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PROCESS FOR ENZYMATICALLY MODIFYING ORGANIC TANNING AGENTS AND PRODUCTS THEREOF

Richard W. Simmons, Bellingham, Wash., assignor to Georgia-Pacific Corporation, Portland, Oreg., a corporation of Georgia

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The present invention relates to products and processes of novel character and, in particular, to methods for improving the efficacy and general usefulness of a certain group of substances which are termed organic tanning agents.

In the process of tanning leather, animal skins, which consist largely of protein, are brought into contact with any of a wide class of organic materials having the property of combining with the protein of the skin so as to form leather. A rather different type of leather may be obtained by using heavy metal inorganic salts, notably chromium salts, but these are not organic and are not of the type contemplated in the present invention, for reasons which will appear hereinbelow.

Since prehistoric time, leather has been tanned with plant extracts known as tannins. In more recent times, other sources of materials of composition rather similar to the classical tan stuffs (or plant tannins) have been found, comprising notably sulfonated lignins, as obtained preeminently in the delignification of wood in the manufacture of cellulose pulp, and synthetic phenolic compounds made generally from coal tar and like aromatic raw materials representative of which are a group of organic compounds known as "syntans". These three classes, viz., plant tannins, lignosulfonates, and syntans, constitute a well-recognized group which may be described as organic tanning agents, and which term will be adopted for the purposes of this disclosure. For example, the authoritative book, "Die Gerbstoffe und Gerbmittel," by H. Gnam (Stuttgart, 1933), the title of which may be translated as, "Tanstuffs and Tanning Agents," contains a section on the plant tannins, another section on the syntans, and a third section on lignosulfonates. Examples of all three of these classes will be given below.

While the individual members of the three classes constituting the group of organic tanning agents all possess some tanning ability, they naturally differ greatly among themselves as to over-all usefulness in tanning leather, in efficacy in other uses besides leather tanning for which the members of this group have been found operative and, finally, in the degree to which they achieve all of the desiderata of the practical tanner. My invention contemplates, in brief, the modification of organic tanning agents so that their properties for some or all of the uses for which they are employed will be ameliorated. For example, the various members of this group of materials will tan leather to a certain degree of tannage and to a certain shrink temperature, which differs for the individual members. Generally speaking, modification of these materials in accordance with the invention increases the degree of tannage, or the shrink temperature, or both.

Organic tanning agents modified in accordance with this invention are also useful in fields other than that of tanning leather, the most important of which is in the modification of aqueous clay slurries and suspensions as occur in the ceramic industry and in the oil well drilling industry, where the clays may be those deliberately added to the drilling slurry or drilling mud, or may be the clay material drilled up during drilling, such as shales. The action is essentially one of dispersing the clays or the clay aggregates.

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Other related uses of the products of the present invention are: as dispersants in wet ore beneficiation processes, including grinding, tabling, and flotation steps; as dispersants in the grinding of Portland cement clinker; as dispersants in various aqueous mixtures such as polishes, particularly containing suspended mineral polishing agents; in detergent formulations, such as soaps and cleansers; and in the dispersion of dyestuffs, particularly of vat dyes, acetate dyes, and the like.

Another field of use for the modified tan-stuffs of this invention is that of boiler water treatment. Not only are they effective as dispersants, but some of them are specifically effective in retarding caustic embrittlement of boiler plate. The oxygen absorbing ability of the tannins in alkaline solutions is also of important benefit in the prevention of tube corrosion.

In summary, therefore, it is an object of the present invention to provide a process for modifying organic tanning agents so as to increase their usefulness, both for tanning leather and for other uses, and it is a further object of the invention to provide the products which arise from carrying out the inventive process, and further to use such products in their appropriate fields, such as tannage, clay treatment and the like.

Other objects of the invention will appear as the description thereof proceeds.

The invention in a generally stated form may be stated to contemplate the treatment of organic tanning agents, with the enzymes of the class of oxidases, followed by the optional step of chemical reduction, and eventually followed, where desired, by the employment of the products so obtained in leather tanning, in clay treatment, in well drilling, and the like.

THE ORGANIC TANNING AGENTS

As mentioned, in the group of organic tanning agents, not only as the term is used in chemical industry but also as I use it in this disclosure and the claims which follow, and as more particularly defined herein, is constituted by the three classes of plant tannins, lignosulfonates, and syntans. Plant tannins are of wide occurrence in the vegetable kingdom, but as a practical matter only those have become of importance which by virtue of their concentration in readily available plants can be commercially produced. By way of example, but not in a limiting sense, I may mention quebracho, urunday, mangrove, mimosa, catechu, gambier, valonea, dividivi, tara, myrobalams, chestnut, osage orange, wattle, sumac, and hemlock, all of which are well known and for the most part commercially available plant tannins generally provided in the form of an extract which has been made from that part of the plant rich in tannin, which may be the bark, the wood, the leaves, the fruit, and the like. In some cases the tannins will have been subjected to a sulfiting treatment, which probably results in a sulfonated tannin. This is especially common with quebracho extract. Such sulfited tannins are likewise well suited for the practice of the invention.

The lignosulfonates are various sulfonated lignin derivatives, lignin of course being the major constituent of wood besides cellulose. Sulfonated lignins are most generally obtained as a by-product in those processes of freeing the cellulose constituent of wood in which the lignin constituent is solubilized with a sulfite. The largest single source of lignosulfonates is the so-called sulfite waste liquor obtained from the sulfite pulping of wood in accordance with any of several processes, all of which have the common feature that a sulfite (or sulphur dioxide) is caused to react with the lignin in such a way that a sulfonate is formed, which under the particular conditions used is solubilized. Lignosulfonates, sometimes referred to herein as "sulfonated lignin-containing

materials," are most commonly encountered in the form of their calcium salt, but are also obtainable in the form of their sodium, magnesium, or ammonium salt, or mixtures of these. Pulping processes other than sulfite methods such as the neutral and alkaline pulping processes in some cases produce a lignin which is not sulfonated as it is produced, but which may later be sulfonated, to produce a lignosulfonate which again may be provided in the form of a calcium or sodium salt or the like. Lignosulfonates, indeed, form such a well-recognized chemical class that it is unnecessary to go into further details of their manufacture here.

In general, any type of wood or lignocellulosic material, the same including straw, cornstalks, bagasse and the like, which can be resolved to pulp with the separation of the lignin-containing material, may be used as a source for providing lignosulfonate in following my invention. Furthermore, changes in the final properties of the product are influenced by the conditions of the pulping process, but particularly good results are obtained using the commercial spent sulfite liquor from paper grade quality pulp.

The degree of purity of the lignosulfonate, although not being a matter of limitation in regard to my invention, is a matter of importance in regard to the quality of the final product obtained by the process of my invention. For example, it is desirable, though not essential, to remove the free and loosely combined sulfur dioxide as well as other hydrolyzable compounds in the spent sulfite liquor, for example by steam stripping in accordance with the disclosure of United States Letters Patent No. 2,430,355 to Joseph L. McCarthy. Beneficial results are also obtained by mild alkaline treatment for example, at pH 7 to 10 at a temperature commensurate with the time. The spent sulfite liquor may be further refined to provide a clarified lignosulfonate starting material by such methods as fermentation with either yeast or bacteria, dialysis, or fractionation procedure such as the Howard process using lime or separations using organic solvents. By such procedures the purity of the lignosulfonate can be improved and for tanning purposes the purification can be characterized by the so-called hide powder test which is the standard procedure of the American Leather Chemists Association for determining the tannin content of tanning material. According to this test, the tanning content of spent sulfite liquor products will range from roughly 30 to 50 percent by weight of solids, and for fermented spent sulfite liquor from about 50 to 55 percent. Through fractionation, spent sulfite liquor products are obtained with substantially higher tannin contents, viz., in excess of 55% by the test just mentioned, and such materials are more desirable as starting materials or substrates for carrying out the process of my invention and preparing an improved compound. Thus, any of these purified sulfonated lignin-containing materials can be used in the process of my invention.

