mullen (p.s.i.)	Ring Crush (lbs.)	Brightness (Percent)
5-a	166	55.0	30.9	39.6	146	81	69.0	18.0
5-b	188	55.0	29.5	35.6	184	77	54.1	18.1

The data in Tables V-A and V-B show the more selective and complete delignification that is obtained, and the improved properties of papers made from the resulting pulps, when the treating liquor employed in pulping a softwood, specifically Southern pinewood, is comprised of both (a) an organomercaptan, more particularly TGA in the form of a salt thereof, and (b) a minor but substantial amount of NaSH as compared with the results obtained using a synthetic kraft-type liquor under comparable cooking conditions of time, temperature, and active alkali concentration.

The improvement in delignification is shown by the fact that at the comparable pulp yields (i.e. 66.6% and 66.8%) of these cooks, the pulp from organomercaptan/NaSH Cook No. 5-a contains less lignin (21.4% vs. 24.4%) and more carbohydrate material (52.3% vs. 50.5% of the initial O.D. wood) than does the pulp from the kraft-type Cook No. 5-b. The low pH range of the treating liquor both initially and at the end of the cook and the high yield of carbohydrate in the pulp resulting from organomercaptan/NaSH Cook No. 5-a is evidence of the pH control and decreased carbohydrate degradation obtained by practicing the method of this invention.

The data on the papers made from the respective pulps show (Table V-B) the better properties with respect to tensile strength (39.6 vs. 35.6), Mullen (81 vs. 77), and ring crush (69.0 vs. 54.1) that characterize the papers prepared from the organomercaptan/NaSH pulp of Cook No. 5-a as compared with those of papers made from the kraft-type pulp of Cook No. 5-b.

EXAMPLE 5

This example illustrates three different simulated labo-

of the pulps are given in Table VI-A. The results of tests on papers (handsheets) made from the pulps identified in Table VI-A are given in Table VI-B.

FORMULATION FOR THE COOKS

Chip Charge: 400.0 g. (O.D. weight) of air-dried chips; pre-extracted with isopropanol.

Liquid Composition:

- 11.1 g.p.l. Na₂CO₃ (2.9% as Na₂O on the O.D. wood)
- 14.8 g.p.l. Na₂S (5.3% as Na₂O on the O. D. wood)
- 30.7 g.p.l. NaOH (10.7% as Na₂O on the O. D. wood)
- Active alkali as Na₂O: 35.6 g.p.l. (16.0% on the O.D. wood)
- Total alkali as Na₂O: 42.0 g.p.l. (18.9% on the O.D. wood)
- Sulfidity: 33.1% of the active alkali
- Liquor-to-wood ratio: 4.5 to 1
- Total liquor volume: 1800 ml.

The above liquor is prepared by dilution of conventional mill white liquor. The active alkali (A.A.) concentration of 16% A.A. based on the O.D. wood is the same as that of a mill cook. The liquor-to-wood ratio of 4.5 to 1 differs from the usual 3.4 to 1 ratio of a mill cook.

The apparatus and general procedure employed in carrying out the cooks are the same as described in Example 1. The time at the maximum cooking temperature of 170° C. is varied from 4 to 39 minutes to provide pulps at various yields for comparison with those of comparable yields and wherein were utilized the treating liquors of Examples 1, 2 and 3.

Tables VI-A and VI-B follow.

TABLE VI-A
Laboratory Kraft Cooks of Southern Pinewood at 16% Active Alkali ¹

Cooking Conditions						Pulp Data		
Cook No.	Chem./100 g. Wood	Sulfidity (Percent)	Effective Alkali ¹	pH Range	Time (min.)	Yield (Percent)	Pulp Lignin (Percent)	Pulp Carbohydrate (Percent of Initial O.D. Wood)
6-a	6.7 g. Na ₂ S, 13.8 g. NaOH 5.0 g. Na ₂ CO ₃	33.1	13.4	13.5 to 13.1	39	55.9	13.4	48.4
6-b	Same as above	33.1	13.4	13.5 to 13.3	12	60.8	18.9	49.3
6-c	do	33.1	13.4	13.5 to 13.3	4	64.3	20.6	51.1

¹ Calculated as Na₂O and based on the O.D. weight of the wood.

