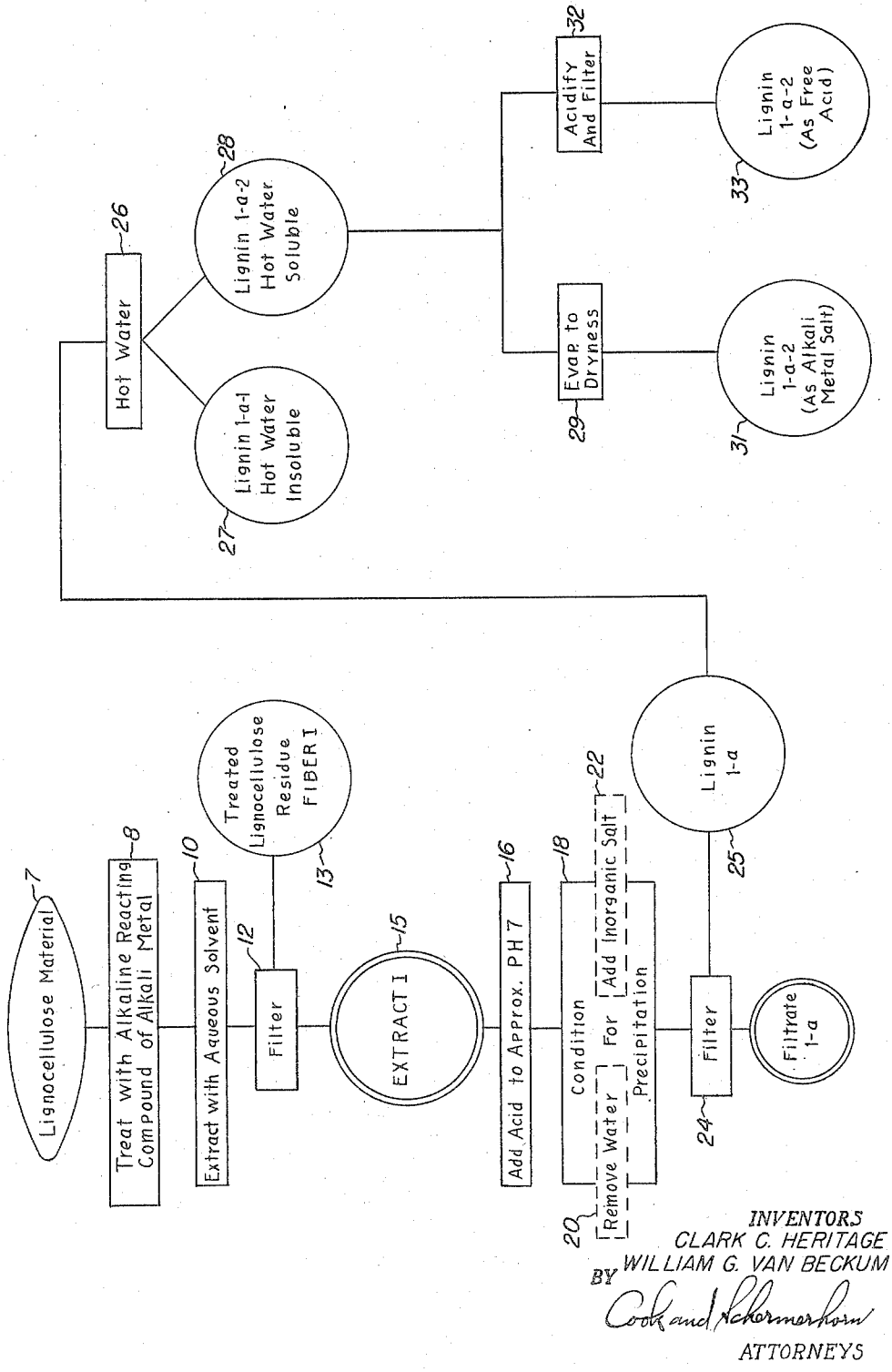
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PROCESS FOR PRODUCING LIGNIN PRODUCTS

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INVENTORS
CLARK C. HERITAGE
WILLIAM G. VAN BECKUM
BY Cook and Ackermorhorn
ATTORNEYS

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PROCESS FOR PRODUCING LIGNIN PRODUCTS

Clark C. Heritage, Cloquet, Minn., and William G. Van Beckum, Longview, Wash., assignors to Weyerhaeuser Timber Company, Longview, Wash., a corporation of Washington

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This invention relates to a method for producing lignin products from materials containing cellulose and lignin, such as wood, cornstalks, straw, bagasse, flax shives, hemp, etc., these and other similar raw materials being hereinafter referred to as lignocellulose materials. The process of the invention is particularly applicable to woods of various species, representative and suitable woods being aspen, jack pine, western larch, Douglas fir, and western red cedar. This application is a continuation-in-part of our abandoned application Serial No. 602,917, filed July 2, 1945.