Both the plant tannins and the lignosulfonates have certain common chemical properties, arising from a community of chemical structure, which may be set forth in general terms even though the detailed chemical structure of these naturally occurring materials may not be completely known because of their complicated nature. Common features are that these materials are essentially organic; they are acidic in nature, whence arises the possibility of being provided either in an acid form or in the form of simple salts such as those of sodium and calcium; they are of relatively high molecular weight, being indeed describable to some extent as anionic polyelectrolytes; their molecular weight is however not so high that they are not still soluble at least in their salt form, in hot water if not in cold; and, of especial importance for the present invention, they are phenols, and generally polyphenols. In addition, certain phenolic compounds of synthetic origin have the properties de-

scribed above and for the purpose of practicing this invention it is believed that to be useful such compounds should have an active hydrogen ortho to the phenolic hydroxyl group. Representative of this group of compounds are synthetically prepared organic tanning agents which have all the properties mentioned above, and in particular are polyphenolic materials and frequently referred to as "syntans." Another example of the important use of my invention is the upgrading of the nontans present in vegetable tan-stuffs by reaction of the phenol oxidase enzyme. Here again, since syntans form a well-recognized class, it is not considered necessary to go into much detail here. Reference may be made to the pioneer article of Stiasny entitled, "Systans, New Artificial Tanning Materials," *J. Soc. Chem. Ind.*, 1913, p. 775, as well as the article by Turley in *J. Am. Leather Chem. Assoc.*, 40, 58 (1945). Methods of preparation of the syntans are further given in the patent literature, e.g., German Patents Nos. 262,558, 266,139, 280,233, 291,457, 433,292, 409,984, 493,795, 537,451 and 539,474. Very broadly speaking, the syntans are made by the condensation of various phenolic materials with such reactants as formaldehyde, benzaldehyde and the like.

THE ENZYMATIC OXIDASE

The field of the known enzymes is of course vast. A relatively small and indeed little known type of enzyme is one which is characterized, among other things, by the functional presence of a heavy metal, viz., copper or iron, in the enzyme molecule, and which has the property of catalyzing the oxidation of phenols and polyphenols. This group of copper (or iron) bearing enzymes includes members which have been previously named by the different investigators in the field, but which may conveniently and particularly for the purposes of this disclosure be termed the phenol oxidase enzymes, this term being herein defined to include the various copper oxidases known as tyrosinase, polyphenol oxidase, lacasse, sweet potato phenolase, and peroxidases. They are described with particular thoroughness in Chapter 57 of the book, "The Enzymes," edited by J. B. Sumner and K. Myrbäck, volume II, Part I, New York, 1951. Another recent treatment is given in Chapters 38 and 39 of the book, "Enzymologie," by O. Hoffmann-Ostenhof, Vienna, 1954. In spite of the highly specific chemical activity of the oxidases, they are found rather widespread throughout the plant kingdom, and likewise throughout the animal kingdom except much more in invertebrates than vertebrates. That part of my process in which the organic tanning agent is modified with the oxidase is carried out by simply bringing together, conveniently in an aqueous slurry or mash, the organic tanning agent or mixture of such agents, with the enzyme, which in general will be contained in its natural source, although for some purposes may be an expressed enzyme-bearing juice or a purified enzyme preparation. The best natural source that I know for oxidase is the common white potato. Other sources are mushrooms, particularly the cultivated edible variety, of which the trimmings may be used; spinach leaves, apples, apple leaves, sugar beets, sweet potatoes, carrots, turnips, cabbage, and horseradish. I do not exclude the use of animal sources of oxidase, such as chicken livers, rabbit skins, grasshoppers, and the like, although in general it is not only much more economical, but also generally more satisfactory to work with simple plant sources such as the white potato. Oxidases are found in some bacteria, also, as well as molds, but care must of course be taken that preparations of these be free of undesired enzymes which may have a quite unwanted effect. For example, certain molds contain enzymes of the tannase group which split tanstuffs by de-esterification. This is another reason why I prefer simple vegetable sources such as the white potato. Methods of isolation of the enzyme from various source materials are described in the literature, references being given

for example in the Sumner-Myrbäck work cited, and while these may be used, particularly in investigational studies, in general the cost of preparing the purified enzyme makes the latter not economically attractive. In some cases it will be found convenient to press the source material, and use the watery juice so obtained, since the oxidase component appears to be water-soluble in the general case.

Where any doubt exists as to the content of oxidase in a given source material, this can readily be determined by methods familiar to enzymologists. A discussion of methods is given on pages 560, 561 and 571 of the Hoffmann-Ostenhof work cited; another account is given in the article by H. Haehn entitled, "Die Bestimmung der Tyrosinase," which appears at pages 1364-1372 of volume III of the work entitled, "Die Fermente," edited by Oppenheimer, Leipzig, 1927.

It should perhaps be mentioned that some enzyme chemists use the term "enzyme" to designate only a single species of enzyme, and prefer to use the word "enzyme system" for the naturally occurring enzymatic material which indeed may contain a mixture of closely related enzymes. For simplicity in disclosure, and since the point is not at all important here, I have used the simple term "enzyme" throughout, to include both isolated, pure enzymes and the enzyme systems which occur in the oxidase-bearing source material, such as, for example, potatoes or mushrooms.

THE OXIDASE REACTION

As mentioned, in order to carry out the enzymatic treatment of the organic tanning agent, I bring together the latter with the enzyme or enzyme source material in such a fashion that the enzyme is accessible to the organic tanning agent to be treated. As a practical matter, the organic tanning agent is suspended or dissolved, as the case may be, in an aqueous medium so as to form a slurry or even a paste, all mixed with the enzyme or source material thereof, for which again practical considerations indicate comminution. Thus, I may grind whole fresh white potatoes to a pulp and mix this with an aqueous slurry of a tanning agent such as quebracho extract or calcium lignosulfonate. The treatment is carried out generally at room temperature; excessively cold temperatures make for longer treating times, whereas excessively high temperatures tend to inactivate the enzyme.

Considerable leeway is available in the pH range during the treatment. Unless pilot tests are made to determine the suitability of some quite different pH's, however, it is wise to carry out the treatment at about the natural pH of the enzyme source, e.g., that of fresh potato juices when these are used, and so on. The pH range of 6.0 to 6.8 will most often be found to be optimum but also operative pH's lie in the range 4 to 8.

Treating times naturally vary with the starting materials and the concentrations employed, but generally it will be found that treatment times within the range of four hours to twenty-four hours suffice. After the tanning agent and the oxidase have been in contact for a suitable length of time, the tanning agent solution or slurry is filtered away from the enzyme source material, and the latter is discarded. In order to conserve material, of course, normal washing of the filtered enzyme source material pulp during filtration may be employed.

The times and other conditions pertaining to the reaction which are set forth herein and especially in the examples which follow may be used as a guide to those wishing to practice the invention. In the event of unusual conditions of temperature, choice of raw materials, and the like, it may be useful to test the reacting slurry from time to time in order to determine the progress of the oxidase reaction. This may readily be done by removing some of the treated tanning agent from the reacting slurry, using it to tan some hide, and making

shrinkage temperature tests of the type standard in the leather art. An effect of the oxidase treatment of the tanning agent is to raise the shrinkage temperature, and this forms a convenient way of determining optimum reaction times. Such determinations are, of course, best carried out as pilot tests, since the tanning step which is part of the determination takes some time to complete.