TABLE VI-B

Tests on 26 lb./MSF Papers Made from Pulp of Cooks of Table VI-A

Papers From Cook No.	Mead Refine Time (Sec.)	Williams Slowness (Sec.)	Density (p.c.f.)	Dry Tensile (lbs./in.)	Tear (g./16 sh.)	Mullen (p.s.i.)	Ring Crush (lbs.)	Brightness (Percent)
3-a-----	153	55.0	33.2	53.9	197	109	70.0	18.8
3-b-----	205	55.0	30.1	44.3	177	90	65.0	17.8
3-c-----	217	55.0	30.2	42.5	178	81	60.0	18.7

EXAMPLE 6

This example illustrates the pulping of isopropanol-extracted southern pinewood by means of a one-stage treatment with alkaline liquor comprised of varying amounts of 2-mercaptoethanol (instead of TGA in the form of its sodium salt as in the other examples utilizing and organomercaptan) at 8 and 16 weight percent effective (and active) alkali calculated as Na₂O based on the O.D. wood. The time at maximum temperature (i.e., 170° C.) is varied from 39 to 120 minutes. A soda cook at 16 weight percent effective (and active) alkali concentration is provided for comparison. The apparatus and general procedure are the same as that described in Example 1.

In all cooks the maximum temperature of digestion is 170° C. and the liquor-to-wood ratio is 4.5 to 1. Other details on the cooking conditions are given in Table VII-A and the properties of the papers made from the pulps are given in Table VII-B. The data on one-stage alkaline pulping with 2-mercaptoethanol that are given in these tables provide additional evidence of the improvements that result in the pulping of lignocellulosic material when the alkaline liquor is comprised of an organomercaptan. The pH data of the cooks in Table VII-A show the lowering and control of the liquor pH that is

than that which results from comparable soda pulping is shown to be achieved when 2-mercaptoethanol is included in the pulping liquor. The higher yield of carbohydrate (i.e., 51.1% of the initial wood) and the lower lignin content of the pulp (i.e., 20.1%) resulting from the 2-mercaptoethanol Cook No. 7-b, when compared with the results from soda Cook No. 7-a (i.e., 47.4% carbohydrate yield and 24.4% pulp lignin), provide evidence of these facts.

In addition, the data show that a one-stage process of this invention wherein 2-mercaptoethanol is utilized as the organomercaptan (also with TGA in the form of its sodium salt) provides a pulp of good quality in a high yield. Considerable improvement (except for brightness) in the paper properties of the pulp over that of the soda pulp is shown to result even at the higher pulp yields. Pulp with paper properties (tensile, Mullen, ring crush, tear, and brightness) near to or comparable with the values of papers made from kraft-process pulp is shown by the data as being obtained even up to 63.9% yield. It is further to be noted that, except for brightness, papers made from the pulp of Cook No. 7-c that was obtained in a yield of 76.4% had unusually good properties when the very high pulp yield is considered.

Tables VII-A and VII-B follow.

TABLE VII-A

Soda and 2-Mercaptoethanol (ME) Pinewood Cooks at 8% and 16% Active and Effective Alkali ¹

Cook No.	Cooking Conditions Chem./100 g. Wood	Effective Alkali ¹	pH Range	Time (min.)	Pulp Data		
					Yield (percent)	Lignin (percent)	Pulp Carbohydrate (Percent of Initial O.D. Wood)
7-a-----	20.7 g. NaOH, 5.0 g. Na ₂ CO ₃ -----	16.0	13.5 to 13.3..	39	62.7	24.4	47.4
7-b-----	42.4 g. ME, 20.7 g. NaOH-----	16.0	10.4 to 11.4..	39	63.9	20.1	51.1
7-c-----	21.2 g. ME, 10.3 g. NaOH-----	8.0	10.2 to 9.5...-	120	76.4	27.5	55.4

¹ See Footnote to Table I-A.