When wood is used as a source of lignocellulose materials, it is preferably first reduced to fibrous form by mechanical or other methods which do not subject the wood to the action of added chemicals other than water. This reduction is carried to the point where it results in the conversion of the wood substance to fibers physically consisting substantially of ultimate fibers and opened-up bundles of ultimate fibers, and constitutionally consisting primarily of cellulose, lignin, and polysaccharides-other-than-cellulose, these three constituents being present in ratios in the range of contents falling between that characterizing the raw wood from which the fiber is derived and that characterizing the water-insoluble content of the raw wood from which the fiber is derived. Fiber containing cellulose, lignin, and polysaccharides-other-than-cellulose in the range characterizing the water-insoluble content of the raw wood from which the fiber is derived is exemplified by raw wood fiber which has been so treated with water as to extract the water-soluble constituents and leave as a fibrous residue the water-insoluble content of the wood. The production of such fiber from woods such as the species hereinabove mentioned is of particular interest, since these woods contain high percentages of water extractable substances, e. g. about 25% in the case of western larch. It may, therefore, be commercially desirable in the case of these woods to extract them with water in order to isolate as commercial products the water-soluble fraction of the wood substance. A fiber residue is thus obtained which may be employed to advantage as a raw material for the process of the instant invention.

The wood fibers to which the process of the invention may be satisfactorily applied may be pro-

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duced, for example, by the method described in U. S. Patent No. 1,913,607 to McMillan. This patent describes a mechanical defibering process entirely free from chemical action, which comprises combing out substantially ultimate fibers from wood by contacting logs of wood with high speed rotary radial elements such as pointed pins projecting from an axle, like bristles. Fiber produced by this process is herein referred to as McMillan fiber, or pin fiber.

Wood fiber suitable for use in the process of the present invention may also be prepared by the method described in U. S. Patent No. 2,008,982 to Asplund. In this method wood substance is defibered by mechanically reducing the wood while simultaneously applying sufficient steam pressure to soften the lignin in the middle lamella, thus permitting easy defibration of the softened wood. The fiber resulting from this practice in efficient operation of the commercial Asplund machine is termed herein normal Asplund fiber, or normal defibrator fiber. It is prepared, for example, by reducing wood while exposing it for about one minute to high pressure steam at a temperature sufficient to effect the desired softening.

Other processes may be employed for reducing wood substance to said ultimate fiber or opened-up bundle form. The wood substance may be affected by steam at any time or times before, during or after such defibration. Action by steam should be such as to avoid any substantial gasification of the wood substance which thus leads to loss or decomposition of wood substance, usually with the formation of furfural, as well as to altered proportions of the three primary constituents, and unduly altered forms of said constituents. The fibers resulting from processes involving both defibering and steaming, which includes those resulting from the Asplund process, differ from the raw wood in that their water-soluble content has been to a greater or lesser degree increased by the action of the steam. In the case of normal Asplund aspen fibers made in about one minute at about 128 pounds' steam pressure, the increase in water-soluble content is 4% to 5%.

Other methods for producing fibers from wood substance may also be used, provided said methods do not subject the wood to the action of added chemical agents other than liquid water or steam. No known attempts have heretofore been made

to isolate lignin products resulting from relatively mild treatments of lignocellulose materials and having such characteristic and reproducible properties as to be useful as raw materials for a variety of industrial applications. In the past, lignocellulose material such as wood chips has been converted to pulp suitable for use in the manufacture of paper, fiber-board, and other products, by relatively severe chemical treatment. Paper-making pulp has been commonly prepared, for example, by treating raw wood chips with strong solutions of bisulfite salts, e. g. calcium bisulfite or magnesium bisulfite, under conditions of high temperature, high pressure, and for long periods of time. It has also been common practice to subject raw wood chips to the action of numerous alkaline chemicals alone or in admixture, as in the soda, kraft or sulfate, and monosulfite processes, again employing strong solutions under conditions of high temperature, high pressure, and prolonged operating periods. Although lignin derivatives have been produced by all of these processes, it has been the general practice heretofore either to discard them in the waste liquor, to burn them to recover the alkali, or to recover part of them as a crude aggregate product of indefinite properties. Such products as have been obtained from these processes have been so modified by the drastic chemical treatment to which the wood substance has been subjected as to differ materially from lignin as it is originally found in wood, and to represent chemically altered or degraded forms of lignin.

Lignin is obtained from lignocellulose material in accordance with the present invention by treating such material with an aqueous alkaline reagent comprising a weak aqueous solution of an alkali-metal hydroxide, e. g. sodium hydroxide, at a temperature in the range between about normal room temperature and about the boiling temperature of the solution at normal atmospheric pressure for a time sufficient substantially to exhaust the extracting action of the alkali, thereby dissolving from the said material lignin and polysaccharides-other-than-cellulose and leaving a fibrous residue, separating the said fibrous residue from the alkaline extract which contains lignin and polysaccharides-other-than-cellulose, conditioning the said alkaline extract to provide a substantial quantity of salt concentration whereby a lignin material is precipitated therefrom, separating the precipitated lignin from the resulting solution in which polysaccharides-other-than-cellulose and other lignins remain dissolved, and extracting the precipitated lignin with a solvent comprising water to effect the separation thereof into water-soluble and water-insoluble fractions.

