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ALKALI-LIGNIN TANNING AGENTS AND METHOD OF PREPARATION

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This invention relates to tanning compositions derived from the spent liquors resulting from the alkaline digestion of wood in the manufacture of wood pulp and to a method of preparing the same. Specifically the invention relates to tanning agents prepared from alkali-lignin as hereinafter defined.

Many proposals have been made to prepare tanning agents from "lignin." The term "lignin" unfortunately has been used loosely to cover both the material as it occurs in combination with cellulose in wood and other natural products, and the lignin compounds separated from wood and the like, such as those formed in the process of making pulp. These lignin compounds vary considerably in composition and properties depending upon the method of separation employed.

For example, the lignin compound occurring in the usual spent acid sulfite liquors is present there as a calcium lignosulfonate; it is soluble in acid solutions but is precipitated by lime and is infusible.

Another form of lignin, sometimes referred to as acid lignin, is the residue left when wood is subjected to an acid hydrolysis or is "saccharified" by treatment with strong sulfuric or hydrochloric acid. Acid lignin is insoluble in acid solutions, insoluble in dilute alkalies and is infusible.

Some of the lignin products derived from the spent liquors of the wood pulp industry have a certain degree of usefulness in the leather industry, but to the best of my knowledge, no successful tanning agents have been prepared heretofore except those from waste liquors from the sulfite process, and these are all used as supplements or extenders to the natural vegetable tans such as those extracted from oak, chestnut, quebracho, wattle, etc.

One object of this invention is to provide tanning agents derived from the spent black liquors from an alkaline digestion of wood or other form of ligno-cellulose.

Another object is to provide tanning agents from spent alkaline liquors of the wood pulp industry that compare favorably with the better commercial natural vegetable tanning agents.

Another object is to provide a method of preparing valuable tanning agents from alkali-lignin.

The raw material for the present invention is what may be termed "alkali-lignin." By alkali-lignin I mean the lignin derivatives formed when wood or other lignocellulosic material is subjected to hot alkaline digestion usually under pressure. It is present in the spent black liquor resulting from pulping wood by, for example, the soda process, the sulfate or kraft process, and the alkaline sulfite process. Although there may be some more or less minor differences in the specific constitution of the alkali-lignins, depending on whether they are derived from the soda, sulfate, or the alkaline sulfite process, I have found that all these alkali-lignins may be used as starting materials for the present invention.

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The alkali-lignins as herein defined are soluble in 2% sodium hydroxide at room temperature. They may be precipitated by the addition of an acid or acidic material to the spent black liquor from the aforementioned alkaline pulping processes. The precipitated alkali-lignins melt generally at a temperature in the range of 160 to 210° C., depending upon the alkaline cooking process employed, the species of plant cooked, and the recovery cycle. Alkali-lignins will generally have an ultimate analysis of 64.5% to 68% carbon, 5.5% to 6% hydrogen, and a methoxyl content of from 11% to 20%. The alkali-lignins correspond in general to the material known as meta-lignin.

I have discovered that if finely divided alkali-lignin suspended in water is abundantly treated with chlorine and the resulting alkali-lignin chlorine composition is treated with alkali, there results a composition which is soluble in water on the acid side as well as the alkaline side, and which has a high tanning potency.

The process of my invention is advantageously carried out as follows: "black liquor" resulting from an alkaline digestion of wood or other lignocellulosic material is first treated with an acid or acidic material, such as for instance, sulfuric or hydrochloric acid, carbon dioxide, sulfur dioxide, etc. The black liquor may be used in the dilute form after the cellulosic pulp has been filtered off, but I prefer to use it after it has been partially concentrated, as, for instance, in the multiple effect evaporators of the recovery system. As the pH of the black liquor is reduced to about 9 or 8 by the addition of the acid, alkali-lignin is precipitated in a form known as "sodium lignate." This readily salts out from the black liquor but can be dissolved in water.

The sodium lignate may be removed from the black liquor and treated with chlorine as hereinafter described, or more acid may be added to the black liquor to bring the pH down as low as 4 at which point a maximum yield of alkali lignin is obtained; this acid precipitated (at a pH below 7) alkali-lignin separates out as a dark some-

what slimy precipitate. This is then separated from the liquid by filtration or other means.