TABLE VII-B

Tests on 26 lb./MSF Papers Made from Pulp of Cooks of Table VII-A

Papers From Cook No.	Mead Refined Time (Sec.)	Williams Slowness (Sec.)	Density (p.c.f.)	Dry Tensile (lbs./in.)	Tear (g./16 sh.)	Mullen (p.s.i.)	Ring Crush (lbs.)	Brightness (percent)
7-a-----	193	55.0	27.8	39.5	147	71	52	19.7
7-b-----	153	55.0	28.6	47.8	192	88	59	16.4
7-c-----	124	55.0	31.9	46.7	150	82	74	12.5

provided by the organomercaptan employed, viz, 2-mercaptoethanol. The advantages resulting from this pH control (i.e., in decreasing the high loss of carbohydrate material that normally results from hydrolytic attack by alkali during alkaline pulping) and from the reaction of the 2-mercaptoethanol with the lignin of the wood are shown most pronouncedly by comparison of Cook No. 7-b with soda Cook No. 7-a which is carried out under the same cooking conditions and concentration of effective (and active) alkali.

The data in these tables show that improvements similar to those demonstrated in previous examples with TGA in the form of its sodium salt also result with 2-mercaptoethanol. More complete and more selective delignification

EXAMPLE 7

This example illustrates the pulping of a hardwood, specifically black gum, with an alkaline liquor comprised of TGA in the form of its sodium salt, i.e., sodium thioglycolate (NaTGA). The liquor is comprised of varying amounts of NaTGA at 8 weight percent effective (and active) alkali concentration calculated as Na₂O and based on the weight of the O.D. wood. Two soda cooks, one under the same cooking conditions as the NaTGA cooks and the other differing from the NaTGA cooks only in the time (12 minutes) at the maximum cooking temperature, are provided for comparison. The apparatus and the general procedure are the same as that described

in Example 1. In all cooks the maximum temperature of digestion is 170° C. and the liquor-to-wood ratio is 4.5 to 1. Other details on the cooking conditions are given in Table VIII-A and the properties of papers made from the pulps are given in Table VIII-B.

The data in Tables VIII-A and VIII-B show the improvements that result over comparable soda pulping when black gum is pulped with soda liquor comprised of an organomercaptan, specifically NaTGA. Evidence of improvements similar to those described in the previous examples directed to the pulping of a softwood (specifically pinewood), is, in general, provided. The only major difference between the organomercaptan pulping of the two different woods, that is, black gum and pine, appears to be the relatively low tear strength of the paper made from the black gum pulp. This is a normal characteristic for paper made from this type of hardwood by prior-art pulping methods.

The pH data of the NaTGA Cook Nos. 8-a and 8-b in Table VIII-A, when compared with that of soda Cook Nos. 8-c and 8-d, show the control of the liquor pH that is provided by the organomercaptan, specifically NaTGA, and which has been described more fully in previous examples. The effect that this control has in decreasing the loss of carbohydrates is shown (Cook Nos. 8-a and 8-b) by the higher yields of carbohydrate (53.5-55.3% based on the initial weight of the O.D. wood) in the pulps resulting from the NaTGA cooks as compared with the pulp carbohydrate yields (51.5% based on the weight of the initial O.D. wood) resulting from soda Cook Nos. 8-c and 8-d.

The data also show the improved dissolution of the wood lignin (i.e., the more complete delignification) that is obtained by pulping with NaTGA as compared with soda pulping. Much less lignin (16.4-17.1%) is left in the pulps of Cooks Nos. 8-a and 8-b as compared with the amount of lignin (25.0%) left in the pulp of soda Cook No. 8-d and wherein the cooking conditions are the same including the time at the maximum temperature.