It is therefore an object of the present invention to provide a method for the isolation of lignin from lignocellulose materials.

It is a further object to provide a method for the isolation from lignocellulose materials of lignin in forms which have not been drastically altered by the action of strong chemical reagents.

Still another object of the invention is to provide a method for the isolation of lignin from lignocellulose materials whereby more than one lignin product is obtained, each of said products having characteristic and differentiating properties.

Another object is to provide a method for the isolation of lignins having properties differing from those of lignins heretofore known to the art and being applicable, therefore, to unique and varied applications.

It is still a further object to provide a method for the separation of lignin from aqueous solutions containing, in addition to lignin, polysaccharides-other-than-cellulose.

It has been found that the above and other objects of the invention may be accomplished by subjecting lignocellulose material, e. g. wood fiber, to the action of a dilute aqueous solution of a basic-acting compound of an alkali-metal, separating the resulting solution from the treated material, and separating lignin from the said resulting solution.

In a specific embodiment of the invention, wood fiber containing substantially all of the water-insoluble content of the wood from which the fiber is derived and prepared by the hereinabove referred to McMillan, Asplund or other processes, and physically consisting substantially of ultimate fibers and opened-up bundles of ultimate fibers and constitutionally consisting primarily of cellulose, lignin, and polysaccharides-other-than-cellulose, said three constituents being present in mutual ratios in the range of contents from those characterizing the wood from which the fiber is derived to those characterizing the water-insoluble content of the said wood from which the fibers are derived, is treated with a dilute aqueous extracting solution of alkali-metal. The alkaline reagent employed is typically exemplified by sodium hydroxide, e. g. a ¼ normal solution of sodium hydroxide, in a total amount, with respect to fiber, sufficient to maintain an extracting alkalinity during the operation. This treatment is preferably carried out at atmospheric pressure and at about the boiling point of the said solution. The time of treatment is variable depending upon the type of wood being treated and the other conditions of the treatment, but in general may be up to about two hours, or such time as shows the extraction to be substantially complete. This treatment extracts from the wood substance a substantial proportion of its lignin and polysaccharides-other-than-cellulose content and leaves a fibrous lignocellulosic residue. After separation of the residue from the caustic solution, the caustic solution is treated for isolation of lignin therefrom. As is more fully explained hereinbelow, this may be accomplished by an integrated series of process steps comprising in variable combinations neutralization, concentration, filtration, extraction and the addition of chemical reagents.

The drawing illustrates a suitable method for the separation of lignin products from an alkaline solution resulting, together with a fibrous product, from the extraction of lignocellulose materials, e. g. wood fiber, with a dilute aqueous solution of alkali. The procedure outlined provides for the isolation from lignocellulosic material of lignin products, herein arbitrarily designated as lignins *l—a*, *l—a—1*, and *l—a—2*, as the free lignin acids and as the lignin salts. These lignin products differ from each other in several respects, principally in their solubility characteristics, analyses, softening and melting points, and chemical reactivity. Because of these differences in constitution and properties, these diverse lignin products may obviously be applied to diverse uses.

In accordance with the procedure outlined in the drawing, it will be seen that the process of the invention is practiced by treating lignocellu-

lose material 7, e. g., wood fiber, as the starting raw stock, with an alkaline reacting compound of alkali metal as indicated at step 8. The alkaline reagent employed is typically exemplified by sodium hydroxide. The treatment is conducted at an atmospheric pressure and at a temperature in the range from room temperature to about 140° C. The time of treatment is variable, depending upon the type of wood being treated, but in general may be up to about two hours, or such time as shows the extraction to be approaching completion. The reacted mass is extracted at step 10 to separate the soluble matter from the thus treated fiber.

Step 8, or steps 8 and 10, herein referred to as the alkali treatment, extract from the wood substance a substantial proportion of the content of lignin and of other organic materials such as polysaccharides-other-than-cellulose, and leave a fibrous residue. Step 8 may be practiced by a batchwise procedure or by a counter-current or recycling procedure as hereinafter more fully discussed. Water is usually employed as the solvent in step 10, but the water may also be admixed with other materials in order to contribute specific properties to the solvent or for specific purposes. Water alone, or with such other materials admixed therein is herein referred to as an aqueous solvent. Steps 8 and 10 may be efficiently combined when an aqueous solution of sodium hydroxide is used, but when moist wood fiber is treated with solid sodium hydroxide, or with solutions so concentrated as to amount to syrups, the separate aqueous extraction step 10 will be necessary.

