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**BARK TREATMENT PROCESS AND PRODUCT**  
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This invention relates to the digestion of bark to derive chemicals therefrom, and has for its object the provision of an improved process of digesting certain coniferous barks, and an improved chemical product resulting from the digestion. The process of the invention comprises digesting the barks, in a suitable state of subdivision, with an aqueous acid solution of a sulfurous acid salt of sodium or potassium at a suitably elevated temperature to recover a water-soluble product containing sulfonate salts of hydroxy aromatic polymeric compounds which is outstandingly effective as a drilling mud additive.

When certain barks are digested with alkali metal salts of sulfurous acid, for example sodium sulfite, in an aqueous alkaline solution, the resulting bark derivative when added to some alkaline drilling muds to control the rheological properties promotes the entrainment of air which results in air-cutting or foaming. As a result of extensive investigations of the chemistry of bark we have found that the air-cutting or foaming is due to saponifiable chemicals which have been removed from the barks of certain trees as a result of the alkalinity of the solution, and that the contaminating chemicals which appear to be derivatives of fats and waxes from the bark can be practically eliminated from our improved bark derivatives by digesting such barks in an aqueous solution of an alkali metal salt of sulfurous acid at a pH below 7.0. Our invention accordingly provides a process for deriving our improved products from the barks of Douglas fir (*Pseudotsuga menziesii*), Amabilis fir (*Abies amabilis*), and southern pine (*Pinus elliotii*, *Pinus palustris*, *Pinus taeda*, and *Pinus echinata*). Our invention also provides an improved alkaline drilling mud comprising our bark derivative.

The foregoing coniferous barks have peculiar compositions which cause them to respond in an unexpected manner to chemical digestion with aqueous acid solutions of sodium or potassium bisulfite, or mixtures of bisulfite and sulfite, at a pH below 7.0 and at an elevated temperature. In accordance with the process of the invention, the bark is digested with a dilute aqueous solution of an alkali metal bisulfite or one in which up to about 50% of the bisulfite is substituted with a sulfite. Our preferred digestion liquor comprises an aqueous solution of about 75% bisulfite and 25% sulfite, since the use of a digestion liquor containing only bisulfite sometimes yields a product with a slightly inferior ability to control the rheological properties of a drilling mud, and furthermore, the lower pH of such a liquor increases its corrosive action on processing equipment. Digestion is carried out at a temperature of from 105° C. to 200° C. and for a time sufficient to solubilize the extractable chemicals, which is usually less than four hours. The pH of the digestion liquor varies from about 4.5 for a pure bisulfite solution to just below 7.0 for a 50-50 mixture of bisulfite-sulfite, while that for the preferred 75-25 bisulfite-sulfite mixture ranges from about 5.5 to 6.0.

In carrying out digestion operations of the invention the bark which is usually obtained in large pieces is preferably reduced in size to pass screens of about 1 to about 20 meshes to the inch in order to avoid an excessive amount of void space in the charge and to aid penetration of the reacting solution. This may be accomplished by conventional means, as by a hammer mill or attrition mill. As an operating expedient, it is also desirable to

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avoid excessive amounts of fines, such as bark dust, which sometimes clog filters, although such fines are in condition for rapid digestion. It has been found that digestion temperatures ranging from about 105° C. to about 200° C. can be used. In using the lower temperatures, longer digestion periods are desirable but temperatures as high as 200° C. can be used for digestions of considerable length, say, for example, an hour, without consuming all of the sulfurous acid salts or materially decomposing the organic products. For digestions which are both rapid and relatively efficient, temperatures of about 170° C. to about 175° C. are preferred. When temperatures much above 175° C. are used, some degradation of the extracted product sets in and no important increase in yield is obtained, and where temperatures much below 125° C. are used, the advantages of high yield and short extraction time are lost, and the products at temperatures below 100° C. are not very good deflocculants for drilling muds. Digestion periods of about fifteen minutes to about 4 hours are used, but at all events the digestions are stopped while there still remains some content of sulfurous acid salt in the charge. Two hours is ordinarily the practical time limit at the higher temperatures. A smaller proportion of the alkali sulfurous acid salt than that equivalent to about 0.03 part of sulfur dioxide per part of oven-dry bark is insufficient, but more salt than that equivalent to about 0.20 part sulfur dioxide per part of oven-dry bark is more than is needed to carry out the reaction satisfactorily. The slight excess of chemicals acts to protect the extractants at the high temperatures, and this action may be lost at concentrations below 0.03%. However, an excess over 0.20% can be used, provided the inorganic salts resulting from such excessive amounts are not deemed deleterious in the solutions of water-soluble products derived from the processes.