The paper data in Table VIII-B show that black gum pulp made by the method of this invention (Cook Nos. 8-a and 8-b) can be expected to provide papers having much better properties, especially as to tensile, Mullen, ring crush, and brightness values than soda pulp at comparable yields. In fact the properties, except for tear strength, are exceptionally good when one takes into consideration the high yield and the fact that the pulp originates from a hardwood.

Tables VIII-A and VIII-B follow.

Instead of using thioglycolic acid or 2-mercaptoethanol as the organomercaptan that is incorporated into the alkaline treating liquor in Examples 1 through 4, 6, and 7, similar results are obtained by using an equivalent amount of other organomercaptans including other mercaptocarboxylic acids such as mercaptopropionic acid, HS-CH₂-CH₂-COOH, and higher members of the homologous series of monomercaptomonocarboxylic acids, and acids the formulas of which previously have been identified in Formulas VI through X. Or, one may use 3-mercaptopropanol or higher members of the homologous series of mercaptoalkanols; or other organomercaptans of which numerous examples previously have been given. Also, instead of pulping a softwood (e.g. southern pinewood), or a hardwood (e.g., black gum wood) by digestion with a treating liquor containing an organomercaptan as described in Examples 1 through 4, 6, and 7, a similar treatment may be applied to a mixture of a softwood and a hardwood, e.g., a mixture of southern pinewood and black gum wood.

From the foregoing description it will be seen that the present invention provides a method of treating lignocellulosic material for the removal of lignin therefrom which comprises:

(A) Digesting said material with a treating liquor containing an agent reactive with the said lignocellulosic material and which is comprised of an organomercaptan in an amount corresponding to at least about 2 weight percent and preferably at least about 5 weight percent based on the weight of the O.D. lignocellulosic material. The treating liquor contains alkali equivalent to at least about 2 weight percent effective alkali calculated as Na₂O, or at least 4 weight percent total alkali also calculated as Na₂O, these weight percentages being based on the weight of the O.D. lignocellulosic material.

The amount of the aforesaid effective alkali or of the aforesaid total alkali, the ratio of treating liquor to O.D. lignocellulosic material, and the time and temperature of digestion are such as to cause the organomercaptan component of the treating liquor to react with the lignin in the lignocellulosic material and concurrently to extract therefrom the resulting mercaptan-reacted lignin so that there is obtained in a single stage digested, solid, cellulose-containing material which is amenable to refining to a pulp, more particularly a paper-making pulp. Ordinarily, this cellulose-containing material also contains lignin in varying amounts.

As previously has been indicated the treating liquor also may contain an inorganic thio compound, more par-

TABLE VIII-A

TGA and Soda Black Gum Cooks at 8% Active and Effective Alkali ¹

Cook No.	Cooking Conditions			Pulp Data		
	Chem./100 g. Wood	pH Range	Time (min.)	Yield (percent)	Pulp Lignin (percent)	Pulp Carbohydrate (Percent of Initial O.D. Wood)
8-a	31.0 g. NaTGA, (25.0 g. TGA), 10.3 g. NaOH	10.6 to 10.2	39	64.5	17.1	53.5
8-b	61.9 g. NaTGA, (50.0 g. TGA), 10.3 g. NaOH	9.2 to 8.7	39	66.1	16.4	55.3
8-c	10.3 g. NaOH	13.0 to 11.7	12	69.9	26.4	51.5
8-d	10.3 g. NaOH	12.9 to 11.7	39	68.7	25.0	51.5

¹ See Footnote to Table I-A.