The mass or slurry, with the treated fiber in aqueous suspension, is next filtered at step 12, or otherwise processed to separate the treated lignocellulose residue 13, herein arbitrarily designated as Fiber I from the soluble matter in the filtrate or solution 15 arbitrarily herein designated Extract I, which contains lignin and the other organic materials including the polysaccharides-other-than-cellulose.

As solution 15 is initially obtained it may be relatively dilute where a single batch of fiber is treated with an extracting solution, or it may be more concentrated where a recycling or counter-current procedure has been used to minimize the water in the system—lignocellulose, alkali, and water. In all cases the pH value of solution 15 will range from neutral to about 10, depending on the extent to which the alkali content has been spent during the reaction with the lignocellulose material. The solution is neutralized at step 16 by addition of inorganic acid, such as hydrochloric acid, sulfuric acid or sodium acid sulfate, bringing it to a pH of approximately 7. The solution as thus acidified is then conditioned for precipitation at step 18. This conditioning may take one of two forms, or a combination of both—by either the removal of water of solution, step 20, or by the addition of inorganic salts, step 22. Both treatments have in common the fact that they result in the concentration of the solution to a point at which completion of the lignin precipitation is effected. The precipitated lignin is then filtered at step 24 and recovered at 25 as product lignin I—*a*.

It is desired at this point to elaborate on step 18 of conditioning the solution for precipitation of the lignin, especially since this same step is generally applicable at other steps in the process, or in other sequences, to the separation of the other lignin products at other pH ranges. While some precipitation of lignin may occur by virtue of establishment of the pH range for separation of the lignin product concerned, the separation of the lignin in this manner is not sharp, and it is advisable to condition the solution in order to effect the complete precipitation of all the lignin which will separate at the particular pH range. After neutralization, the solution may be concentrated by evaporation, which step, if practiced, is included in step 18. The concentration is continued to a point where the lignin content is precipitated in substantial amount. The solution is preferably maintained neutral during this concentration step by the addition of acid as necessary. It will be obvious that the need for concentration by removal of water will depend upon the usage of alkali and the concentration of the alkali in the solution 15. The more the salt content formed by the interaction between the alkali and the acid, the less will be the extent to which the removal of water needs to be continued. It will be further appreciated in this connection that steps 16 and 18 are more or less interdependent and that either step may be performed first; that is, either the removal of water or the addition of the salt may precede acidification. It is generally more advantageous, however, for step 18 to follow step 16, because, in this manner, full advantage can be taken of the salts formed by the neutralization of the alkali present.

When the conditioning of the solution for precipitation is to be accomplished by the addition of inorganic salts as at 22, sodium acid sulfate is preferably used, and is added until the solution is near saturation with respect to this compound. At this point, precipitation of lignin I—*a* can be expected to be substantially complete. The neutral, concentrated solution containing undissolved lignin, preferably at room temperature, is filtered at 24, thereby separating lignin I—*a*, designated 25, in the solid form. Division of this lignin product may be effected by extracting it at 26 with hot water. This results in the formation of a hot-water-insoluble lignin fraction I—*a*—1 (27) and a hot-water-soluble lignin fraction I—*a*—2 (28). Although the relative amounts of these two fractions are variable depending in part on the nature of the material treated, in the case of woods such as aspen, jack pine and western red cedar about two-thirds of lignin I—*a* is soluble in hot water while about one-third is insoluble in that solvent.

The hot-water-soluble fraction 28 which contains lignin I—*a*—2 may be evaporated to dryness at 29 to yield the lignin content of the solution in the salt form 31. Alternatively, the aqueous solution may be acidified to a pH of about 1.5 at 32, and the free lignin acids 33 thereby precipitated. These may be separated by filtration of the solution, preferably after heating to about 60° C. to facilitate filtration.

It will be apparent that the process of the invention is flexible and may be varied as desirable or necessary when processing different species of woods or when employing a range of operating conditions and reagent concentrations. For example, various alkaline materials may be employed in the treating step 8. Suitable alkaline materials include in general the hydroxides of the alkali metals as well as those alkali metal compounds which, being salts of strong bases and weak acids, undergo hydrolysis in aqueous medium to form the alkali-metal hydroxides, or their equivalent in alkali-metal ions and hydroxyl

ions. Such compounds are, therefore, the basic-acting compounds of the alkali-metals, i. e. of lithium, sodium, potassium, rubidium and caesium. The hydroxides of this group of metals, especially sodium hydroxide, are preferred reagents for effecting the herein described extraction, although the carbonates, e. g. sodium carbonate, may also be used.

