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PROCESS FOR METAL RECOVERY

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1

This invention relates to a process for metal recovery, and particularly to a process whereby metals may efficiently and economically be recovered from liquors in which they are contained in solution as metal salts.

Numerous situations exist in the metallurgical and metal working arts wherein there are obtained solutions of metal salts from which it is impractical or impossible to obtain the metal content by known methods of metal recovery. In other instances, methods of recovery exist but are not usually applied because they are too costly or too difficult of operation. In the electroplating industry, for example, electrolytic baths containing metal salts are used. These baths often become unsuited for use after operating periods of varying duration, principally because of contamination during the electroplating process by undesirable ions. This is particularly true in the electroplating of chromium and nickel, in which arts it is common practice to discard the electrolytic baths after a period of use, since no known method exists for economically recovering the substantial chromium and nickel content thereof.

Likewise, in various metallurgical procedures, solutions of metal compounds are obtained or encountered from which it is desirable to extract the metal content. Thus, in the mining of certain zinc ores, a dilute solution termed "mine water" is encountered. This solution contains in quite dilute concentrations salts of several metals, especially zinc and cadmium. It usually is not processed, however, because of the low concentration of metal salts present and because of the expense of recovering them. Solutions of metal salts are also encountered when metal ores, e. g. silver or gold ores, or various mill wastes or tailings, are leached with acids or other chemical reagents, thereby forming solutions of metal salts in water. It would obviously be desirable in these and other situations wherein solutions of metal salts are obtained to provide a practical method for the recovery of the metal content thereof.

Accordingly, it is an object of the present invention to provide a process whereby metals may efficiently and economically be recovered from solutions in which they are contained as metal salts. Other objects and advantages of the invention will in part be obvious and in part appear hereinafter.

It has been discovered that a large number of metals may economically and efficiently be recovered from solutions in which they are contained as metal salts by mixing with the said

2

solutions lignin products which, being comprised of alkali metal salts or ammonium salts of one or more lignin acids, form insoluble lignate salts with the metal content of the said solutions, and separating the thus formed metal lignates from the residual solutions.

The process of the invention may be applied to the recovery of a wide variety of metals, and is particularly applicable to the recovery of all metals which form insoluble lignin salts. The alkali metals and the metal-like ammonium ion form soluble lignates which may be recovered by concentrating the solutions to a point where the solubility concentration is exceeded. Metals forming insoluble lignates comprise substantially all metals to be found in group I, sub-group B, to group VIII, inclusive, of the periodic chart of the atoms. Stated otherwise, they comprise silver and substantially all the metals having a valence higher than 1. Certain lignin products react with various groups of metals to form insoluble lignates and are included in the scope of the invention. Such groups are the alkaline earth metals, the light metals excluding the alkali metals, the heavy metals, and the noble metals. Representative metals selected from these groups are beryllium, magnesium, aluminum, calcium, strontium, barium, copper, silver, gold, zinc, cadmium, tin, lead, chromium, manganese, iron, cobalt and nickel. The process of the invention is particularly applicable to the recovery from aqueous solutions of metal salts of lead, copper, zinc, nickel, chromium and silver.

The operating procedure whereby the metal lignates are prepared comprises, in its simplest embodiment, forming a solution containing the desired metal and reacting therewith a lignin product. The said lignin product may be introduced into the mixture in solid form as the free lignin acids, or in the form of the solid water-soluble lignin salts, e. g. the alkali metal salts. Alternatively and preferably, the lignin product may be introduced as an aqueous solution of the soluble lignin salts. Metathetical or double decomposition reactions then occur whereby the salts of the lignin products are obtained.

Should it be desired to convert one soluble lignin salt to another soluble lignin salt, as, for example, to convert sodium lignate to potassium lignate, a solution of the sodium lignate is acidified and the precipitated free lignin acid is removed and redissolved in a solution of the desired base, e. g. potassium hydroxide, whereupon the potassium lignate is formed. The soluble ammonium salt of a lignin may be formed by subjecting a lignin acid to an atmosphere of am-

monia, or the salt may be formed by reaction between a solution of a lignin product and the ammonium ion.