In case the black liquor is derived from a kraft or sulfate process I prefer to use sulfur dioxide as the acid material as sulfur dioxide supplies a source of sulfur in the recovery system of the black liquor processing. With black liquor from a soda process carbon dioxide is advantageous.

The alkali-lignin is next subjected to the action of chlorine. A suspension or solution in water as the case may be containing from about 3% to 10% of alkali-lignin is normally employed. Higher concentrations can be used, or if desired, the alkali-lignin can be treated in the form of a wet paste, but in general a relatively dilute slurry is preferred. Advantageously, if the alkali-lignin is in the acid precipitated form, it is reduced to fine particle size as by passing the slurry through a colloid mill.

When an aqueous solution of sodium lignate is used for the chlorine treatment, the hydrochloric acid, which is formed by reaction of chlorine with alkali-lignin, rapidly reduces the pH of the solution below 7 whereupon the alkali-lignin is precipitated. Further treatment with chlorine proceeds as when a slurry of acid precipitated alkali-lignin is used as the starting material.

The chlorine treatment is conveniently carried out by introducing chlorine gas into the suspension or solution of alkali-lignin; or the alkali-lignin can be added to an aqueous chlorine solution containing sufficient proportion of chlorine to carry out the desired reaction. Good agitation is desirable. From a study of the reaction rate it appears that one atom of chlorine together with an atom of oxygen is introduced into the lignin molecule rapidly. Additional chlorine enters the molecule more slowly.

The reaction of chlorine and alkali-lignin is continued until the alkali-lignin product analyzes 15% or more chemically combined chlorine on the dry weight of the product. I have discovered that the potential tanning properties of the alkali-lignin increase as the chlorine content increases above 15% until, at a chlorine content of about 25% to 30%, a maximum in potential tanning content is attained. This normally requires from 1 to 3 hours, but may require only a fraction of an hour or may take as long as 15 hours depending upon the rate of introduction of chlorine, and whether or not the reaction vessel retains the chlorine until it is consumed. This reaction may be carried out as a batch process or continuously and either at atmospheric pressure or above. Additional chlorine may be introduced into the product by severe treatment but with difficulty and with no substantial improvement in tanning content. At around 32% chlorine content the potential tanning properties appear to decrease. A chlorine content of at least 20% is preferred in order to insure adequate solubility of the final product. It is characteristic of the products thus prepared that they are soluble in dilute solutions of mild alkalies at room temperature, for example, in a 2% solution of sodium carbonate.

The temperature of the chlorine treatment has not been found critical although cooling of the aqueous alkali-lignin system (either slurry or solution) may be desirable at times to remove the heat liberated in the reaction. Good results have been obtained starting with the system at room temperatures. The system is ordinarily cooled to maintain the temperature below 90° F., but good tanning materials can be produced over the temperature range of 32° to 140° F. As the temperature approaches 200° F. it becomes difficult to combine an adequate amount of chlorine with the lignin. Pressure facilitates the chlorine treatment; pressure of as low as 3 to 25 pounds above atmospheric speed the reaction.

As stated above the treatment of the alkali-lignin in water with chlorine also brings about an oxidation of the alkali-lignin composition. The reaction product ordinarily will contain from about 24% to 28% oxygen depending on the chlorine content, the higher oxygen content corresponding to a lower chlorine analysis and vice versa.

At the end of the chlorine treatment the insoluble reaction product may be separated from the mother liquor, and washed free of hydrochloric acid and treated with alkali, or alternatively alkali may be added directly to the suspension. The alkali used is advantageously taken from the class consisting of alkali-metal hydroxides, carbonates and bicarbonates. There is reason to believe that in the chlorine treatment two atoms of chlorine and one atom of oxygen are introduced into each alkali-lignin unit. One of the chlorine atoms is readily reactive while the other is relatively non-reactive. As a result of the treatment with alkali apparently the reactive chlorine is replaced by hydroxyl to give a product which is soluble in water in the acid pH range commonly used in vegetable tanning and on the alkaline side as well. A certain amount of chlorine remains in the product and cannot be readily removed even by heating with a strong caustic solution. In the case of a chlorine-treated alkali-lignin having an initial chlorine content of 25% to 30% on dry basis, the chlorine content remaining after dissolving in caustic will be about 15% to 18%, while a product having a chlorine content of 15% to 16% will, after treatment with alkali, have a chlorine content of about 12%.