The operating conditions of the extraction step, wherein lignocellulosic fiber is extracted with a dilute aqueous solution of a basic-acting alkali-metal compound, may be varied within limits as desirable or necessary to suit the particular lignocellulose material being treated. It is the teaching of the invention, however, and critical to its success in practical operation, to use and maintain operating conditions and reagents of such a mild character as to effect the cleavage of the lignin-polysaccharide complexes existing in the lignocellulose materials, and the separation of lignin without causing substantial or drastic changes in composition of the constituents, thereby preserving the inherently great reactivity of naturally occurring lignin. Thus it is preferred to use a solution having a relatively low concentration of alkali-metal hydroxide, i. e. a solution which contains sufficient alkali-metal hydroxide to be about ¼ normal with respect to that reagent. A preferred solution for effecting the extraction is a 0.6% solution of sodium hydroxide.

Usages of alkali largely in excess of those necessary to obtain the desired fractionation are also avoided. The total amount of alkali-metal hydroxide used is usually based upon the weight of fiber treated. Thus, for example, a usage of 15% sodium hydroxide signifies that 15 parts by weight of sodium hydroxide is used to extract 100 parts of dry fiber.

Where a mixing procedure is employed in the extraction with alkali-metal hydroxide, the consistency of the reaction mixture (i. e. the weight of fiber per 100 parts by weight of solution) is maintained at a level such as to afford ease of manipulation and thoroughness of treatment. The optimum consistency is obviously dependent upon many factors, principally upon the method of handling the fiber mixture. Varying consistencies may be used depending upon whether the fiber is treated batchwise, or continuously, as in counter-current operation.

It will be apparent that concentration, usage and consistency are interrelated factors and that variations in one will affect the others. Thus, when the concentration and usage are varied, the consistency changes. Various combinations of these variables are possible, the practical limiting factors being, as disclosed above, the desirability of keeping the operating conditions relatively mild, and also of providing consistencies such as to favor ease of handling, drying, processing and relatively complete separation of extract from treated material. A representative combination of these variables suitable for use in extracting woods in fibrous form in accordance with the process of the invention comprises the use of an aqueous sodium hydroxide solution having a concentration of 0.6% by weight sodium hydroxide in an amount equal to 15% by weight of the fiber treated, whereupon the consistency of the mixture will be about 4%.

As stated hereinabove, the alkaline extraction is carried out at a temperature which is preferably about the boiling temperature of the mixture at about normal atmospheric pressure. In ordinary operation where the process is carried out at normal atmospheric pressure in open vessels and where the described dilute solutions are employed, the temperature of operation will be about 100° C.

Treating times of up to about two hours may be employed. In the case of aspen, jack pine, and similar woods, maximum treating times of the order of one hour are used, relatively little advantage obtaining from longer treating durations.

Largely for reasons of economy and efficient operation, it is usually preferred to recycle the alkaline solution used in the extraction when batchwise extraction is being practiced. In this manner, as the caustic-soluble content of the wood substance is built up in the solution, the solution becomes increasingly valuable as a source of extracted materials. Since some of the alkali is consumed by reaction with the wood substance during the extraction process, it is desirable to add a further quantity of alkali before treating fresh wood fiber. In the case of woods such as aspen and jack pine, extracted at 4% consistency with a 0.6% solution of caustic soda, about 60% replacement of the original caustic alkali usage after each extraction is sufficient to fortify the solution to the desired degree, e. g. to a concentration of about 0.6% in the case of caustic soda. Although the number of times an alkaline solution which has been thus fortified may be used for the extraction of raw wood is variable depending largely upon the nature of the wood, it has been observed that extracting eight times in a manner stated above and fortifying the resulting extract with additional alkali before each extraction results in the production of an alkaline extract rich in lignins and polysaccharides-other-than-cellulose and, at the same time, leaves a fiber residue of useful composition and properties.

Recycling, or its equivalent operation, may profitably be practiced until such time as the contribution of alkali solubles of each new batch of fiber equals the amount of extracted alkali soluble material retained by the fibers upon separating the fibers and the extract. Obviously, this involves many factors including the amount of alkali solubles contributed by each successive batch of fiber, as well as the efficiency of the mechanical step of effecting said separation.

Similarly, the conditions of operation for isolating the desired lignin products from the lignin-containing extract are subject to some variation. Thus, various acids may be used for acidifying the lignin-containing extract. Any of the common mineral acids such as sulfuric acid, phosphoric acid or hydrochloric acid, as well as some of the organic acids, e. g. acetic acid, are suitable for this purpose. Sulfuric acid is a preferred member of this group.

The amount of acid used is likewise variable, and depends largely upon the alkalinity of the extract. In general, enough acid is employed to result in the formation of a substantially neutral solution, i. e. one having a pH of about 7.

The neutralized extract is concentrated to a point at which lignin I—*a* is insoluble, but at which its content of inorganic salts (principally sodium sulfate, when caustic soda and sulfuric acid are used in the extraction and acidification steps), polysaccharides-other-than-cellulose, and some types of lignin, are substantially soluble. There is thus obtained a lignin precipitate which is substantially free from contamination by inorganic salts and polysaccharides-other-than-

cellulose. Although the point at which this desideratum is attained varies with the relative proportions of solvent and solute and with other factors, when the proportions and operating conditions are substantially as given in the examples herein it is preferred to concentrate the neutralized solution to about 12% of its original volume.