It has been found that definite stoichiometric relationship exists throughout the metathetical or double decomposition reactions referred to above. Thus, on a weight basis, the amount of lignin required to react completely with a metal decreases with decreasing valency and increasing atomic weight of the metal. Stated otherwise, metals of low atomic weights and high valences require greater amounts of lignin product to effect complete reaction than do metals of high atomic weights and low valences. It is also apparent that the lignin required for complete reaction with a metal decreases with decreasing molecular weight of the lignin and with increasing active basicity, i. e. the number of acid groups actively entering into salt formation.

In practice, however, the amount of lignin product which is admixed with the aqueous solution of metal salts is variable. It may be preferred to add the lignin in an amount greater than that just sufficient to combine with the metal content of the solution, i. e. the stoichiometric amount, to assure substantially quantitative recovery of the lignin salt. In other cases, however, it may be desirable to add an amount of lignin product which is less than the stoichiometric amount. This may be the case, for example, where it is desired to effect the separation of components of the metal salt solution which contains two or more metal salts, this being possible where the lignates of the said metals are of varying solubilities. Thus, if a limited amount of lignin product is added to such a solution, the lignin will react preferentially with that metal compound which forms the most insoluble metal lignate, thereby effecting the precipitation thereof as a product which is to a greater or lesser degree uncontaminated by the lignates of any metals which may be present in the solution.

The solvent employed is generally an aqueous solvent. However, varying proportions of other solvents may be employed, as to desirably affect the solubility of the constituents of the reaction mixture, provided the addition of said solvent does not interfere with the reaction whereby the metal salt content of the solution is converted to the metal lignate. It may also be possible, and even desirable in some instances, to add other substances to the reaction mixture. Thus, various suitable inorganic salts commonly known as "salting out" agents may be introduced in order to decrease the solubility of the metal lignate.

The reaction between the lignin product and a metal salt solution may be carried out at any suitable temperature. For the preparation of insoluble metal lignates, suitable temperatures are, in general, those at which the metal lignates are substantially insoluble in the solvent used, whereas the other products of reaction are soluble and remain in solution. In most instances, the operation may satisfactorily be effected at normal room or atmospheric temperatures.

Diverse methods may be employed to separate the insoluble metal lignate product from the resulting solution. Suitable methods are, for example, allowing the precipitated product to settle and drawing off the supernatant liquor; filtering the admixture of precipitated metal lignate and residual solution; centrifuging the said admixture, etc. In general, however, it is preferred to effect the separation of the desired metal lignate product by filtration, using either gravity type

or vacuum type filters or filter presses. Soluble lignates are conveniently separated from solutions by evaporation or by other methods of concentration.

The metal lignate products have per se many uses and may be applied thereto without further treatment. It has been found, for example, that the metal lignates are advantageously employed in the preparation of paints and other coating compositions. If desired, however, they may be further purified by suitable techniques or converted to other useful metal compounds by reaction with an appropriate acid or other chemical reagent. In metallurgical operations, for example, it will usually be desirable to obtain from the metal lignates the free metals or various inorganic metal salts or the metal oxides. The conversion of metal lignates to the free metals or metal oxides may readily be accomplished in most instances by simply heating the metal lignates to a temperature at which the organic content thereof is destroyed, as by volatilization, oxidation or burning. Such processes are termed herein the roasting, ignition, or burning of the metal lignates. In the case of some of the heavy metals, as, for example, the noble metals, the metal is obtained in the uncombined state, i. e., as the free metal, this result being favored by the presence of the organic content of the metal lignates which serves as a reducing agent. However, in the case of the more active metals, the metal lignates may be converted to the corresponding metal oxides. These may be used as such or may be converted to useful metal salts, as by reaction with a suitable acid. It is obviously desirable to carry out this roasting or igniting procedure in the presence of oxygen in order to destroy and remove the organic content of the metal lignates. It is likewise desirable to carry out the ignition or roasting under conditions such as to prevent the volatilization of the metals or of the metal oxides, or, if this is impossible or impractical, to provide means for condensing and collecting the volatilized metal products.