For the alkali treatment, I prefer to use sodium hydroxide because of its convenience. Sufficient alkali is added to solubilize the lignin product completely and this usually necessitates bringing the pH up to a value of 7 or above, e. g., 8 to 8.5. Solubilization can be achieved at a pH of 5.5 to 6 if the alkali is added slowly over a period of several hours. High pH values, as for example 10 and 11, are not detrimental but entail an increase in inorganic content. A chlorine treated alkali lignin containing about 25% chlorine will ordinarily require about 0.20 g. sodium hydroxide per gram of material, while one containing 15% chlorine will require about 0.13 g. sodium hydroxide, but this will vary depending upon the amount of residual hydrochloric acid.

One method of processing the chlorinated-oxidized alkali-lignin is to dry the material after it has been washed, mix it with the proper amount of dry alkali to convert it into the water-soluble form, and market the powdered mixture. The tanning properties of the material in this case are developed when the tanner prepares his solution.

In any case, after the chlorine-treated alkali-lignin is put in solution, the pH is adjusted to the value desired for the tanning operation.

The hydrolyzed chlorine-treated alkali-lignin produced as described above carries with it a substantial amount of inorganic salts, particularly sodium chloride formed in the hydrolysis step. In certain tanning operations such as the tanning of calf skin, "mordanting," and vegetable

retan of chrome tanned hides, the presence of inorganic salts is not objectionable, and often salts are deliberately added to prevent undesirable effects in the leather such as undue swelling, etc. The salt accompanying the alkali lignin tanning agent of this invention is therefore a suitable ingredient for certain types of tan liquors.

On the other hand, in the preparation of sole leather and for many other types of tanning, only a small amount of inorganic salt can be tolerated. This is particularly true in cases where recirculating systems involving countercurrent movement of hides and liquors are employed. As the tanning liquor is used to treat successive batches of hides or skins the tannin will approach exhaustion much more rapidly than the dissolved salts. When such weakened liquors are successively restrengthened an increase in salt concentration can occur which may influence leather quality.

I have found that if the above defined chlorine-treated alkali-lignin, subsequent to being hydrolyzed in aqueous alkali, is contacted with an aqueous acid solution having a pH of from about 0.1 to 3, the lignin derivative is substantially insoluble therein, whereas the salt and other impurities are soluble in the acid and can thus be removed. Preferably the pH should be in the range of about 1 to 2; as the pH increases, the lignin derivative becomes more soluble and more difficult to filter; low pH conditions, 0.1 and below, are not deleterious but require more acid than is necessary. If the hydrolyzed product is first dried to form a finely divided material or if the filter cake of acid precipitated material is dried the extraction of the impurities with the acid is greatly facilitated. In any event the filter cake or the dried material is washed by being slurried in water at a pH below 3 and then filtered; the operations are repeated as many times as desired. One washing is usually sufficient to reduce the inorganic salt content to below 5% and two washings usually reduces it to 1% or less.

The acid treated material is substantially freed of acid, then resolubilized by adding alkali in sufficient amount to form a solution having a pH above about 5; much less alkali is needed than in the first solubilizing step. As a net result, the inorganic content will usually be in the range of from 10% to 20% of the soluble solids as compared to an inorganic content of from 25% to 50% of the soluble solids of a solution after the first solubilizing step. By thus reducing the salt content, the lignin product is converted into a material having a much wider field of application in tanning operations.