The concentration of the organic tanning agent in the solution or slurry is not critical. While it may be quite dilute, for example 10% by weight of total solution, it is more economical to use as concentrated solutions as can readily be handled by the usual chemical process equipment. For most of the organic tanning agents treated in accordance with the invention, I use a solution of these in water of about 50% solids.

Normally, I use the enzyme in the form of its plant source material, for example, ground fresh potatoes, and this is added directly to the aqueous solution or suspension of the tanning agent. Here again, a wide variation is permissible in relative proportions. Using white potatoes and calcium lignosulfonate, as well as white potatoes and sulfited quebracho extract, I have obtained improved products in accordance with the invention over a range of ratios of tanning agent solids to potato pulp of 1:3 to 50:1. For any given combination of tanning agent and oxidase, a few simple experiments as mentioned above will serve to determine the lowest concentration of oxidase-containing material, which of course, is an aid in the economical practice of the invention. If cost is no object, of course, one can always use a substantial quantity of oxidase source material, for example, a 1:1 ratio, and obtain good results in accordance with the inventive process.

So far as is known to me, these oxidases are all copper (or iron) bearing, and it has been found that the oxidase may be inactivated if there is present a material which combines with copper (or iron) ions, such as cyanides, sulfides, and the like. Those skilled in the art of enzyme chemistry will, of course, realize that it is desirable to avoid the presence of such inactivating chemicals during the processing in accordance with the invention. Indeed, the addition of a trace of a simple copper salt such as copper sulfate does no harm to the reacting system and will do some good by scavenging out any material such as sulfides or cyanides if those are present. About 1/40 of 1% copper sulfate on the total reacting mix may be used as a matter of course.

So far as is known to me, the action of the oxidase is to add another phenolic OH group to both mono- and polyphenols which form constituents of the organic tanning agents treated. The oxygen required for this reaction must, of course, come from somewhere, but I have found that that which is present in the reacting solutions as a result of the normal access of air during mixing and reaction is adequate. It is conceivable that under unusual conditions, where for example make-up water was used which for some reason was free of dissolved air, and where the reaction might be carried out in a system of closed pipes or tanks or the like, sufficient oxygen might not normally be present to complete the reaction. In such cases it is a wise precaution to introduce air at some suitable point in the process, such as bubbling air into the reaction mixture when it is first prepared.

A sub-group of the oxidases are the peroxidases, which have the peculiarity of requiring the presence of oxygen in its peroxide form in order to carry out the oxidase reaction. When a source material for which the oxidase constituent is chiefly a peroxidase, such as for example ground fresh horse-radish, then some peroxide oxygen should be supplied, which is readily done by adding hydrogen peroxide or any of the other commercially available peroxides such as urea peroxide, sodium pyrophosphate peroxide, and the like.

It has been found that peroxidase (mediated) oxidation of the product of this invention—that is, following the

phenoloxidase reaction and with or without the optional reduction step—results in a tanning agent of somewhat different characteristics. The greatest difference between leather tanned with the regular product described above and the leather tanned with this product after treatment with hydrogen peroxide and horse-radish roots as the peroxidase source, is in the color. While the regular product of the reaction using spent sulfite liquor as the base yields leather of pink to red hues, the additional treatment with peroxidase and hydrogen peroxide considerably lightens the color and produces beige colored leather when dried. This result is surprisingly different from the color of hide treated with ordinary spent sulfite liquor solids which results in black to dark brown horny material when dried.

It is well within the scope of the invention, of course, to use mixtures of organic tanning agents, even from different classes within this group. The different species may be premixed and then subjected to the oxidase reaction, or they may be separately treated with oxidase and later mixed. The treated organic tanning agents may also be used with untreated organic tanning agents in the various uses for these. Examples of such joint employment are the following: In the extraction of barks of various plant species with the aid of sulfites, both a sulfonated tannin and a sulfonated lignin constituent may be obtained. Such a mixture really represents two different classes of organic tanning agents, but, of course, may be treated in a single oxidase reaction. Again, since all of the different tanning agents have somewhat different effects on the materials treated, such as on skins in forming leather, it is often desirable to combine different organic tanning agents to get a combination of properties, e.g., in the finished leather. Thus, oxidase treated calcium lignosulfonate may be used with quebracho extract as a tannage; or it may be used jointly with oxidase-treated quebracho or other plant tannin extract. The permutations and combinations are, of course, very numerous and need not be detailed further here.

THE OPTIONAL REDUCTION STEP

I have found that organic tanning agents which have been oxidase-treated in accordance with the invention may in general be improved still further for the purposes for which tanning agents are employed, by subjecting the oxidase-treated tanning agent to a chemical reducing agent, such as, for example, nascent hydrogen. Generally speaking, it is not necessary to remove the enzyme source material, but the reduction step may conveniently be carried out after the oxidase reaction has been completed, by simply adding the chemical reducing agent to the liquid slurry. Of course, due attention must be paid to the pH range within which the particular reducing system is effective. For example, when nascent hydrogen is employed as formed from zinc and sulphuric acid, one adds sufficient sulphuric acid to the oxidase reaction mixture after the conclusion of the oxidase treatment so that the pH is reduced to 4 or below, and then adds powdered zinc to the acidified slurry in order to release hydrogen. Quite small amounts of reducing agent suffice for this further amelioration of the tanning agent. For example, as little as 0.1% of powdered zinc based on the weight of the original organic tanning agent solids suffices as a general rule. It is advisable when zinc and acid is used to raise the temperature of the mixture after addition of the zinc to a high enough temperature for rapid hydrogen evolution, such as 60° C. After the reduction with hydrogen in this manner, the pH of the mixture may be raised again with lime or other alkali to the desired pH for the final product, as for example by using lime or other alkali to a pH of 4 or 5 or indeed higher. Where the relative proportion of enzyme source material is large, it may be more satisfactory to carry out the reduction step on the treated organic tanning agent solution after removal of the enzyme source material therefrom.

While zinc and a mineral acid such as sulfuric acid is

generally the cheapest reducing agent and quite satisfactory, it is within the purview of the invention to use other chemical reducing agents, such as stannous chloride, sodium borohydride, sodium hydrosulfite, sodium sulfoxalate, or other simple salts of these reducing anions such as, for example, calcium hydrosulfite, as well as catalytic and electrolytic methods. The use of these for chemical reduction is carried out under conditions appropriate to the agent chosen, which is known to those skilled in the art and need not be detailed here. See, for example, Organic Chemical Bulletin, 30 (2), (1958), "Newer Methods of Reduction," by M. H. Stern. The term "chemical reduction" is used here and in the claims which follow to include reduction procedures, whether effected electrolytically or by the addition of chemical reducing agents, with or without catalysts.

For various reasons such as the desire to reduce the ash content of the tanning mixture, to raise the tannin content of the mixture, or to intensify the tanning ability of various treated agents, it is frequently convenient to replace the calcium cation of the product of this invention with a different cation. Examples of such modifications are the corresponding chromium, zirconium, ammonium, magnesium, sodium, or aluminum salts. Any of these compounds may be prepared by methods well known to those skilled in the arts, for example, by using ion exchange resins. A preferred method if the enzyme treated tanning agent is in the calcium form is to add the stoichiometric quantity of the soluble sulfates of the above cations to the product of this invention. The precipitated calcium sulfate may be removed by centrifugation or other clarification process. It is to be noted that other soluble salts than the sulfates of these metals may be used provided their anions form insoluble calcium compounds.

The chromium salt of the product of this invention is of particular interest. If it is desired to produce a leather which combines the high temperature resistance of the chromium tannage with the plumpness, fill, and dyeing properties of vegetable leathers, it is quite possible to use any of the enzyme treated agents herein described as "retan" materials for fuller chrome tanned leather.