The lignin products employed in the metal recovery process of the invention comprise one or more lignin acids or the soluble salts of lignin products, e. g. the alkali metal salts, of the said lignin acids. They are obtained as products of a process which subjects lignocellulose material to the action of one or more chemical reagents of such a nature as to effect the cleavage of the ligninpolysaccharide complexes present in the said lignocellulosic material and thereby form soluble aromatic and aliphatic organic acids. These acids, or their alkali metal salts, comprise the herein referred to lignin products. Suitable lignin products are described, and their method of production disclosed, in our co-pending applications for Lignin Products, Serial No. 711,790, filed November 22, 1946 (PA 27–6–C), and for the Process for Producing Lignin Products, Serial No. 602,917, filed July 2, 1945 (PA 27–6–A). These applications are abandoned.

The procedure described therein was applied to the treatment of western red cedar and to jack pine, both woods being preliminarily defibered according to the process of Asplund, U. S. Patent 2,008,892. Each of the above prepared fiber samples 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 atmospheric pressure for a duration of one hour. The fiber was then separated from the 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 8 extractions of raw wood fiber was carried out in this manner, replenishing the concentration of sodium hydroxide in the extracting solution between each extraction. This resulted in the production of an alkaline extract rich in materials removed from the wood, i. e. rich in lignins and in polysaccharides - other - than - cellulose. The yield of treated fiber obtained upon filtration of the reaction mixture was about 77% for both wood species.

The alkaline extract was then processed for the recovery of its content of lignins. This was accomplished by neutralizing with sulfuric acid the alkaline extract, which had a pH of about 10, 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. Acidification of this neutralized and concentrated extract to a pH of 1.5 with sulfuric acid produces a suspension of precipitated lignin which is coagulated upon being heated to about 60° C. The mixture is then cooled and filtered and the recovered lignin 1 acid washed and dried.

Alternatively, the neutralized and concentrated extract when cooled and filtered yields solid lignin 1–*a*. When dried, the sodium salt of lignin 1–*a* is obtained, or when made into a thin slurry with water and acidified to a pH of 1.5 with sulfuric acid, lignin 1–*a* is obtained in the free acid form. The suspended precipitate of lignin 1–*a* acid is coagulated by heating the solution to about 60° C. and the resulting precipitate washed and dried.

Lignin 1–*a* when extracted with about five times its weight of hot water for about 2 hours separates into water-soluble lignin 1–*a*–2 and water-insoluble lignin 1–*a*–1. Lignin 1–*a*–1 is dried to produce the lignin in the form of its sodium salt, or is acidified to a pH of 1.5 as discussed above to obtain the lignin 1–*a*–1 acid. The water solution of lignin 1–*a*–2 is concentrated by evaporation or other methods to recover the lignin in the form of its sodium salt, or is acidified to a pH of 1.5, heated to coagulate the suspended lignin, filtered, and the lignin 1–*a*–2 acid washed and dried.

The neutral solution remaining after the separation of lignin 1–*a* is acidified with sulfuric acid to a pH of about 1.5, and, if desired, sufficient sodium sulfate is added to form a solution saturated with respect to this compound. The acidified saturated solution is then filtered in order to separate lignin acid 1–*b*.

Alternatively, the neutral solution remaining after the separation of lignin 1–*a*, when acidified to a pH of 5.0 by the addition of sulfuric acid, results in the precipitation of lignin 1–*b*–1, which is separated by filtration. The precipitated lignin 1–*b*–1 may be suspended in water and further acidified to pH 1.5 to obtain the full acid form thereof. The solution of pH 5.0 remaining from the above filtration may then be saturated with sodium sulfate if desired, acidified further to a pH of 1.5 with sulfuric acid, and then filtered thereby separating lignin 1–*b*–2 from the residual acidified solution.

The various lignin free acids obtained as described above were subjected to exhaustive chemical and physical analyses to determine their respective properties and chemical constitution. Elementary analyses showed all of the lignins to consist of carbon, hydrogen and oxygen. Since lignins in general decompose upon prolonged exposure to high temperatures, melting points were ascertained by suddenly exposing each lignin to various known high temperatures for a short time. This was accomplished by dropping the samples upon the surface of a regulated hot plate and observing the temperature at which melting occurred.