The process of removing salt by the method described modifies the tanning properties of the hydrolyzed chlorine-treated alkali lignin in that the rate of tanning is reduced. It is possible that the strong hydrochloric acid used in the process may, in some little understood manner, polymerize or otherwise change the alkali-lignin derivative to bring about the slower tanning rate. The tannin content, which is based on a ten minute test with hide powder is also lowered, but if the test is extended for 24 hours the material will be found to have substantially as high a tannin content as a portion not precipitated with acid and tested for 24 hours. In this respect, the tanning agents of this invention differ from the natural vegetable tans which normally show no substantial increase in tannin content values when tested for longer than 10 minutes.

In dissolving the chlorine-treated alkali-lignin with an alkali, either from the chlorine step or after the hydrolyzed material has been acid precipitated, heat is not required to put it in solution or to develop the tanning properties.

The ultimate product after the chlorine and alkali treatments is a highly effective tanning agent having a tannin content of from 40% to 75% based on the dry weight of the chlorine treated alkali-lignin, as determined by the standard hide powder method. This value compares favorably with the better natural vegetable tanning agents. The tannin content values given throughout the specification were determined according to the hide powder test described in the manual, Methods of Sampling and Analysis, American Leather Chemists Association, Proposed Methods, 1946, pages A–7 to A–13. In brief, the test consists of agitating a standard amount of hide powder with a solution of the tanning agent, filtering out the hide powder, and determining the percentage of agent removed by the hide powder; the standard time of contact between the hide powder and tanning agent solution is 10 minutes, and the tannin content values given herein were determined on a 10 minute basis unless otherwise specified. The test solution of tanning agent was adjusted to a pH of 4.0±0.5 in each determination.

Furthermore, the tanning agents of my invention produce commercial quality leather and are suitable for use in various vegetable tanning processes. They have been used alone and in blends with other commercial tans including quebracho, wattle, and sulfite spruce in operations such as chrome retan, mordanting, pickle skin and flesh split tanning, etc. The leather tanned with my agents has good resistance to tear and cracking, has a medium to light brown color, exhibits shrink temperatures of 75° F. to 82° F. and is highly resistant to mold growth. No mold is encountered during the tanning processes, thereby eliminating the necessity of adding a disinfectant. Furthermore, the finished leather is moldproof.

The invention will be lilustrated further by the following examples:

Example 1

Concentrated black liquor from a conventional sulfate digestion of southern pine was used as the starting material. Sulfur dioxide was introduced into 525 pounds of the liquid at 18° Bé. at room temperature with thorough agitation until the pH was reduced to about 4.5. The temperature of the liquor was then raised to 155° F. to render the precipitate more easily filterable. After cooling the liquor, the precipitate was separated by decantation, reslurried in water, and separated by filtration. A dry sample of this precipitate showed the following analysis: 67.3% carbon, 6.04% hydrogen, a methoxyl content of 12.74%, and an oxygen content of 26.66% by difference.

About 25 pounds dry weight of the precipitate was mixed with sufficient water to form a 10% slurry and run through a Premier colloid mill at 0.003 inch clearance. Chlorine was bubbled in for about 13 hours while the mixture was thoroughly agitated; the temperature was maintained between 45° and 55° F. by the addition of ice. About 37 pounds of chlorine was used. The product was separated from the supernatant liquor,

then reslurried with water, and filtered twice. It analyzed as follows on a moisture free basis:

	Per cent
Chlorine	25.2
Carbon	45.4–45.8
Hydrogen	2.6– 2.9
Sulfur	0.67
Methoxyl content	1.93
Oxygen (by difference)	25.57

The yield was about 27.2 pounds, dry weight. The product was dissolved in water by the addition of sodium hydroxide to a pH of 8 and then acidified to pH of about 4 with sulfuric acid. Tested by the American Leather Chemists Association hide powder technique it had a tanning content of approximately 75% on the dry basis of the chlorine-treated alkali-lignin.