In addition it is possible to simplify this process, which requires two separate and distinct tannages, by tanning leather with the chromium salt of my enzymatic oxidized tanning agent. Thus to the valuable properties of the chromium-tanned leather are added the special advantages of vegetables tannage. The economy of a single step "retan" is readily apparent.

To prepare such a chromium salt of my treated agents it is only necessary to add the step of treating the calcium or other salt of the enzymatic oxidation product, before or after reduction, with a basic chromic sulfate solution to accomplish precipitation of calcium as calcium sulfate. Indeed it is possible in the case of the treated lignosulfonate product to add chromium in amounts substantially greater than required for the cation exchange. The additional chromium is apparently held in solution by the chelating capacity of the lignosulfonate product. Chromic sulfates of varying degrees of basicity can be prepared, and different properties can be observed in the leather prepared from them. These chromic sulfates may be made by the acid reduction of sodium dichromate with molasses, glucose, or other sugar, with sulfur dioxide, or with spent sulfite liquor. The basicity may be regulated by adjustment of the amount of acid added to the reactants. Then any of these preparations can be added to the calcium salt of the tanning agent of my invention; and the precipitated calcium sulfate removed. The resultant chromium compound of the enzyme-oxidized and preferably reduced product of my invention may be used as a "one-bath, Retan" tanning agent.

By way of example, and not limitation, I have found that a preferred range of between 4% and 14% by weight of chromium on the total solids produces tanning agents of good balance between the chrome type and the vege-

table type. Agents of lower chrome content yield leathers of improved shrink temperature; yet, with them, full advantage is not taken of the chrome effect. With agents of higher chrome content than the upper limits of the range specified above, the full benefits of the vegetable retan type of tanning are not as evident.

The chromium, zirconium, and aluminum salts of the products modified in accordance with the invention are especially valuable for tanning purposes, as compared with the corresponding sodium, potassium, ammonium, calcium, or magnesium salts, as has been especially noted herein for the case of chromium, as these three metallic ions participate themselves in the tanning process.

Some detailed examples showing procedures in accordance with the invention will now be given.

Example 1

Spent liquor from the calcium sulfite pulping of hemlock wood chips was steam stripped to remove sulfur dioxide, hydrolyzable sulfur compounds and volatile organic compounds, fermented with brewer's yeast, steam stripped to remove the alcohol, and evaporated to a viscous liquid containing 50% solids, all in accordance with procedures well known in the art. To 400 g. of this viscous liquid at room temperature there was added 200 g. of a slurry of Irish potatoes, prepared by shredding the potatoes in a Waring blender. The pH of the solution was raised to 7.0 by the addition of sodium hydroxide solution, and the mixture was stirred gently at room temperature for 24 hours. It was then allowed to settle, and the clear supernatant liquid was decanted off. The pH of this liquid was reduced to 4.0 by the addition of sulfuric acid, after which the liquid was put in a steam bath and heated to 90° C. After heating, it was allowed to cool, and then diluted to 4.2° Baumé for tanning tests.

Example 2

The liquid recovered in Example 1 was concentrated by heating over a water bath, air dried at 60° F. and powdered.

Example 3

Spent sulfite liquor from the calcium sulfite pulping of hemlock wood chips was steam stripped to remove free sulfur dioxide, hydrolyzable sulfur compounds and volatile organic compounds, fermented with brewer's yeast, and steam stripped of its alcohol content (which process is fully described in the article on pages 165 to 167 of Chemical Engineering Progress, vol. 43, 1947) and concentrated by evaporation to a concentration of 48.9% solids. Two hundred twenty gallons of this concentrated liquor, at a pH of about 4.2, was placed in a tank and allowed to cool, while sodium hydroxide was added to raise the pH. The cooled liquor, at 23° C., had a pH of 6.3. One hundred eighty pounds of potato slurry was obtained by the fine grinding of whole fresh Irish potatoes, and was mixed into the said neutralized liquor. Mixing was continued for about 46 hours, the temperature ranging between 23° and 31° C. during this period. Live steam was then blown into the suspension, raising the temperature to 91.5° C., and sulfuric acid was added slowly. A total of 30.9 lbs. of 96% acid was added over a period of 1.5 hours. During the addition of the acid, zinc dust (5.02 lbs.) was added. The sulfuric acid reduced the pH considerably, but this effect was partly compensated by the action of the zinc.

Mixing was continued for another day, during which time the solution was allowed to cool. The pH was increased to 4.5 by the addition of sodium hydroxide. The solution was then screened to remove the major part of the solid sludge, which was discarded. The sludge contained the residue from the potatoes and a considerable quantity of calcium sulfate.

Example 4

The liquid product of Example 3 was dried in a spray drier to give a dry solid product.

Example 5

Approximately equal parts by weight, and totaling 383 grams, of a mixture of sulfonated kraft liquor solids manufactured and sold by the West Virginia Pulp and Paper Company under the names, respectively, of Polyfon T and Polyfon R were dissolved in 1.5 l. of water. (Polyfon T contains 2 sulfone groups per lignin unit while Polyfon R contains 3. These products are described in Polyfon Technical Bulletin No. 301 entitled, "Sodium Lignosulfonates," published by West Virginia Pulp and Paper Company, May 1954.) The solution was divided into two equal portions, one of which was used as a control, and one of which was treated with approximately 65 grams of whole, finely ground, potatoes. This mixture was allowed to stand overnight, the pH being approximately neutral, having been adjusted with hydrochloric acid, since the Polyfons are somewhat alkaline. The potato residue was then filtered off, the solution was acidified with sulphuric acid to a pH of just under 2, and 8 grams of zinc dust were added. The mixture was heated to 65° C. and maintained there until hydrogen ceased evolving, which required about an hour. The pH was then returned to 4.0 with sodium hydroxide, and the solution eventually diluted to 4.2° Bé.

Example 6

The process of Example 1 was carried out except that "clarified" quebracho extract, that is quebracho extract that has been given a bisulfite treatment in order to improve its cold water solubility, was substituted for the alcohol-stripped lignosulfonate material of Example 1.

Example 7

The product of Example 6 was treated with sulphuric acid and zinc and eventually sodium hydroxide as set forth in Example 3.

Example 8

Twelve hundred and eighty-seven grams of air dried quebracho extract (not bisulfited or clarified) were dissolved in 3 l. of water. One-half of this volume (containing 643.5 grams of quebracho solids) was reserved for direct tanning tests. The other half was adjusted to a pH of 7.0 with sodium hydroxide, and 214 grams of Irish potatoes (unpeeled, ground in a Waring Blender) were stirred into the mixture and the whole allowed to stand one day at room temperature. The supernatant liquid was decanted off the sludge. The liquid solution was heated to 90° C. on a steam bath. After attaining temperature, 20 grams of zinc dust were added along with enough sulfuric acid to drop the pH below 2.0. After gas evolution, from the zinc and acid, had slowed down, the reaction mixture was cooled and the pH was brought to 3.5 with lime slurry. The supernatant liquid was decanted off the residue of gypsum and unreacted zinc, and the clear solution was diluted to 4.2° Bé.

Example 9

Spent liquor from calcium bisulfite pulping of hemlock bark, containing about 12% solids, was treated with 1/3 by weight of solids in the liquor of finely ground Irish potatoes, the pH having first been adjusted to neutrality with lime. The mixture was allowed to stand overnight whereupon it was decanted from the sludge, acidified with sulphuric acid and treated with powdered zinc as set forth in Example 3 above. After cooling, the pH was brought up to 3.5 with lime, the clear fraction was decanted off the sediment, and diluted to 4.2° Bé.