Selective methylation of lignins 1–*a*–1; 1–*a*–2; 1–*b*–1 and 1–2 was used to determine portions of their chemical constitution, utilizing dimethyl sulfate to methylate phenolic and alcoholic hydroxyl groups and diazomethane to methylate phenolic and carboxylic hydroxyl groups. Methylation and determination of methoxyl contents were performed according to well-known laboratory methods. By determining the initial methoxyl content, the methoxyl content after methylation with dimethyl sulfate, the methoxyl content after methylation with diazomethane, and the methoxyl content after methylation with both reagents, it is possible to calculate the minimum whole number of groups per combining weight of each lignin.

To illustrate a method for performing the above calculations, i. e. to ascertain the number of methoxyl, phenolic hydroxyl, alcoholic hydroxyl and carboxyl groups:

Let w=the combining weight of the lignin;
Let m=the whole number of methoxyl groups per combining weight;
Let a=the whole number of alcoholic groups per combining weight;
Let p=the whole number of phenolic groups per combining weight; and
Let c=the whole number of carboxylic groups per combining weight.

It is apparent that the per cent methoxyl is

$$\frac{(31m)\ 100}{w}$$

Since one CH_2 unit is added for each alcoholic, phenolic, or carboxylic hydroxyl group upon methylation thereof, the combining weight of the lignin increases by 14 for each group methylated. Thus, after methylation with dimethyl sulfate, the per cent methoxyl is

$$\frac{(31m+31p+31a)\ 100}{w+14\ (p+a)}$$

after methylation with diazomethane, the per cent methoxyl is

$$\frac{(31m+31p+31c)\ 100}{w+14\ (p+c)}$$

and after methylation with both reagents, the per cent methoxyl is

$$\frac{(31m+31a+31p+31c)\ 100}{w+14\ (a+p+c)}$$

After determining the per cent methoxyl for one lignin experimentally, the above equations may be solved simultaneously. Since five unknowns are represented in four equations, it is necessary to solve the equations in terms of one of the unknowns, preferably in terms of the combining weight. By trial and error methods, the value of combining weight must be found such as to give simple whole numbers for the values of *m*, *a*, *p* and *c*. Having thus calculated the number of respective groups, the percentage of those groups per combining weight of the lignin may readily be determined. Although the above described method of calculation imposes a limit upon the degree of accuracy to which the unknowns may be evaluated, it will be apparent to those skilled in the art that it is superior to one conventional method wherein the unknown quantities are evaluated from assumed molecular weights.

The percentages and numbers of the various groups found in the above mentioned lignins fractionated from western red cedar (WRC) and from jack pine (JP) are given in the following table. Electrotitration data indicate that the reaction whereby the lignin acid is formed from the alkali metal salt occurs more readily than does the reverse reaction.

Lignin	Number of Groups				Percentage of Groups			
	Methoxyl	Phenolic	Alcoholic	Carboxyl	Methoxyl	Phenolic	Alcoholic	Carboxyl
WRC, 1-*a*-1	8	6	3	0	13.2	5.5	2.7	
WRC, 1-*a*-2	5	7	1	0	11.4	8.7	1.1	0
WRC, 1-*b*-1	2	3	0	0	10.8	8.9	0.0	0
WRC, 1-*b*-2	3	5	2	2	8.2	7.5	3.0	7.9
JP, 1-*a*-1	7	11	3	0	10.0	8.5	2.4	0
JP, 1-*a*-2	4	7	1	0	9.0	8.6	1.2	0
JP, 1-*b*-1	1	2	0	0	8.0	8.7	0.0	0
JP, 1-*b*-2	2	5	2	1	5.9	8.0	3.2	4.2

The lignin free acids and their methylated derivatives are found to be substantially completely isoluble in water, butanol, di-n-butylamine, diethylether, benzene and carbon tetrachloride, and substantially completely soluble in the methyl ether of ethylene glycol and formic acid. Degrees of solubility were found in such solvents as acetone, methanol, acetic acid, hot glycerol, and in a mixture of equal parts of acetone and butanol.

The lignin free acids were found to be insoluble in dioxane while their respective methylated derivatives were soluble in that solvent. The lignin free acids were found to be soluble in an aqueous solution containing about 4% sodium hydroxide, a 50% aqueous solution of ammonium hydroxide, hot ethylene glycol, triethanolamine and furfuryl alcohol, while their respective methylated derivatives were insoluble in those solvents. It was found that no one of the lignins were precipitated from alkaline solution by reaction with carbon dioxide, and that they were soluble in a 40% aqueous solution of sodium xylene sulfonate and in a mixture of equal parts of methanol and ethylene dichloride.