A calf-skin was tanned under conditions equivalent to commercial tanning using as the tanning agent the chlorine-treated alkali-lignin dissolved in dilute aqueous caustic using about 24 grams of sodium hydroxide per 100 grams of alkali-lignin product, dry basis, and then acidified. The skin was pickled, depickled, and then treated in a series of eight tan baths over a period of 8 days starting with a liquor having a tannin content of 0.5 gram per 100 cc. and a pH of 4.9, and ending with a liquor having a tannin content of 2.2 grams per 100 cc. and a pH of 3.46, the intermediate baths being graduated between these two. The skin was then bleached, retanned, fatliquored, and oiled off. A good grade of leather was obtained having a shrink temperature of 80° C. comparable to that obtained with other vegetable tanning agents; firmness and temper were as good as obtained when using chestnut extract; color was brown similar to that produced by oak bark extract; rate of penetration was better than for chestnut extract; good plumpness was obtained and the yield of leather is comparable to that obtained with quebracho, i. e. the leather contained about 40% hide substance and 60% tannins, etc. The leather as well as the liquor showed no signs of mold growth during the tanning process nor did the leather when innoculated with mold organisms.

Example 2

Carbon dioxide was introduced into hot partially concentrated black liquor from a conventional sulfate pulp digestion until a pH of 8.6 was reached; a precipitate of sodium lignate was formed. The sodium lignate was filtered out and dissolved in hot water; hydrochloric acid was added to precipitate the alkali-lignin and this product was then washed by decantation until substantially free of sodium salts. About 25 pounds (dry basis) of the precipitated lignin was slurried with water at 5.7 solids. Chlorine was bubbled into the slurry at a moderate rate for 6½ hours. The slurry, thoroughly agitated throughout, varied in temperature from 93° to 140° F. The lignin product contained 28.9% chlorine and assayed 62.7% tannin content by the hide powder method. The product was dissolved in water with caustic at a pH of about 7 and acidified to a pH of about 4. A sheepskin skiver tanned with this solution had a light brown color and good feel properties. It exhibited a shrink temperature of 79.6° C. which compares favorably with skivers prepared with commercial vegetable tans.

Example 3

Meadol, a commercial sodium lignate obtained by carbon dioxide precipitation of soda process black liquor from a digestion of deciduous wood and then washed with dilute sulfuric acid until ash-free, was used. The lignin derivative analyzed 65.1% carbon, 5.97% hydrogen, and methoxyl content 20.2%. One pound of the powdered lignin material (insolubilized by an acid wash) was suspended in water to form a 5% slurry; chlorine was introduced into the agitated slurry for 6½ hours during which the temperature rose from 67° to 102° F. The chlorine-treated alkali-lignin contained 26% chlorine and assayed 63.5% tannin content. A skiver was tanned using the above product dissolved in dilute caustic at a pH of about 8 and brought to a tanning pH of 4 by the addition of sulfuric acid. Shrink temperature was 79° C. and exhibited properties of good commercial quality.

Figure 4

Cooking liquor from an alkaline sulfite digestion of southern pine was acidified to a pH of 3 by the addition of sulfuric acid to precipitate the alkali-lignin. The digestion had been carried out holding a temperature of 345° F. for 1⅔ hours and using a liquor having an initial composition of about 55 grams of sodium hydroxide and 28 grams of sodium sulfite per liter. On analysis the precipitated alkali-lignin contained 64.5% carbon and 5.98% hydrogen. The precipitate was washed, then slurried in water at a solids content of 1.4% and the slurry treated with chlorine gas for 1¾ hours at 72° to 85° F. The product contained 26.8% chlorine and had a tannin content of 58%. A skiver tanned with the product had a shrink temperature of 75° C. and was of good color and quality. For the determination of tannin content and the skiver tanning, a solution of the product was prepared by dissolving in cold caustic at a pH of 8 and then acidifying to a pH of 4.