Example 10

A syntan consisting of the formaldehyde condensation product of beta naphthol sulfonic acid made in accordance with the teachings of German Patents 292,531, 318,948 and 409,984, and available commercially from the firm of Rohm and Haas, Philadelphia, as "Leucanol"

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was added to an equal part of water, adjusted to a pH of 6.5 with sodium hydroxide, and 18 parts of whole, finely ground Irish potatoes added per 100 parts of "Leucanol." The mixture was allowed to stand overnight at room temperature, then heated to 90° C., the pH lowered to 2 with sulfuric acid, and zinc dust in the proportion of 0.4% by weight of the "Leucanol" was added. The zinc dissolved quickly, and after 30 minutes the evolution of hydrogen was complete, whereupon the mixture was cooled and clarified by decanting, and adjusted to a pH of 4 with sodium hydroxide, water being added to give a 4.2° Bé. solution.

Example 11

The process of Example 8 was repeated with two condensed tannins other than quebracho. These were wattle and gambier.

Example 12

The process of Example 8 was applied to tannins other than condensed tannins. These were chestnut, myrobalams and nutgall.

Example 13

A quantity of the 50% concentration solution of a calcium base spent sulfite liquor, fermented and alcohol stripped, and the same material as used in Example 1, containing a total of 400 grams of solids, was admixed with the juice expressed from 127 grams of edible commercially grown white mushrooms, a hydraulic press being used, and the pH being adjusted to 6.9. After 24 hours at room temperature, the pH was lowered to 2 with dilute sulfuric acid and 2.5 grams of zinc dust added. The mixture was heated to 85° C., kept there for about one-half hour, then cooled and clarified. The resulting pH was 3.65.

Example 14

The procedure set forth in Example 13 was carried out except that the juice expressed from 276 grams of fresh common spinach was substituted for the mushroom juice.

Example 15

The procedure set forth in Example 13 was carried out except that a highly purified commercial preparation of tyrosinase (500 units/mg.) obtained from Mann Research Laboratories, Inc., 136 Liberty Street, New York 6, New York, was substituted for the mushroom juice at 1 mg., 5 mg., and 14 mg. per 200 grams of spent sulfite liquor solids.

Example 16

The procedure set forth in Example 8 was carried out except that spent sulfite liquor derived from the sulfite pulping of hardwood (alder) was substituted for quebracho extract.

Example 17

A portion of the solution treated in Example 3 was removed before the reduction with zinc and sulfuric acid, and 10.2 grams of stannous chloride were used to reduce 580 grams (containing 43% solids, by weight) of this liquid product. This reduction was carried out at a pH of 6.0 overnight at room temperature.

Example 18

The procedure of Example 17 was carried out except that 10.0 grams of sodium borohydride were substituted for the stannous chloride as the reducing agent. This reduction with sodium borohydride was made at a pH adjusted to 9.1 with sodium hydroxide and at room temperature.

Example 19

A portion of the liquid product of Example 3 weighing 610 g. (250 g. of solids, 41%) was converted to the zirconium salt. This process involved the following steps: Zirconium sulfate tetrahydrate, 53.3 grams, was dissolved

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in about 100 ml. of warm water. This amount of zirconium sulfate was calculated to be equivalent to 4.8% of calcium in the treated spent sulfite liquor (the approximate proportion found in the raw material of Example 3). The solution, at about 40° C., was added slowly with mixing to the solution of the product of Example 3, which was initially at 77° C. After mixing, the pH of the solution was about 2. About 50 ml. of 18% sodium hydroxide solution was added, raising the pH to about 5. The mixture was then allowed to stand for a day, meanwhile cooling to room temperature. After standing, the solution was centrifuged to remove the sludge of insoluble calcium sulfate, which was washed once with water and discarded. The washings were combined with the solution recovered from the centrifuging, and the resulting solution was diluted to 4.2° Baumé for tanning tests.

Example 20

An amount of the clarified liquid product derived from Example 3 containing 2400 grams of dry solids was measured out. Meanwhile 381 grams of sodium dichromate were treated with 290 grams of sulfuric acid, plus enough water to clarify the solution, and to this mixture was slowly added 610 grams of spent sulfite liquor containing 122 grams of solids. After the addition was completed and the reaction had subsided, the resultant reduced chromic salt solution was added to the above portion of the product of Example 3. This mixture was maintained at 90° C. for twelve hours to give the maximum precipitation of calcium sulfate which was then removed by decanting and centrifuging. The pH was adjusted to 4.0 and the product was ready for tanning tests. The chromium content of the dry solids was 5.2%.

Example 21

A product was prepared as exhibited in Example 20 except that 381 grams of sodium dichromate and 290 grams of sulfuric acid reduced by 610 grams of spent sulfite liquor were added to 900 grams of solids from Example 3. This product contained 10.0% by weight of chromium based upon dry solids.

Example 22

One hundred grams of solids obtained in Example 4 were redissolved in water and treated with 100 grams of whole shredded horseradish root. To this mixture were added sixty ml. of 30% hydrogen peroxide. After standing over night at room temperature, the solution was clarified by centrifuging and diluted to 4.2° Baumé for tanning tests.

Example 23

A quantity of calcium base spent sulfite liquor at 48% concentration of solids, fermented and alcohol stripped in the manner set forth in Example 3, and containing a total of 1,000 grams of solids, was neutralized to pH 6.4 by adding 10 grams of sodium hydroxide as a 10% solution. This solution was mixed with 300 grams of the fresh juice of white potatoes, prepared by grinding together potatoes and water in the proportion of 300 parts to 150 parts respectively and pressing the resulting pulp to separate the potato juice. This said solution of fermented spent sulfite liquor containing the potato juice was allowed to stand for 20 hours at 27° C. and then heated to 90° C. Thirty grams of sulfuric acid was added as a 10% solution, giving a pH of 3.4 in the solution. Five grams of zinc dust was added and the solution stirred for 3 hours. Then it was allowed to digest overnight at 80-90° C., and the calcium sulfate removed by decantation. The pH of the solution was 3.6.

A number of examples showing the use of the products obtained in the foregoing examples will now be given.

Example A

The soluble material recovered in Example 1 was diluted to 4.2° Baumé with water. To 40 grams of de-

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greased pickled sheep skin in a jar, there were added 2000 ml. of 10% sodium chloride brine (a 5000% float) and one hundred ml. of the 4.2° Bé. stock liquor were added to the jar. The following day, the tanning solution in the jar was enriched by the addition of another 200 ml. of 4.2 Bé. stock liquor. For six days daily additions of 200 ml. each of stock liquor were made to the tanning solution. On the ninth day, the jar was emptied, and the skin (then fully penetrated) was covered with the stock liquor and left for three days at room temperature. After this time the fully tanned leather was removed, washed, fat liquored, set-out, and dried.

Example B

The process of Example A was carried out except that the liquid product recovered in Example 3 was used instead of that recovered in Example 1.

Example C

The process of Example A was carried out except that the product obtained in Example 5 was used in place of that obtained in Example 1.

The shrinkage temperature of the leather obtained in Examples A, B and C was determined by a method as shown, for example, in *The Chemistry and Technology of Leather*, vol. II, F. O'Flaherty, W. T. Roddy, R. M. Lollar 1958, Reinhold Publishing Co., New York, p. 31, and the quality of the leather was noted. The following table shows the results, together with that of leather obtained in the same fashion as in Examples A, B and C except that the alcohol-stripped spent sulfite liquor described in Example 1, as well as the sulfonated kraft liquor which was the starting material of Example 5 were used without any oxidase treatment in order to furnish a "blank" for comparison. The following table represents the results obtained:

TABLE I

Example	Tanning agent	Shrinkage temperature, ° C.	Quality of leather
(Blank)...	Untreated spent sulfite liquor.	61	Black, tinny, flat.
A.....	Product of Example 1.....	63	Brown, mellow.
B.....	Product of Example 3.....	66	Pink, soft, full.
(Blank)...	Untreated sulfonated kraft liquor.	54	Black, untanned.
C.....	Product of Example 5.....	70	Brown, full, soft.