In using the subdivided bark of the sizes indicated, about 10% to about 20% of the bark on the basis of its equivalent oven-dry weight is desirable in the charge, the rest of the charge being water and the sulfurous acid salts. We prefer to use a water solution containing from 50% to 75% of the active chemical as sodium bisulfite, and the balance sodium sulfite. However, the amount of water is not critical. The amounts of water indicated are preferable since such amounts provide water to act as solvent for the inorganic material and for the aromatic sulfonates formed, as well as to provide the presence of water and sulfurous acid radical in the reaction mass. Amounts of water in excess of the proportions indicated may be present when barks of the size indicated are used, but water in excess of such proportions tends to slow the reaction by dilution of the chemical, serves in general to require excessive space in the digesters, and eventually gives a very dilute product solution requiring a correspondingly costly evaporation to produce the solids in the form of concentrated solutions or in dry form. In general it is desirable but not necessary to agitate the charge in the digester, although continuous mixing reduces somewhat the time of reaction. The digestion equipment and physical condition of the bark must be capable of bringing the bark material and water solution of alkali sulfurous acid salt into intimate contact. Either batch or continuous operations may be carried out in a single stage or in a multiplicity of stages.

Following the digestion, the products of the reaction as well as any other water-soluble material are separated from the insoluble bark residue. Some of the products of reaction are contained in solution occluded in the bark residue, and in view of their relatively high molecular weight and slow diffusion rates, the separation of this material by washing operations dependent on diffusion has disadvantages, however, still representing consider-

able improvement over older procedures of lixiviating undigested bark. Such separation of occluded reaction materials simply by washing involves uneconomic dilution, and is not even relatively complete unless many changes of water and prolonged soaking periods for diffusion are provided.

Effective and rapid separation of all soluble products of digestion is preferably accomplished by mechanical dislodging aids. Such mechanical dislodging aids or expressing means effectively separate occluded solution and the soluble reaction product contained therein from the bark residue. Expressing, as by compressing the mixture of watery material and bark residue in a continuous screw press or in a batch hydraulic press, is especially effective, in that solutions of maximum concentration are producible. Using batch pressing, it will frequently be found desirable to reslurry the pressed residue in water and repress.

The solutions usually contain a small amount of insoluble material such as bark in fine subdivision which, if desired, may be separated by filtration. The products may be used in the form of water solutions of suitable concentrations or in the form of solids. Concentration of the solutions may be effected by known methods of evaporation, and the like, either at atmospheric or reduced pressure, but temperatures not exceeding those used in the digestion of the bark are preferable in order to avoid degradation of the phenolic material present. Solid products may be produced by known methods, such as spray drying and drum drying, conducted at atmospheric or reduced pressures, preferably avoiding excessive temperatures and oxidizing conditions which would affect the tannins where further reactions are not desired.

The bark of the aforementioned coniferous trees is composed of various materials which are significant to the invention, including a large proportion of insoluble hydroxy aromatic compounds, varying small proportions of various water-soluble tannins and saponifiable fats and waxes. With the exception of the fats and waxes, a considerable proportion of the insoluble part of the bark is converted by the present process of digestion into water-soluble alkali sulfonate salts of hydroxy aromatic compounds. The saponifiable fats and waxes are practically unaffected. Besides these organic salts, the water-soluble solids in the reaction product comprise alkali sulfurous and sulfuric acid salts derived from the charged inorganic salts. A small but varying proportion of such salts are sulfurous acid salts. The ratio of organic to inorganic material present in the solid product varies and depends upon a number of factors among which are the amount of convertible material in the bark, the amount of the insoluble proportion of the bark material converted and the proportion of bark to inorganic sulfurous acid salt used in the charge. The organic material contains aromatic compounds and will have relatively large proportions of phenolic hydroxy groups in important amounts, so that the compositions derived from the products of the present reaction constitute an important source of raw organic material of the kinds indicated. All of the products are useful as reactants or raw materials from which to manufacture other organic compounds or compositions, especially drilling muds.

The bark derivatives in aqueous solution as initially recovered from the bark are acid chemicals and our invention provides a variation of this derivative obtained by reacting it with an alkali, such as sodium hydroxide, to give a product having a pH of about 8.5 before drying. This product is especially advantageous for use in alkaline drilling muds as a viscosity control agent.