Example 5

Partially evaporated black liquor from a conventional sulfate digestion of southern pine chips was treated with carbon dioxide until the pH was lowered to about 9; it was then heated to about 190° F., allowed to cool, and the precipitate filtered out. This sodium lignate precipitate was dissolved in water to form a solution (sp. gr. of 1.018) containing 4.5% solids and having a pH of about 8.5. The solution was fed into an enclosed continuous reaction chamber as a small stream while chlorine was simultaneously introduced through the same inlet and intimately blended with the solution with vigorous turbulence. The chlorine was introduced at the rate of about 8 pounds per hour and the sodium lignate solution at the rate of 17 gallons per hour. As the chlorine was introduced, acid was formed and the pH dropped immediately to a value well below 7 with concomitant precipitation of the alkali-lignin derivative as very fine particles. The precipitated lignin derivative and the chlorine were retained in intimate contact for about one hour at a pressure of about 6 pounds per sq. in. and a temperature between 85° and 90° F. The reaction slurry was filtered, reslurried in water at about 5% solids, and filtered. The product analyzed 26% chlorine. The tannin content on an ash-free basis was 49% for 10 minute hide powder test, 67% for 60 minutes, and 88% for 24 hours.

The above product made up as a 10% slurry in water was hydrolyzed and dissolved by adding

a 12% solution of sodium hydroxide to bring the pH up to about 8.5 quickly and then holding at a pH of about 8.5 for 5 minutes by adding additional caustic. The soluble solids of this solution contained 26% inorganic matter.

The above hydrolyzed chlorine-treated alkali-lignin solution was mixed with sufficient concentrated hydrochloric acid to reduce the pH to about 0.8, the solution was heated to about 186° F. and filtered, the precipitate was reslurried in water at about 6% solids and a pH of about 1.5 (due to the retained acid), and the slurry was heated to about 182° F. and filtered. The filtrant analyzed 3.5% ash, dry basis.

The final product, low in salt content, is a new organic intermediate and capable of tanning leather commercially when dissolved with alkali. A solution of this resolubilized product contained about 14% inorganic on the soluble solids.

The product after salt removal contained 18% chemically combined chlorine and analyzed 28% tannin content for a 10 minute test; although this may appear to be a low assay the product was not an inferior tanning agent. The product analyzed 45% tannin content for 60 minutes contact and 75% tannin content for 24 hours contact with the hide powder.

The ultimate analysis of the alkali-lignin and the chlorine-treated product is determined by standard analytical procedures except for chlorine content which is determined as follows:

One liter of the acid slurry from the chlorine-treating step carrying about 45 grams of suspended solids is filtered on a Buchner funnel, using vacuum. The filter cake is slurried with one liter of cold distilled water and filtered. This step is repeated once more. The filter cake is then allowed to air dry, after which it is powdered and used for analysis. A 0.5 gram sample of the chlorine-treated alkali-lignin is mixed with 2.5 grams of sodium carbonate in a nickel crucible, one ml. of water is added with mixing, and 2.5 grams of sodium peroxide is added in approximately 0.5 gram portions. The crucible is added in a cold muffle furnace and heated to 1300° F. The fusion mixture is allowed to cool somewhat, then about 2 grams of additional peroxide is added. After a second fusion the crucible is allowed to cool; the fusion mixture is dissolved in hot water and made up to 250 mls. in a volumetric flask. Aliquot portions of 50 mls. are acidified with nitric acid. A known excess of standard silver nitrate solution is added, about 5 mls. of nitrobenzene is introduced to immobilize the suspended silver chloride, and the excess silver nitrate is titrated with a standard potassium thiocyanate solution using ferric alum as the indicator.

The term "alkali-lignin" as used in the appended claims includes both the water soluble forms thereof, in particular, sodium lignate which is precipitated in a pH range of 8 to 9 and to the insoluble forms thereof, in particular to the material precipitated at a pH below 7.

I claim:

1. A chlorinated, oxidized, hydrolyzed alkali-lignin tanning agent made in accordance with the method recited in claim 2 containing on a dry ash-free basis from about 12% to 18% chlorine, said tanning agent being soluble in dilute alkaline solutions and when dissolved with an aqueous solution of alkali showing a tannin content, as determined by the standard hide powder test, of at least 25%.

2. Method of preparing a tanning agent which comprises reacting chlorine with alkali-lignin in the presence of at least sufficient water to form a wet paste, continuing the reaction until said alkali-lignin contains from about 15 per cent to 30 per cent of combined chlorine, separating said alkali-lignin derivative from the accompanying liquor, dissolving said alkali-lignin in water by adding alkali in an amount sufficient to raise the pH to between about 6 and 10, and adjusting the pH of the resulting solution to an acid value for tanning hide.