TABLE VIII-B

Tests on 20 lb./MSF Papers Made from Pulps of Cooks of Table VIII-A

Papers From Cook No.	Mead Refine Time (Sec.)	Williams Slowness (Sec.)	Density (p.c.f.)	Dry Tensile (lb./in.)	Tear (g./16 sh.)	Mullen (p.s.i.)	Ring Crush (lbs.)	Brightness (percent)
8-a	80	55.0	35.3	49.6	102	80	80	27.7
8-b	118	55.0	34.2	52.2	105	76	77	31.9
8-c	138	55.0	27.5	30.6	98	46	64	20.3
8-d	146	55.0	28.2	31.8	82	45	61	18.0

cularly an inorganic sulfide such as Na_2S or an inorganic hydrosulfide such as NaSH , in an amount that may be varied considerably depending upon the particular results that are desired. Usually, if an inorganic thio compound is added to the treating liquor in practicing the present invention, it is employed in a minor amount (i.e., less than 50 weight percent) of the total $-\text{SH}$ content of the treating liquor. Preferably such a modifying inorganic thio compound is a water-soluble inorganic hydrosulfide, e.g., an alkali hydrosulfide such as sodium, potassium, lithium or other alkali-metal hydrosulfide, or their obvious equivalents; and the amount thereof is generally from about 3 to about 45 weight percent, more particularly from about 5 to about 30 weight percent, of the total $-\text{SH}$ content of the treating liquor.

(B) At the end of the digestion period, the excess liquor is removed by any suitable means from the digester, e.g., by draining, siphoning, etc., thereby separating the excess liquor from the treated material resulting from Step A.

Preferably the residue that remains after removing the excess liquor from the organomercaptan-treated lignocellulosic material is washed, e.g., with water and, more particularly, with hot water. The washed residue may then be refined, as desired or as may be required, to yield a pulp suitable for paper-making or other purposes. Additionally, if desired, it may be bleached or further processed as desired or as required for the particular end use.

From the foregoing description of the instant invention it will be seen that it is materially and unobviously different from that described by Holmberg in the early part of this specification, and is separately and patentably distinct from that disclosed and claimed in our aforementioned copending application Ser. No. 605,978 and in our copending application Ser. No. 606,025. It is also separately and patentably distinct from the inventions disclosed and claimed in the copending applications of Carl A. Johnson, Ser. No. 606,024 and Ser. No. 606,012. The first-identified Johnson application is concerned with the use of a combination of an organomercaptan and a hydrotrope agent in a method for pulping (digesting) lignocellulosic material. The latter Johnson application is concerned with a particular two-stage treatment to delignify (pulp) lignocellulosic material first with a treating liquor containing an organomercaptan and having an alkaline pH up to about 12.0; and, in a second stage, extracting mercaptan-reacted lignin retained by the digested lignocellulosic material by contacting it with a dilute solution of a water-soluble inorganic base. All of the aforementioned applications, filed concurrently herewith, are assigned to the same assignee as the instant invention.

We claim:

1. The method of treating lignocellulosic material for the removal of lignin therefrom in a single stage which comprises:

(A) digesting said material with a treating liquor containing an agent reactive with the said lignocellulosic material and which is comprised of an organomercaptan in an amount corresponding to at least about 2 weight percent based on the weight of the oven-dried lignocellulosic material, said treating liquor containing alkali equivalent to at least about 2 weight percent effective alkali calculated as Na_2O , or at least 4 weight percent total alkali also calculated as Na_2O , said weight percents being based on the weight of the oven-dried lignocellulosic material,

the amount of the said alkali, the ratio of treating liquor to oven-dried lignocellulosic material, and the time and temperature of digestion being such as to cause the said organomercaptan to react with the lignin in the said lignocellulosic material and concurrently to extract therefrom the resulting mercaptan-reacted lignin so that there is obtained in a single stage a digested, solid, cellulose-containing material that is amenable to refining to a pulp; and

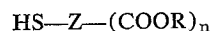
(B) removing the excess liquor from the treated material from Step A.

2. The method as in claim 1 wherein the lignocellulosic material is softwood.

3. The method as in claim 1 wherein the lignocellulosic material is hardwood.

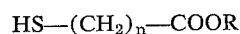
4. The method as in claim 1 which includes the step of washing the residue that remains after removing the excess liquor from the organomercaptan-treated lignocellulosic material.