In accordance with this invention, nine separate digestions were made, three each from Douglas fir, Amabilis fir and a mixture of the four listed southern pine barks. Three portions of wet bark equivalent to ten to fifteen pounds of bone-dry material of each of the foregoing species were hammermilled to pass through a  $\frac{7}{16}$  by

inch screen. These samples were then digested, one in each of the three following ways:

(A) These samples were digested for 30 minutes at 150° C. with an aqueous solution of sodium sulfite equivalent to 0.09 parts SO<sub>2</sub> per part of dry bark. After completion of the digestion, the aqueous solution of the bark extract was separated from the bark residue and, upon suitable concentration, was spray dried.

(B) These samples were digested for 60 minutes at 170° C. with an aqueous solution of sodium bisulfite equivalent to 0.07 parts SO<sub>2</sub> per part of dry bark. (The pH during extraction was approximately 4.5.) After completion of the digestion, the aqueous solution of the bark extract was separated from the bark residue and alkalinized with sodium hydroxide to a pH of 8.5 (to produce a sodium content equivalent to the "A" products). It was then suitably concentrated and spray dried.

(C) These samples were digested for 45 minutes at 170° C. with an aqueous solution of a mixture of 75% NaHSO<sub>3</sub> and 25% Na<sub>2</sub>SO<sub>3</sub> equivalent to 0.07 parts SO<sub>2</sub> per part of dry bark. The pH during extraction was about 5.85, varying somewhat, of course, as chemical was used up, but always remaining below 7.0. After completion of the digestion the aqueous solution of the bark extract was separated from the bark residue and alkalinized to a pH of 8.5 with sodium hydroxide. It was then suitably concentrated and spray dried.

In each of the above digestions, a sufficient amount of water and chemical was used to give a 12% consistency based on the weight of the dry bark during the reaction.

The yields are given in the following table:

Table I

| Bark               | Extraction Method | Yield, percent |
|--------------------|-------------------|----------------|
| Southern pine..... | A.....            | 47.9           |
| Do.....            | B.....            | 50.3           |
| Do.....            | C.....            | 48.9           |
| Douglas fir.....   | A.....            | 49.0           |
| Do.....            | B.....            | 51.2           |
| Do.....            | C.....            | 48.5           |
| Amabilis fir.....  | A.....            | 47.3           |
| Do.....            | B.....            | 47.0           |
| Do.....            | C.....            | 41.3           |

The bark derivatives of the invention are excellent viscosity control agents in drilling muds, and have little, if any, tendency to promote air-cutting in the mud to which they have been added.

A large quantity of a base mud for use in testing the various bark derivatives was prepared by mixing a blend of 75% of native Texas clay and 25% of a Wyoming bentonite clay with distilled water at the rate of 58 lbs./bbl. solids to water. Sample muds for testing were prepared using the base mud and the previously-described nine bark derivatives as follows:

(a) The bark derivative being tested was added to an aliquot of the base mud at the rate of 3 lbs./bbl., along with 0.3% of NaCl (based on mud volume), and the resultant blend mixed at high speed for one minute.

(b) Caustic soda (NaOH) was then added to (a) at the rate of 3 lbs./bbl., and this mixture was mixed for 5 minutes at high speed.

(c) Lime was then added to (b) at the rate of 5 lbs./bbl. and the whole again was mixed at high speed for 5 more minutes. At this time the so-called "break-over" mud weights were determined.

This synthetic drilling mud is representative of a conventional lime-treated mud under operating conditions. The mud samples were then aged overnight in a roller cabinet at 70° C., remixed for 5 minutes at high speed and given the usual mud tests, as indicated in Table II. The extent of the air-cutting is determined by the "mud weight" of the mud to which the additive is added under fixed conditions. Mud weights, as such, were determined by the standard A.P.I. procedure as set out in the Ameri-

can Petroleum Institute bulletin entitled "Recommended Practice for Standard Field Procedure for Testing Drilling Fluids," API RP 29, third edition, May 1950.

The other physical properties of the drilling muds, as set out in the examples, were tested in the laboratory by procedures developed by the American Petroleum Institute also, as described in the said bulletin, modified, however, by substitution of a Fann V. G. viscometer for the Stormer, as suggested by Rogers in "Composition and Properties of Oil Drilling Fluids," 1953 ed., pp. 103 and 104. The important properties pertinent to a viscosity control agent that were determined for use herein were viscosity, 0 and 10 minute gel strengths and fluid loss (often also termed "water loss," "filter loss," or simply "filtration").