The lignin acids 1, 1-*a*, 1-*a*-1, and 1-*a*-2 are only slightly soluble in a mixture of equal parts of methanol and acetone while the lignin acids 1-*b*, 1-*b*-1, and 1-*b*-2 are substantially completely soluble in that solvent.

Lignin 1 acid obtained from both western red cedar and jack pine has a melting point of between about 200° and 213° C. Lignin 1 acid from western red cedar is dark brown in color and that fraction from jack pine is dark tan in color.

Lignin 1-*a* acid obtained from western red cedar has a melting point of between about 225° and 236° C. and is dark brown in color, while the corresponding lignin from jack pine has a melting point of between about 250° and 275° C. It is dark tan in color.

Lignin 1-*a*-1 acid obtained from either species has a melting point of between about 250° and 275° C. The initial acidity of western red cedar lignin is pH 4.8 and that of jack pine is pH 4.0. The lignin from western red cedar is dark brown in color while that from jack pine is dark tan. Methylation of the western red cedar lignin with dimethyl sulfate and with diazomethane produces a tan color product having a melting point between about 213° and 225° C. Methylation of the lignin derived from jack pine with dimethyl sulfate produces a cream colored product melting between about 237° and 250° C. while methylation with diazomethane results in a cream colored product melting between about 225° and 237° C.

Lignin 1-*a*-2 acid obtained from western red cedar has a dark reddish brown color and melts at a temperature between 225° and 237° C. Its initial acidity is pH 3.2. The derivative obtained by methylation with dimethyl sulfate is light brown in color and has a melting point of between about 275° and 300° C., while the derivative produced by methylation with diazomethane is light brown in color and melts between about 213° and 225° C. The lignin obtained from jack pine is medium dark tan in color and melts between about 275° and 300° C. Its initial acidity is pH 3.2. Methylation with dimethyl sulfate produces a dark tan derivative melting between 250° and 283° C. and the derivative from the diazomethane methylation is light tan in color and has a melting point of between 225° and 237° C.

Lignin 1-*b* acid obtained from western red cedar is medium brown in color and has a melting point of between 200° and 213° C., while that derived from jack pine is dark tan in color and melts between about 190° and 200° C.

Lignin 1-*b*-1 acid from western red cedar is dark brown in color and melts between 213° and 225° C. Its initial acidity is pH 3.5. Methylation with dimethyl sulfate produces a medium brown colored derivative melting between 237° and 250° C., while the derivative obtained by methylation with diazomethane is medium brown in color and melts between 213° and 225° C. The corresponding lignin derived from jack pine is dark tan in color and melts between 225° and 237° C. The initial acidity is pH 3.3. Dimethyl sulfate reacts to produce a methylated derivative having a dark tan color and melting between 250° and 283° C. The derivative produced by methylation with diazomethane is light tan in color and melts between 225° and 237° C.

Lignin 1–b–2 acid obtained from western red cedar is medium dark brown in color and has a melting point between 213° and 225° C. Its initial acidity is pH 3.1. The methylated derivative obtained upon reaction with dimethyl sulfate has the same color and melts between 225° and 237° C., while the derivative obtained from diazomethane methylation is dark tan in color and melts between 213° and 225° C. The lignin obtained from jack pine has the same melting point as that obtained from cedar and is dark reddish brown in color. Its initial acidity is pH 2.9. Methylation with dimethyl sulfate produces a dark tan derivative melting between about 275° and 288° C. and the product from methylation with diazomethane is light brown in color and melts between 225° and 237° C. During methylation of the various lignins with dimethyl sulfate, lignin 1–b–2 remained completely soluble in the alkaline methylating solution whereas the other lignins became insoluble. This observation and the methylation percentage data indicate the presence of carboxyl groups in lignin 1–b–2.