3. Method of preparing a tanning agent which comprises reacting chlorine with alkali-lignin in the presence of at least sufficient water to form a wet paste, continuing the reaction until said alkali-lignin contains from about 15 per cent to 30 per cent combined chlorine, separating said alkali-lignin derivative from the accompanying liquor, dissolving said alkali-lignin in water by adding alkali in an amount sufficient to raise the pH to between about 6 and 10, reducing the pH of the resulting solution to below 3 whereby the solubilized alkali-lignin derivative is precipitated from solution, separating the precipitate from the mother liquor, washing said precipitate with water at a pH below 3, and redissolving said precipitate with aqueous alkali.

4. Method of preparing a tanning agent which comprises reacting chlorine with alkali-lignin in the presence of at least sufficient water to form a wet paste, continuing the reaction until said alkali-lignin contains from about 15 per cent to 30 per cent of combined chlorine, separating said alkali-lignin from the accompanying liquor, dissolving said alkali-lignin in water by adding alkali in an amount sufficient to raise the pH to between about 6 and 10, evaporating the resulting solution to dryness, washing the dried product obtained with water having a pH of below 3, separating said washed alkali-lignin derivative from the wash liquor, and redissolving said alkali-lignin with aqueous alkali.

5. Method of preparing a tanning agent which comprises reacting sodium lignate with chlorine in the presence of at least sufficient water to form a wet paste until the lignin derivative present contains from about 20 per cent to 30 percent of combined chlorine, and dissolving said chlorine-treated lignin derivative in water by adding alkali in an amount sufficient to raise the pH to a value of about 7 to 8.5, said sodium lignate having been obtained from alkaline wood pulp black liquor by carbon dioxide precipitation at a pH between about 8 and 9.

6. Method of preparing a tanning agent which comprises precipitating alkali-lignin from waste liquor of an alkaline digestion of ligno-cellulosic material by reducing the pH of said waste liquor to a value between about 3.5 and 9, separating said alkali-lignin from said waste liquor, reacting said alkali-lignin with chlorine in the presence of at least sufficient water to form a wet paste until said alkali-lignin contains from about 20 per cent to 30 per cent of combined chlorine, and solubilizing said chlorine-treated alkali-lignin in water by adding alkali in an amount sufficient to raise the pH to a value of about 7 to 8.5.

7. Method of preparing a tanning agent which comprises reducing the pH of black liquor from an alkaline wood pulp digestion to a value between about 3.5 and 9 by the introduction of sulfur dioxide whereby alkali-lignin is precipitated, separating said precipitated alkali-lignin from said black liquor, reacting said alkali-lignin

with chlorine in the presence of at least sufficient water to form a wet paste until said alkali-lignin contains from about 20 per cent to 30 per cent of combined chlorine, and solubilizing said chlorine-treated alkali-lignin by adding an alkali in an amount sufficient to raise the pH to a value of about 7 to 8.5.

8. A tanning agent made in accordance with the method recited in claim 6.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,567,395	Schmidt	Dec. 29, 1925
1,844,018	Sailer	Feb. 9, 1932
2,130,550	Koch	Sept. 20, 1938
2,161,748	Samaras et al.	June 6, 1939

Number	Name	Date
2,186,509	Wallace	Jan. 9, 1940
2,209,289	Wallace	July 23, 1940
2,244,410	Wallace	June 3, 1941
2,418,981	Muller	Apr. 15, 1947
2,433,227	Lewis et al.	Dec. 23, 1947
2,491,499	Katzen et al.	Dec. 20, 1949

OTHER REFERENCES

"Wood Chemistry" (Wise), pub. by Reinhold Publishing Co., New York, 1946, Kress and Vorgtman reference appears in lines 18 to 22 on page 310 of "Wood Chemistry." Feustel and Byers reference appears in lines 29 to 30 on page 310 to line 1 on page 311 of "Wood Chemistry."

"Progress in Leather Science 1920 to 1945," page 113, published 1948, by B. L. M. R. A., London, England.