5. The method as in claim 1 wherein the organomercaptan is one represented by the general formula



wherein Z represents an alkylene radical containing from 1 through 10 carbon atoms; R represents a member of the group consisting of (a) hydrogen, (b) alkyl radicals containing not more than 10 carbon atoms, and (c) a salt-forming cation; and n represents an integer from 1 up to that of the combining power of the alkylene radical represented by Z; and which includes the step of washing the residue that remains after removing the excess liquor from the organomercaptan-treated lignocellulosic material.

6. The method as in claim 5 wherein the organomercaptan introduced into the treating liquor is one represented by the general formula



wherein n represents an integer from 1 to 8, inclusive, and R represents a member of the group consisting of (a) hydrogen, (b) alkyl radicals containing not more than about 8 carbon atoms, and (c) a salt-forming cation.

7. The method as in claim 6 wherein the organomercaptan is thioglycolic acid.

8. The method as in claim 7 wherein the amount of the thioglycolic acid is less than the chemically equivalent amount of the effective alkali.

9. The method as in claim 1 wherein the weight percent of organomercaptan is at least about 2.5.

10. The method as in claim 1 wherein the weight percent of organomercaptan is at least about 5.

11. The method as in claim 1 wherein the treating liquor contains from 2 to about 250 weight percent of effective alkali, calculated as Na_2O , based on the weight of the oven-dried lignocellulosic material; the organomercaptan is present in the treating liquor in an amount corresponding to from 2.5 to about 100 weight percent based on the weight of the oven-dried lignocellulosic material; the ratio of treating liquor to oven-dried lignocellulosic material corresponds to from about 15 to about 200 ml. of the former for each 10 grams of the latter; and the maximum digestion temperature is within the range of from 100°C . to 250°C .

12. The method as in claim 1 wherein the organomercaptan, as introduced into the treating liquor, is thioglycolic acid in an amount corresponding to from about 5 to about 50 weight percent based on the weight of the oven-dried lignocellulosic material; the treating liquor contains at least 6.5 weight percent of effective alkali, calculated as Na_2O , based on the weight of the oven-dried lignocellulosic material; and the ratio of treating liquor to oven-dried lignocellulosic material is from about 30 to about 60 ml. of the former for each 10 grams of the latter.

13. The method as in claim 1 wherein the organomercaptan, as introduced into the treating liquor, is thioglycolic acid in amount corresponding to from about 5 to about 50 weight percent based on the weight of the oven-dried lignocellulosic material; the maximum digestion temperature is within the range of from 100°C . to 250°C .; and the time of digestion at the maximum temperature is within the range of from a few minutes to 6 hours.

14. The method as in claim 13 wherein the digestion temperature is within the range of from 120°C . to 210°C .; and the time of digestion at the maximum tempera-

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ture is within the range of from about ¼ hour to about 3 hours.

15. The method as in claim 13 wherein the maximum digestion temperature is within the range of from 150° C. to 190° C.; the time of digestion at the maximum temperature is within the range of from about ¼ hour to about 3 hours; and which includes the step of water-washing the residue that remains after removing the excess liquor from the organomercaptan-treated lignocellulosic material.

16. The method as in claim 4 which includes the additional step of refining the washed residue to a paper-making pulp.

17. The method as in claim 15 wherein the organomercaptan-treated lignocellulosic material is organomercaptan-treated pinewood; the ratio of treating liquor to oven-dried lignocellulosic material corresponds to about 45 ml. of the former for each 10 grams of the latter; the digestion temperature is about 170° C.; and the time of diges-

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tion at the maximum temperature is from about ½ to about 1 hour.

18. The method as in claim 1 wherein the organomercaptan is 2-mercaptoethanol.

19. The method as in claim 1 wherein the organomercaptan is a mercaptoalkanol.

20. The method as in claim 1 wherein the treating liquor also contains a minor amount by weight of an inorganic thio compound.

References Cited

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HOWARD R. CAINE, Primary Examiner

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