In preparing metal salts of the above identified lignins, each lignin acid is preliminarily converted to the form of its soluble sodium salt by treatment with a dilute aqueous solution of sodium hydroxide. A solution containing about 5% lignin soda salt was thus obtained and an excess thereof was used in preparing the several lignin metal salts. It should be emphasized that the solid lignin alkali metal salts or ammonium salts, as well as partially soluble lignin acids, may equally well be added to the solution of metal salt as disclosed above. Solutions containing metal salts in known concentrations of about 2% by weight were mixed with the above prepared lignin solutions whereupon the metal lignates were obtained.

The insoluble metal lignates may be weighed and then ignited to destroy the organic matter, and the ash residue of metal or metal oxide weighed to ascertain the amount of metal recovered. By dividing the weight of metal lignate by the weight of metal recovered, a ratio of parts of lignin required to precipitate one part of metal is determined. Knowing the original amount of metal present in the solution and the amount of metal recovered therefrom, the per cent metal recovery is readily obtained. It should be recognized that solubility of the metal lignates will affect the degree of recovery obtainable, and that suitable techniques known to those experienced in the art may be employed to decrease the solubility and thus increase the efficiency of metal recovery.

Having determined the weight of ash obtained by igniting the metal lignate recovered from solution, calculation of the minimum combining weights of the various lignins may be made. This is accomplished by dividing the molecular weight of the ash, e. g. the molecular weight of the metal or metal oxide, by the percentage of ash obtained, subtracting therefrom the atomic value of weight of metal combined with the lignin and dividing the result by the number of combining valences of the metal. For example, an aluminum lignate was prepared which, upon ignition, was shown to contain 4.2% Al_2O_3. The molecular weight of Al_2O_3 is 101.94, the atomic value of weight of metal combined with the lignin is twice the atomic weight of aluminum, or 53.94, and the number of combining valences of the metal is twice the valence of aluminum in its oxide state, or 6. Thus the value of combining weight of the lignin is found to be

$$\frac{(101.94)(100)-(53.94)(0.042)}{(0.042)(6)}=395$$

It is apparent that the combining weights of the desired lignins may be utilized to advantage in determining the ratio of parts of lignin required to combine with one part of a desired metal. Thus, by merely multiplying the combining weight of the lignin by the valence of the metal in its salt form and dividing the product by the atomic weight of the metal, the parts of lignin required to combine with one part of that metal is determined.

Solutions of various metal salts were admixed with various lignins and the respective metal lignates were recovered as described hereinabove. From analytical data obtained as described above it was found that the amount of lignin required to precipitate a metal decreases with increasing atomic weight and decreasing valency of the metal. Thus, aluminum with a high valence and low atomic weight requires a greater amount of lignin for precipitation than does silver or lead which have lower valences and higher atomic weights. Because the univalent silver has an atomic weight of about one-half that of the bivalent lead, the lignin requirements for both metals are substantially the same.

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. The process comprising subjecting lignocellulose material in a defibered state to the action of a dilute aqueous solution of a basic-acting compound of an alkali metal and thereby dissolving from said lignocellulose material a lignin consisting of carbon, hydrogen and oxygen, said lignin being insoluble in dioxane and incapable of being precipitated from an alkaline solution by reaction with carbon dioxide, concentrating the so-produced lignin solution, acidifying the latter to a pH of about 1.5 whereupon a lignin product is precipitated leaving a residual solution, separating said lignin precipitate from said residual solution, forming an aqueous solution from said lignin precipitate, said aqueous solution containing a lignin material selected from the group consisting of water-soluble lignic acid and water-soluble salts of lignic acid, reacting said aqueous solution with a solution of a salt of a metal which forms a water-insoluble metal lignate whereupon a metal lignate is precipitated, and recovering said precipitate.

2. The process comprising subjecting lignocellulose material in a defibered state to the action of a dilute aqueous solution of a basic-acting compound of an alkali metal and thereby dissolving from said lignocellulose material a lignin consisting of carbon, hydrogen and oxygen, said lignin being insoluble in dioxane and incapable of being precipitated from an alkaline solution by reaction with carbon dioxide, neutralizing the so-produced solution, concentrating the neutralized solution until the lignin content thereof precipitates leaving a residual solution, separating said lignin precipitate from said residual solution, forming an aqueous solution from said lignin precipitate, said aqueous solution containing a lignin material selected from the group consisting of water-soluble lignic acid and water-soluble salts of lignic acid, reacting said aqueous solution with a solution of a salt of a metal which forms

a water insoluble metal lignate whereupon a metal lignate is precipitated, and recovering said precipitate.