Although a substantially aqueous solvent is employed in the extraction of lignin I—*a* to provide insoluble lignin I—*a*—1 and soluble lignin I—*a*—2, relatively minor proportions of other suitable reactive or non-reactive, organic or inorganic, materials may be mixed with the water where desirable or necessary, as where a sharper separation of these two lignin fractions is desired and thereby effected.

The temperature of the aqueous solvent is likewise variable. In general, an extracting temperature is employed, this being in the range at or near the boiling temperature of the solvent. Where water alone is used as a solvent, the preferred extracting temperature is at the boiling temperature of water at ordinary atmospheric pressure, i. e. at about 100° C.

In general, a sufficient amount of water is used to separate completely lignin I—*a*—1, the insoluble fraction, from lignin I—*a*—2, the soluble fraction. Inasmuch as these two lignin fractions differ materially in their solubility characteristics, it is preferred to use a substantial excess of aqueous solvent in effecting their separation. Insoluble lignin I—*a*—1 is obtained in a weakly acidic or neutral form and may be dried and used as such. Soluble lignin I—*a*—2, however, is obtained as a salt, e. g. as a sodium salt when caustic soda is used as the extracting alkali. It may be obtained as such by evaporation of the aqueous extract and drying of the residue. Although this form may be useful for some purposes, it may be desired for other uses to obtain the product in the form of a concentrated aqueous solution or as the free lignin acid. The latter may be accomplished by acidifying the neutral aqueous extract to a pH of about 1.5, using any suitable acid, e. g. a mineral acid such as sulfuric acid, and removing the precipitated lignin acid, as by filtration, followed, if desired, by washing and drying. This lignin acid is not identical with lignin I—*a*—1, described above, since it differs therefrom in solubility, degree of acidity, reactivity and other properties. It probably comprises, as do others of the lignin acids described herein, a mixture of organic acids having approximately similar acidities and somewhat similar properties so as to be precipitated together in the operating procedure.

The process of the invention may be illustrated by the following examples, wherein parts are expressed as parts by weight.

EXAMPLE 1

Western red cedar normal Asplund fiber, i. e. fiber prepared from the wood of the western red cedar by means of an Asplund defibrator, was extracted with a 0.6% aqueous solution of sodium hydroxide. A sufficient amount of this solution was used to provide a total sodium hydroxide content equivalent to 15% based on the dry weight of the raw wood fiber. This resulted in a reaction mixture having a consistency of about 4%, i. e. a mixture containing about 4 parts by weight of fiber per 100 parts of solution. The extraction was effected at the boiling temperature of the solution at normal atmospheric pressure for a duration of one hour. The fiber was then separated from the alkaline extract and washed with water for subsequent uses. The alkaline extract was fortified by the addition of caustic soda in an amount sufficient to build up the sodium hydroxide concentration to a level substantially that of the original solution. This required replacement of about 60% of the original sodium hydroxide. The fortified solution was then employed in the extraction of a further quantity of raw wood fiber. A total of eight extractions of raw wood fiber was carried out in this manner, reestablishing the concentration of sodium hydroxide in the extracting solution after each extraction. This resulted in the production of an alkaline extract rich in materials removed from the wood substances, i. e. rich in lignins and in polysaccharides-other-than-cellulose.

This alkaline extract, which has a pH of about 10, was processed for the recovery of a portion of its lignin content. This was accomplished by neutralizing with sulfuric acid and concentrating the neutralized extract by evaporation while adding further sulfuric acid as necessary to maintain the solution neutral. The solution was thus concentrated to about 12% of its original volume. It was then cooled and filtered. This resulted in the separation of lignin fraction I—*a*. This fraction after separation was boiled with water to further separate it into water-insoluble lignin I—*a*—1 and water-soluble lignin I—*a*—2.

Lignin I—*a*—1 resulting from the above treatment was removed by filtration, dried, and thus made available for utilization in various applications. The neutral, aqueous solution containing lignin I—*a*—2 was subjected to varying procedures in order to obtain the lignin product in any one of various lignin forms.

In one instance, the aqueous solution was evaporated to dryness, thereby forming as a product a dark brown powder comprising the sodium salt of lignin I—*a*—2.

In another case, the neutral, aqueous solution was acidified to a pH of about 1.5. This resulted in the precipitation of a lignin I—*a*—2 in the acid form. The precipitated lignin was separated from the mother liquor by filtration, and dried to form a brown powder as a product.

EXAMPLE 2

McMillan fiber, prepared from aspen wood by means of the McMillan defibrator, was extracted with dilute sodium hydroxide solution and the extract then fractionated, using substantially the same procedure as outlined in Example 1 for the processing of Asplund western red cedar fiber and its extract.