Example D

The process described in Example A was carried out, except that the treated clarified quebracho extract of Example 7 was used as the tanning agent instead of the product obtained in Example 1.

The leather resulting from Example D was examined for shrinkage temperature, degree of tannage, and quality of leather, and these tests were likewise made on leather products in accordance with Example D except that untreated clarified quebracho extract was used for comparison, that is, the same as the starting material of Example 6. The following table presents the results obtained:

TABLE II

Example	Tanning agent	Degree of tannage	Shrinkage temperature, ° C.	Quality of leather
(Blank)....	Untreated clarified quebracho extract.	63	77	Reddish brown, soft, full.
D.....	Treated clarified quebracho extract, Ex. 7.	83	78	Bright pink, very plump, soft, round.

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Example E

The process of Example A was carried out except that the product of Example 8 was used instead of the product of Example 1, as the tanning agent, and pickled calf skin was substituted for sheep skin.

The leather produced in Example E was examined, and the results in the following table compare this leather with that obtained by following the process of Example E except using quebracho extract (not bisulfited or clarified) which was the starting material in Example 8:

TABLE III

Example	Tanning agent	Shrinkage temperature, ° C.	Quality of leather
(Blank)...	Quebracho extract (not clarified).	77.5	Reddish brown, plump, fully tanned.
E.....	Product of Example 8.....	78	Pinkish buff, very plump, full.

Example F

The process of Example E using calf skin was carried out except that the product of Example 9 was used instead of the product of Example 8.

The leather produced was examined, and the following table shows the comparison of this leather with that obtained by proceeding in accordance with Example F except using the untreated hemlock bark liquor which was the starting material of Example 9:

TABLE IV

Example	Tanning agent	Shrinkage temperature, ° C.
(Blank).....	Untreated hemlock bark sulfite liquor.	66
F.....	Product of Example 9.....	69

Example G

The process of Example E was carried out, except that the product of Example 10 was substituted for the product of Example 8.

The following table shows a comparison of the leather produced in Example G with leather produced in a similar fashion except using regular, untreated "Leucanol" which was the starting material of Example 11:

TABLE V

Example	Tanning agent	Shrinkage temperature, ° C.
(Blank).....	Untreated "Leucanol".....	61
G.....	Product of Example 10.....	69

Example H

Sheep skin skiver squares, fresh from pickle, were rolled in a jar containing a 10 fold float of 7% salt brine at room temperature for six days. Daily increments of the tanning solution which was the product of Example 13 were added at a dilution of 4° Bé. to the skiver soaking in the brine. On the fifth day, all of the solution was drained from the skiver and replaced by the straight 4° Bé. tanning solution for the final day. The skivers were thoroughly washed and dried, without fat liquoring.

Example J

The process of Example H was carried out except that the product of Example 14 was used instead of the product of Example 13.

The shrinkage temperature of the leather produced in Examples H and J were determined, in addition to that for leather obtained with the fermented spent sulfite

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liquor which was the starting material of Examples 13 and 14. The following table shows the results obtained:

TABLE VI

Example	Tanning agent	Shrinkage temperature, ° C.
(Blank)-----	Untreated sulfite liquor-----	61
H-----	Product of Example 13-----	65
J-----	Product of Example 14-----	65

Tanning tests were made following the above procedures with the products of Examples 15, 16, 17 and 18 adjusted to pH 4. In each case control tannage with the untreated spent sulfite liquor was run for comparison. In all of these cases, the treated agents showed significant improvement over the parent material, as shown in Table VII.

TABLE VII

Example	Tanning agent	Shrinkage temperature, ° C.
(Blank)-----	Untreated sulfite liquor-----	61
	Product of Example 15 (1 mg.)-----	62
	Product of Example 15 (5 mg.)-----	64
	Product of Example 15 (14 mg.)-----	64
	Product of Example 16-----	63
	Product of Example 17-----	66
	Product of Example 18-----	65

Example K

The tanning procedure of Example A (pickled sheep skins) was carried out except that the product of Example 19 (the zirconium salt of the enzyme treated and reduced spent sulfite liquor) was used as the tanning agent. Parallel tannages with the untreated liquor, and with the calcium salt of the treated liquor (Example 3) was conducted. Table VIII shows the results of this tannage:

TABLE VIII

Example	Tanning agent	Shrinkage temperature, ° C.
(Blank)-----	Untreated spent sulfite liquor-----	61
B-----	Product of Example 3-----	66
K-----	Product of Example 19-----	82

Example L

The tanning procedure of Example E (still tannage of pickled calfskin) was carried out using the chromic salt prepared as disclosed in Example 20.

Example M

The tanning procedure of Example E (still tannage of pickled calfskin) was carried out using the chromic salt of Example 21.

The tanned pieces of hide from Examples L and M were soft grey in color and flexible. On bending sharply they did not crack as did the pieces tanned with chrome compound made by adding spent sulfite liquor solids instead of the product of my invention to the reduced sodium dichromate.

TABLE IX

Example	Tanning agent	Shrinkage temperature, ° C.
(Blank)-----	Untreated spent sulfite liquor-----	61
L-----	Product of Example 20-----	92
M-----	Product of Example 21-----	103

Example N

An 18 lb. cured and soaked calfskin was immersed in sufficient limewater to cover it. Sodium sulfide (200

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grams) was added. After five days the hair was slipped off and the hide was washed and scudded. A bate was prepared by suspending 250 grams of commercial trypsin in 20 gallons of water at a pH of 8.0. The hide was immersed in this solution for 3 hours at 95° F. It was removed, washed, and divided into left and right sides. Squares were cut from the same positions of the butt section of each half and those from the left side were pickled with salt and sulfuric acid. With appropriate adjustments of acidity, a matched pair of squares from each side was still-tanned with daily increments of the product of Example 3. Comparison tannage of neighboring squares with untreated spent sulfite liquor was conducted simultaneously. Table X shows the results of shrinkage temperature tests on the leathers produced.

TABLE X

Example	Skin	Tanning agent	Shrinkage temperature, ° C.
(Blank)-----	Limed-----	Untreated spent sulfite liquor-----	59
N ₁ -----	do-----	Product of Example 3-----	63
(Blank)-----	Pickled-----	Untreated spent sulfite liquor-----	61
N ₂ -----	do-----	Product of Example 3-----	66

Example P

The tanning procedure of Example E (still tannage of pickled calfskin) was carried out using the product of Example 22. The resultant leather was markedly lightened and brighter in color than that from Example B and was yellow rather than pink.

In addition to their important use as a tanning agent, the products of my invention are especially versatile in their practical utility and particularly in their effectiveness as dispersing agents. They are useful in dispersing pigment, in dispersing clays in forming aqueous slurries in the manufacture of structural clay products, in the dispersing of raw materials in manufacture of Portland cement, in the grinding of Portland cement clinker, in the wet mixing of concrete, and in the dispersing of clays in formulating drilling fluids. The following examples are offered by way of illustration and not limitation to illustrate the effectiveness of products of my invention in several applications where dispersing properties are important.

Example Q

A sample of fermented calcium base spent sulfite liquor was fractionated by adding to it stepwise an organic solvent (ethanol) in order to separate the liquor into three fractions. The first fraction separated, constituting 21% by weight of the spent sulfite liquor solids, was composed primarily of high molecular weight lignosulfonates. The second fraction, constituting 34% of the spent sulfite liquor solids, was composed primarily of lignosulfonates having intermediate molecular weight. The remainder, or third fraction, constituting 45% of the spent liquor solids, was composed of low molecular weight lignosulfonates as well as the major part of the unfermented sugars, organic acids, and other minor components of the original spent sulfite liquor.