3. The method defined in claim 1 in which the basic-acting compound of an alkali metal is an alkali metal hydroxide.

4. The method defined in claim 2 in which the basic-acting compound of an alkali metal is an alkali metal hydroxide.

5. The process comprising subjecting lignocellulose material in a subdivided form to the action of a dilute aqueous solution of a basic acting compound of an alkali metal and thereby dissolving from said lignocellulose material a lignin consisting of carbon, hydrogen and oxygen, said lignin being insoluble in dioxane and incapable of being precipitated from an alkaline solution by reaction with carbon dioxide, recovering the lignin from said lignin solution, forming an aqueous solution from the recovered lignin product, said aqueous solution containing a lignin material selected from the group consisting of water-soluble lignic acid and water-soluble salts of lignic acid, reacting said aqueous solution with a solution of a salt of a metal which forms a water-insoluble metal lignate whereupon a metal lignate is precipitated, and recovering said precipitate.

6. The process comprising subjecting lignocellulose material in a subdivided form to the action of a dilute aqueous solution of an alkali metal hydroxide and thereby dissolving from said lignocellulose material a lignin consisting of carbon, hydrogen and oxygen, said lignin being insoluble in dioxane and incapable of being precipitated from an alkaline solution by reaction with carbon dioxide, recovering the lignin from said lignin solution, forming an aqueous solution from the recovered lignin product, said aqueous solution containing a lignin material selected from the group consisting of water-soluble lignic acid and water-soluble salts of lignic acid, reacting said aqueous solution with a solution of a salt of a metal which forms a water-insoluble metal lignate whereupon a metal lignate is precipitated, and recovering said precipitate.

7. The process comprising subjecting lignocellulose material in a subdivided form to the action of a dilute aqueous solution of a basic-acting compound of an alkali metal and thereby dissolving from said lignocellulose material a lignin consisting of carbon, hydrogen and oxygen, said lignin being insoluble in dioxane and incapable of being precipitated from an alkaline solution by reaction with carbon dioxide, recovering the lignin from said lignin solution, forming therefrom an aqueous solution of alkali lignate, said aqueous solution having a concentration of approximately 5% alkali lignate, reacting said alkali lignate solution with a solution of a salt of a metal which forms a water-insoluble metal lignate whereupon a metal lignate is precipitated, and recovering said precipitate.

8. The process comprising reacting an aqueous solution of a material selected from the group consisting of water-soluble lignic acid and water-soluble salts of lignic acid, said lignic acid (*a*) consisting of carbon, hydrogen, and oxygen; (*b*) being insoluble in dioxane, and (*c*) incapable of being precipitated from an alkaline solution by reaction with carbon dioxide; and an aqueous solution of a salt of a metal which forms a water-insoluble metal lignate, said reaction producing a precipitated metal lignate, and recovering the latter.

9. The process comprising subjecting lignocellulose material in a subdivided form to repeated extraction with sodium hydroxide in an amount equivalent to about 15% based on the dry weight of the raw wood fiber to thereby dissolve from said lignocellulose material a lignin consisting of carbon, hydrogen and oxygen, said lignin being insoluble in dioxane and incapable of being precipitated from an alkaline solution by reaction with carbon dioxide, neutralizing the resulting alkaline extract, concentrating the neutralized extract to about 12% of its original volume while adding additional neutralizing agent to maintain the solution neutral, acidifying the concentrated neutralized solution to a pH of 1.5 whereupon a lignin product is precipitated leaving a residual solution, coagulating said lignin precipitate, separating the latter from said residual solution, forming an aqueous solution from said lignin precipitate, said aqueous solution containing a lignin material selected from the group consisting of water-soluble lignic acid and water-soluble salts of lignic acid, reacting said aqueous solution with a solution of a salt of a metal which forms a water-insoluble metal lignate whereupon a metal lignate is precipitated, and recovering said precipitate.

CLARK C. HERITAGE.
WILLIAM G. VAN BECKUM.

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