EXAMPLE 3

McMillan jack pine fiber was treated with dilute sodium hydroxide solution and the extract treated using substantially the same procedure as described in Example 1.

EXAMPLE 4

Normal defibrator (Asplund) jack pine fiber, subjected for about one minute to the action of steam at about 365° F. (150 pounds pressure), was also treated with dilute alkali and the extract processed for lignin separation as described in Example 1.

Certain properties of the various lignin products obtained in the foregoing examples are shown in the table.

Table

LIGNIN MELTING POINTS IN °C.

Lignin	Asplund Western Red Cedar (Example 1)	McMillan Aspen (Example 2)	McMillan Jack Pine (Example 3)	Asplund Jack Pine (Example 4)
1-*a*-1	[1] 300	[1] 300	[1] 300	[1] 300
1-*a*-2 (acid form)	265	250	250	275

[1] Approximate decomposition temperature.

ASH CONTENT (%)

1-*a*-1	5.1	13.8	15.0	11.4
1-*a*-2 (sodium salt form)	26.9	27.1	28.4	33.1
1-*a*-2 (acid form)	1.2		2.2	

SOLUBILITIES

[Of lignin 1-*a*-1 from Asplund western red cedar.]

Solvent	Solubility
water	insoluble.
acid	Do.
alkali	partially soluble.
methanol	very slightly soluble.
acetone	Do.
acetone methyl Cellosolve	Do.
(1-*a*-2, acid form):	
water	insoluble.
acid	Do.
alkali	completely soluble.
methanol	partially soluble.
acetone	Do.
acetone methyl Cellosolve	completely soluble.
(1-*a*-2, sodium salt):	
water	completely soluble.
acid	insoluble.
alkali	soluble.
methanol	insoluble.
acetone	Do.
acetone methyl Cellosolve	Do.

Having now described our invention and in what manner the same may be used, what we claim as new and desire to protect by Letters Patent is:

1. A process for obtaining lignin products from lignocellulose material which comprises treating said material with an aqueous solution of a basic-acting compound of an alkali metal at a temperature of from about normal room temperature to about the boiling point of said solution at atmospheric pressure and in concentration sufficient to provide not substantially more than about 15 parts of said alkali per 100 parts of dry lignocellulose material for dissolving from the material lignin and polysaccharides-other-than-cellulose and leaving a lignocellulosic residue, separating the resulting aqueous alkaline treating solution from the said lignocellulosic residue, reducing the pH of said alkaline solution to a value near the neutral point, conditioning the said aqueous solution by establishing a salt concentration therein sufficient to cause precipitation of a substantial amount of its lignin content, and separating the thus precipitated lignin from the residual solution, and treating the said lignin with an aqueous solvent for extracting components dissolved by said solvent.

2. A process for obtaining lignin products from lignocellulose material which comprises treating said material with an aqueous solution of an alkali metal hydroxide at a temperature of from about normal room temperature to about the boiling point of said solution at atmospheric pressure and in concentration sufficient to provide not substantially more than about 15 parts of said alkali metal hydroxide per 100 parts of dry lignocellulose material for dissolving from said

material lignin and polysaccharides-other-than-cellulose and leaving a lignocellulosic residue, separating the resulting aqueous alkaline treating solution from the said lignocellulosic residue, neutralizing the said aqueous alkaline treating solution and conditioning the said aqueous solution by establishing a salt concentration therein in an amount sufficient to cause precipitation of a substantial amount of its lignin content, separating the thus precipitated lignin from the residual solution, and treating the said lignin with an aqueous solvent for extracting components dissolved by said solvent.

3. A process for obtaining lignin from lignocellulose material which comprises treating said material with an aqueous solution of an alkali metal carbonate at a temperature of from about normal room temperature to about the boiling point of said solution at atmospheric pressure and in concentration sufficient to provide not substantially more than about 15 parts of said alkali per 100 parts of dry lignocellulose material for dissolving from the material lignin and polysaccharides-other-than-cellulose and leaving a lignocellulosic residue, separating the resulting aqueous alkaline treating solution from the said lignocellulosic residue, substantially neutralizing said alkaline solution and conditioning the said aqueous solution by establishing a salt concentration therein in an amount sufficient to cause precipitation of a substantial amount of its lignin content, separating the thus precipitated lignin from the residual solution, and treating the said lignin with an aqueous solvent for extracting components dissolved by said solvent.