Each of the three fractions obtained by solvent fractionation was evaporated to remove the organic solvent and to increase the concentration of solids. A sample of each fraction, at about 35% solids concentration, was treated with the juice obtained from white potatoes and treated with zinc dust, following the procedure described in Example 23.

Using these treated fractions, sheep skin skiver squares weighing 50 grams each were tanned in simulated drum tannage employing endwise revolving cylinders. In each case, a 25 gram portion, dry basis, of one of the fractions was added to the skiver square in the cylinder, along with enough salt and water to give a total of 100 grams

of 10% brine. The cylinders were revolved for 24 hours at room temperature at 20 revolutions per minute. Following tanning the skins were washed, fat-liquored and dried.

The leathers tanned by the different fractions were of different quality. The lower molecular weight fraction gave a more astringent yet more lightly colored leather than the other; while the high molecular weight fraction yielded a full, dark colored leather. The middle fraction yielded leather intermediate between these extremes.

Example R

The dispersing ability of different dispersing agents for titanium dioxide was tested by means of the Daniel-Goldman Test, described in Anal. Adin., Ind. Eng. Chem. 18, 26-31 (1946). According to this test, a solution of the dispersing agent is added with mixing to a known weight of the solid to be dispersed, reaching what is called the "wet point." This volume of solution is recorded. More solution is added, with mixing, until the point called by Daniel and Goldman of "flow point" is reached. The volume of solution required to reach the flow point is recorded. The difference in volumes, ΔV , of solution required to reach the "wet point" and the "flow point," is a measure of the effectiveness of the dispersing agent, a lower ΔV corresponding to a relatively greater dispersing power than a higher ΔV .

In the present tests during the Daniel-Goldman Method, the material to be dispersed was 10 grams of titanium dioxide, and the products being tested were dissolved in water to make solutions containing 3 percent by weight. The products were stripped, fermented spent sulfite liquor solids and the products of Example 23. For further comparison, similar tests were made using water alone with no dispersing agent. Several repetitive tests with each dispersing agent are necessary to provide average values of sufficient accuracy to distinguish the difference in dispersing power of different agents.

TABLE XI.—DISPERSION OF TITANIUM DIOXIDE
[10 g. of TiO_2 was used in each test]

Dispersing solution.....	Wet point	Flow point	ΔV
3% solution of untreated fermented spent sulfite liquor in water.....	4.6	6.0	1.4
Do.....	4.8	6.2	1.4
Do.....	4.8	6.1	1.3
Do.....	4.7	6.1	1.4
Do.....	4.8	6.3	1.5
Average value.....			1.4
3% solution of fermented spent sulfite liquor, treated according to Example 23, in water.....	4.8	6.0	1.2
Do.....	4.8	5.9	1.1
Do.....	4.7	5.7	1.0
Do.....	4.6	5.7	1.1
Average value.....			1.1
Water, with no spent sulfite liquor.....	4.6	9.4	4.8
Do.....	4.6	9.3	4.7
Do.....	4.7	9.4	4.7
Do.....	4.6	9.4	4.8
Average value.....			4.8

It is to be noted that the average ΔV for the untreated fermented spent sulfite liquor, (that is, 1.4) is significantly higher than the ΔV for the product treated according to Example 23 of this invention (that is, 1.1), showing that the product of Example 23 is the better dispersing agent for titanium dioxide. Both products gave ΔV considerably lower than the 4.8 for water containing no dispersing agent. It is further to be noted that although the test may seem somewhat arbitrary in determining the wet point and flow point, the values are reproducible within about 0.1 ml.

Example S

In these experiments the dispersing action on Portland cement mixes of fermented spent sulfite liquor treated according to this invention was compared with that of untreated fermented spent sulfite liquor. The method of testing was to use the "flow table" commonly used in the cement industry to determine the flow characteristics of cement slurries, according to the standard procedure of the American Society for Testing Materials, C230-57T. The test is conducted as follows: the cement-water-Ottawa sand slurry, prepared under carefully controlled conditions, is placed in a form on a horizontal table. The form is removed, and the table is subjected to a series of blows, delivered by the action of a cam driven by an electric motor. As a result of these blows, the mass of cement slurry spreads out over the table to an extent which is a measure of its fluidity. The diameter of the mass of slurry is then carefully measured, and the increase in diameter resulting from the blows is calculated and is reported as the "flow." The resulting of such tests are listed in Table XII. The dispersing agents used were the product of Example 4, which had been redissolved in water and centrifuged to remove any insoluble matter, and the fermented spent sulfite liquor solids without treatment.

TABLE XII.—PORTLAND CEMENT FLOW TABLE TEST RESULTS^a

Dispersant used	Dispersant, g.	Flow Table results, ^b percent	Increase, ^c percent
None.....	0	85	0
Fermented spent sulfite liquor solids.....	7.5	112	32
Product of Example 4.....	7.5	118	39

^a In these tests the weight of cement was 500 g. and the weight of Ottawa sand was 1375 g. The volume of water was 230 ml.

^b The results are expressed as the percent increase in the diameter of the cement-sand slurry after shaking over the diameter before shaking.

^c The "Increase" in this column is the percent of increase in Flow Table figure caused by the dispersant.

Example T

This example illustrates the use of the product of my invention in formulating a drilling mud thinner. For purposes of illustration and not limitation the dried product prepared as described in Example 4 was tested as a limed mud thinner in comparison with dried calcium base fermented spent sulfite liquor solids.

A laboratory drilling mud was prepared from commercial drilling clays and water using 45.5 lbs. bbl. of a mixture of commercial drilling clay having a yield value of 45 bbls. of 15 cp. mud per ton of clay and 1 part by weight of a commercial drilling clay having a yield value of 95 bbls. of 15 cp. mud per ton of clay. The mud was mixed in 500 ml. portions for 30 minutes at high speed on a Hamilton Beach "Drinkmaster" No. 30 milkshake mixer and then allowed to age in a sealed polyethylene bottle for about 24 hours.

For the mud tests, limed muds were made up with 4.0 and 6.0 lbs. per bbl. (4.0 and 6.0 grams to 350 ml. of mud respectively) of the product of my invention and 4.0 and 6.0 lbs. per bbl. of dried fermented spent sulfite liquor. The samples were added to the hereinabove described mud together with 6.0 lbs. per bbl. of calcium hydroxide and 6.0 lbs. per bbl. of 25% sodium hydroxide and the mud mixed for 5 minutes at high speed in the Hamilton Beach mixer. The thinned muds were aged by rolling first overnight at room temperature and then for 20 hours at 150° F. The muds were then mixed 5 minutes and tested for yield, gels, and water loss according to American Petroleum Institute Code No. 29 using a Fann Instrument Corporation, Model 35 V-G Meter and standard API filtration test apparatus.

The product of Example 4 gave a very effective "break-over" of the lime mud to a mud of useable viscosity and low water loss. Without the additive of my inven-

tion the mud containing the lime would be too thick to flow. The results of the tests are shown in the table.

TABLE XIII.—THINNING OF LIMED BASE MUD
[Mud test rolled 20 hours 150° F.]

Sample	Lbs./bbl.	IG.	Y.	10G	WL
Calcium base fermented spent sulfite liquor solids.....	{ 4.0 6.0	{ 3.0 3.0	{ 6.0 3.5	{ 40.0 11.0	{ 15.2 16.7
Product of Example 4.....	{ 4.0 6.0	{ 1.5 1.0	{ 4.0 2.0	{ 19.5 2.5	{ 13.3 15.0

Example U

The wattle product obtained in Example 11 was used to tan hide as set forth in Example H. The shrinkage temperature and degree of tannage were determined with the following results, which include a comparison with untreated wattle:

TABLE XIV

Sample	T _s	Degree of tannage
Untreated wattle.....	68	67
Wattle product of Example 11.....	72	78

Example V

The products of Example 12 were tested as in Example U, with the following results:

TABLE XV

Sample	T _s	Degree of tannage
Untreated chestnut.....	75	74
Chestnut product of Example 12.....	76	87
Untreated myrobalams.....	68	-----
Myrobalams product of Example 12.....	74	-----
Untreated nutgall.....	65	-----
Nutgall product of Example 12.....	69.5	-----

Having fully described my invention, it is to be understood that I do not wish to be limited to the details set forth, but my invention is of the full scope of the appended claims.

I claim:

1. The process of modifying an organic tanning agent selected from the group consisting of plant tannin extracts which have been separated from plant material, lignosulfonates, syntans and mixtures thereof which comprises contacting it with an enzymatic oxidase comprising a phenol oxidase enzyme containing a metal selected from the group consisting of copper and iron under conditions which permit the enzymatic oxidation of said tanning agent to a sufficient extent to improve the tanning properties of said tanning agent, and subsequently subjecting the so-treated tanning agent to chemical reduction.

2. The process of claim 1 in which the organic tanning agent is a plant tannin extract which has been separated from plant material.

3. The process of claim 1 in which the organic tanning agent is a lignosulfonate.

4. The process of claim 1 in which the organic tanning agent is a syntan.

5. A novel product which has been prepared by contacting an organic tanning agent selected from the group consisting of plant tannin extracts which have been separated from plant material, lignosulfonates, syntans and mixtures thereof with an enzymatic oxidase comprising a phenol oxidase enzyme containing a metal selected from the group consisting of copper and iron under conditions which permit the enzymatic oxidation of said tanning agent to a sufficient extent to improve the tanning properties of said tanning agent, and subsequently subjecting the so-oxidized tanning agent to chemical reduction.

6. The novel product in accordance with claim 5 in which the organic tanning agent contacted was a plant tannin extract which has been separated from plant material.

7. The novel product in accordance with claim 5 in which the organic tanning agent contacted was a lignosulfonate.

8. The novel product in accordance with claim 5 in which the organic tanning agent contacted was a syntan.

9. The process of modifying an organic tanning agent chosen from the class consisting of plant tannin extracts which have been separated from plant material, lignosulfonates and syntans, which comprises forming an aqueous suspension of said organic tanning agent with a material containing an enzymatic oxidase comprising a phenol oxidase enzyme containing a metal selected from the group consisting of copper and iron and permitting said suspension to remain for a period of time sufficient to permit the enzymatic oxidation of said tanning agent to occur to a sufficient extent to increase the value of a property chosen from the class of properties consisting of degree of tannage and shrink temperature as determined by tanning hide with the so-modified tanning agent, and subsequently subjecting the suspension to the action of a chemical reducing agent.

10. The process in accordance with claim 9 in which the oxidase is chosen from the class consisting of tyrosinase, polyphenol oxidase, and laccase.

11. The process of modifying a lignosulfonate which comprises contacting it with an enzymatic oxidase comprising a metal selected from the group consisting of copper and iron under conditions which permit the enzymatic oxidation of said lignosulfonate, subsequently subjecting the so-treated lignosulfonate to chemical reduction, and subsequently forming the so-treated lignosulfonate into a salt of a metal chosen from the group consisting of chromium, zirconium and aluminum.

12. The process of modifying a lignosulfonate having a hide powder test value greater than 55% which comprises contacting it with an enzymatic oxidase comprising a phenol oxidase enzyme containing a metal selected from the group consisting of copper and iron under conditions which permit the enzymatic oxidation of said lignosulfonate, and subsequently subjecting the so-treated lignosulfonate to chemical reduction.

13. The process of claim 11 in which the lignosulfonate has a hide powder test value greater than 55%.

14. The process of modifying an organic tanning agent selected from the group consisting of plant tannin extracts which have been separated from plant material, lignosulfonates, syntans and mixtures thereof which comprises contacting it with an enzymatic oxidase comprising a phenol oxidase enzyme containing a metal selected from the group consisting of copper and iron other than a peroxidase under conditions which permit the enzymatic oxidation of said tanning agent, subsequently contacting the so-treated organic tanning agent with a peroxidase in the presence of peroxide oxygen, and thereafter subjecting the so-treated tanning agent to chemical reduction.

15. The process of treating spent sulfite liquor derived from the calcium sulfite pulping of hemlock wood chips which comprises, stripping said spent sulfite liquor with steam to remove free sulfur dioxide, fermenting out the fermentable sugars contained therein with a yeast, removing alcohol from the said fermented spent sulfite liquor, concentrating the so-treated spent sulfite liquor to about half solids and half liquid, adding sodium hydroxide thereto to a pH of about 6.3, grinding whole Irish potatoes to a mash, mixing said potato mash with said concentrated spent sulfite liquor so as to form a mixture, maintaining said mixture at between about 23° C. and 31° C. for about two days, thereafter raising the temperature to near boiling and adding sulfuric acid and zinc thereto, bringing the mixture to room temperature in a period of about a day, adding sodium hydroxide to a pH of 4.5,

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removing sludge from said mixture to produce a liquid product, and removing water from said liquid product so as to form a solid product.

16. The solid product derived from the process of claim 15.

17. The process of claim 1 wherein the source of said oxidase is comminuted white potatoes.

18. The product of claim 5 wherein the source of said oxidase is comminuted white potatoes.

19. A process for tanning hides comprising contacting hides with an organic tanning agent which has been modified by contacting an organic tanning agent selected from the group consisting of plant tannins, lignosulfonates, syntans and mixtures thereof with an enzymatic oxidase comprising a phenol oxidase enzyme containing a metal selected from the group consisting of copper and iron under conditions which permit the enzymatic oxidation of said tanning agent to a sufficient extent to improve the tanning properties of said tanning agent and subsequently subjecting the so-treated tanning agent to chemical reduction.

20. The process of claim 1 wherein said chemical reduction step comprises subjecting the oxidase-treated tanning agent to a chemical reducing agent selected from the group consisting of nascent hydrogen, stannous chloride, sodium borohydride, sodium and calcium hydrosulfites, and sodium sulfoxalate.

21. The process of claim 1 wherein said chemical reduction step is accomplished by the use of nascent hydrogen.

22. The process of claim 1 wherein said chemical reduction step is accomplished by electrolysis.

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References Cited by the Examiner

UNITED STATES PATENTS

1,844,018	2/32	Sailer	195—51
2,437,044	3/48	Robinson et al.	8—94.26
2,491,436	12/49	Barnes	252—8.5
2,594,291	4/52	Cordon et al.	195—2
2,885,325	5/59	Weaver et al.	195—2
2,886,401	5/59	Wells et al.	8—94.33
2,913,304	11/59	Heyden et al.	8—94.33
2,997,363	8/61	Pfiroman	8—94.26

OTHER REFERENCES

F. F. Nord, *Advances in Enzymology*, Interscience Pub. Inc., New York; vol. 2, pages 121, 122, 130, 131 (1942); vol. 6 page 336 (1946); vol. 10, pages 347, 348 (1950); vol. 16, pages 150, 151, 152, 153 (1955).

Biochemical Journal, vol. 34, pages 1472 to 1492 (1940); vol. 35, pages 1106 to 1115 (1941).

Sumner et al., *Chemistry and Method of Enzymes*, Academic Press, Inc., Pub., New York, 1953, pages 213, 240 to 245.

Gustavson, *Chemistry of Tanning Process*, Academic Press Inc., New York (1956), pages 202, 203, and 223.

Gustavson, *Chemistry of Tanning Process*, Academic Press Inc., New York (1956), pages 2 to 4.

A. LOUIS MONACELL, *Primary Examiner*.

TOBIAS E. LEVOW, ABRAHAM H. WINKELSTEIN,
Examiners.