4. A process for obtaining lignin from lignocellulosic material which comprises treating said material with an aqueous solution of a basic-acting compound of an alkali metal at a temperature of from about normal room temperature to about the boiling point of said solution at atmospheric pressure and in concentration sufficient to provide not substantially more than about 15 parts of said alkali per 100 parts of dry lignocellulose material for dissolving from the material lignin and polysaccharides-other-than-cellulose and leaving a lignocellulosic residue, separating the resulting aqueous alkaline treating solution from the said lignocellulosic residue, substantially neutralizing said alkaline solution and conditioning the said aqueous solution by establishing a salt concentration therein in an amount sufficient to cause precipitation of a substantial amount of its lignin content, separating the thus precipitated lignin from the residual solution, and treating the said lignin with an aqueous solvent, separating the resulting lignin residue from the resulting lignin-containing aqueous solution, and concentrating the said lignin-containing solution for forming as a solid product the dissolved components of the total lignin fraction in the form of their alkali metal salts.

5. A process for obtaining lignin from lignocellulose material which comprises treating said material with an aqueous solution of a basic-acting compound of an alkali metal at an elevated temperature not substantially higher than the boiling point of said solution at atmospheric pressure and in concentration sufficient to provide not substantially more than about 15 parts of said alkali compound per 100 parts of dry lignocellulose material for dissolving from the material lignin and polysaccharides-other-than cellulose and leaving a lignocellulosic residue,

separating the resulting aqueous alkaline treating solution from the said lignocellulosic residue, neutralizing the said aqueous alkaline treating solution and conditioning the said aqueous solution by establishing a salt concentration therein in an amount sufficient to cause precipitation of a substantial amount of its lignin content, separating the thus precipitated lignin from the residual solution, and treating the said lignin with an aqueous solvent, separating the resulting lignin residue from the resulting lignin-containing aqueous solution, and acidifying the resulting lignin-containing solution for precipitating as free lignin acids the dissolved components of the total lignin fraction.

6. A process for the production of lignin from lignocellulose material which comprises treating said material with an aqueous treating solution of a basic-acting compound of an alkali metal at a temperature of near the boiling temperature of the said solution at normal atmospheric pressure and in concentration sufficient to provide not substantially more than about 15 parts of said alkali per 100 parts of dry lignocellulose material for a time period of about one hour, thereby forming a solution which contains a composite lignin fraction and polysaccarides-other-than-cellulose and leaving a lignocellulosic residue, separating the said solution from the said residue, neutralizing the said solution and conditioning said aqueous solution by producing therein a salt concentration sufficient to effect the precipitation of a substantial amount of its lignin content, separating the said undissolved lignin from the residual solution, and treating the said undissolved lignin with hot water, thereby extracting therefrom its hot-water-soluble constituents and effecting its separation into hot-water-soluble and hot-water-insoluble fractions.

7. The process for obtaining lignin from lignocellulose material which comprises providing the said material in the form of ultimate fibers and opened-up bundles of ultimate fibers and constitutionally consisting primarily of cellulose, lignin and polysaccharides-other-than-cellulose, providing and maintaining an aqueous treating solution of an alkali metal hydroxide, treating said fibers with said alkaline solution at an elevated temperature and in concentration sufficient to provide not substantially more than about 15 parts of said alkali metal hydroxide per 100 parts of dry lignocellulose material for a time period sufficient substantially to exhaust the extracting

action of said solution for dissolving from the fibers lignin and polysaccharides-other-than-cellulose and leaving a fibrous residue, separating said fibrous residue from said alkaline solution, neutralizing said alkaline solution and conditioning said solution by producing therein a salt concentration in an amount sufficient to cause precipitation of a substantial amount of its lignin content, separating the thus precipitated lignin from the resulting solution, and treating the said lignin with an aqueous solvent for extracting components dissolved by said solvent and effecting the separation of said lignin into fractions characterized by solubility and insolubility in said solvent.

8. The process for obtaining lignin from wood which comprises providing the wood in the form of ultimate fibers and opened-up bundles of ultimate fibers and constitutionally consisting primarily of cellulose, lignin and polysaccharides-other-than-cellulose, providing and maintaining an aqueous treating solution of an alkali metal hydroxide, treating said fibers with said alkaline solution at an elevated temperature and in concentration sufficient to provide not substantially more than about 15 parts of said alkali metal hydroxide per 100 parts of dry wood fibers for a time period sufficient substantially to exhaust the extracting action of said solution for dissolving from the fibers lignin and polysaccharides-other-than-cellulose and leaving a fibrous residue, separating said fibrous residue from said alkaline solution, neutralizing said alkaline solution and conditioning said solution by producing therein a salt concentration in an amount sufficient to cause precipitation of a substantial amount of its lignin content, separating the thus precipitated lignin from the resulting solution, treating the said lignin with a hot aqueous solvent, separating the resulting lignin residue from the resulting lignin-containing aqueous solution, acidifying the said resulting lignin-containing aqueous solution for precipitating the free lignin acids, and separating the precipitated lignin acids from the resulting solution.

CLARK C. HERITAGE.
WILLIAM G. VAN BECKUM.

REFERENCES CITED

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

Wise: "Wood Chemistry, 1944," pages 286–288.