Table II

| Bark Derivative | Mud Weight,<br>lb./gal. |      | Vis-<br>cosity,<br>cp. | Gel Strength,<br>lbs./100 sq. ft. |            | Fluid<br>Loss,<br>ml./30<br>min. |
|-----------------|-------------------------|------|------------------------|-----------------------------------|------------|----------------------------------|
|                 | Break-<br>over          | Aged |                        | 0<br>min.                         | 10<br>min. |                                  |
| Southern Pine:  |                         |      |                        |                                   |            |                                  |
| "A"-----        | <7.0                    | <7.0 | 16                     | 4                                 | 31         | 15.2                             |
| "B"-----        | 8.8                     | 9.0  | 10                     | 2                                 | 21         | 16.4                             |
| "C"-----        | 8.4                     | 9.0  | 10                     | 1                                 | 16         | 16.4                             |
| Douglas Fir:    |                         |      |                        |                                   |            |                                  |
| "A"-----        | 7.3                     | 7.3  | 11                     | 3                                 | 21         | 15.4                             |
| "B"-----        | 9.0                     | 9.1  | 11                     | 2                                 | 22         | 16.2                             |
| "C"-----        | 9.0                     | 9.1  | 10                     | 2                                 | 21         | 17.4                             |
| Amabilis Fir:   |                         |      |                        |                                   |            |                                  |
| "A"-----        | 7.5                     | 7.6  | 12                     | 4                                 | 30         | 15.0                             |
| "B"-----        | 8.8                     | 9.0  | 12                     | 4                                 | 36         | 17.0                             |
| "C"-----        | 8.7                     | 9.0  | 10                     | 3                                 | 28         | 17.4                             |

In the method of testing used above, the high speed mixing whips air into the mud and the mud weight shows the degree of air entrainment resulting from the use of the derivative. Under the given circumstances, a mud having a weight of say 9.0 lbs./bbl. indicates that there has been virtually no entrainment, but one with a mud weight of say 7.5 or lower indicates a highly air-cut mud, so frothy in fact as to be almost completely unusable.

This type of mud was selected for comparative tests because air-cutting may become a serious problem when viscosity control agents are used in such muds. However, the bark derivatives of our invention may be used effectively as viscosity control agents in any type of drilling mud, and they will not cause air-cutting in drilling muds susceptible of air-cutting.

As the lists show, when the aforementioned barks are digested in alkaline solutions of sulfite, the resulting bark derivative will foam or air-cut so badly in an alkaline drilling mud as to be useless. Drillers will not use materials which cause air-cutting for the following reasons:

(1) Foam (especially where mud guns are used) hides the surface of the mud in the pits so the driller cannot watch it for indications of what is happening down below.

(2) Foam-cut muds do not release drill cuttings properly.

(3) Regular mud pumps do not operate properly on foam-cut muds because of the air in it and the resulting compressibility.

(4) It is impossible to maintain a proper weight in a foam-cut mud. A sufficient hydrostatic head must be maintained in a well to prevent dangerous blowouts. Again, if it becomes too heavy, the mud itself can be lost in the formation being drilled. A proper and carefully controlled mud weight, therefore, is essential for successful well drilling.

(5) A driller determines when gas pockets are encountered by watching the mud as it comes from the well. Foam-cut mud, of course, would interfere with this procedure.

We claim:

1. The process of making a bark derivative containing water-soluble sulfonate salts of hydroxy aromatic

polymeric compounds which comprises digesting a bark of the group consisting of Douglas fir, Amabilis fir, and southern pine in an acid water solution at a pH below 7.0 of a salt of the group consisting of sodium and potassium salt of sulfurous acid which is at least 50% alkali bisulfite at a temperature of from 105° C. to 200° C. while maintaining sulfurous acid salt in the reaction mixture, said heating being continued until a portion of the sulfurous acid radical of the inorganic salt is combined in the water-soluble derivatives of the bark, separating from the bark residue the water-soluble bark derivative which is practically free of saponified matter, and alkalizing the solution by the addition of a sodium compound.

2. The process in accordance with claim 1 in which the sulfurous acid salt consists of at least 50% of sodium bisulfite and the bark derivative is practically free of saponifiable material.

3. The process of claim 1 which comprises digesting the bark in a solution containing a mixture of salts of sulfurous acid consisting of from 50% to 75% of sodium bisulfite and from 25% to 50% of sodium sulfite at a pH varying from 4.5 to 6.0.

4. The process in accordance with claim 1 in which the sulfur dioxide of the sulfurous acid salt and bark in the mixture treated are in the proportion of about 0.03 to 0.20 part of sulfur dioxide per part of bark.

5. In the process of claim 1 alkalizing the solution by addition of a caustic sodium compound to change the pH to about 8.5.

6. The process of making a bark derivative containing water-soluble sulfonate salts of hydroxy aromatic polymeric compounds which comprises heating a bark of the group consisting of Douglas fir, Amabilis fir, and southern pine in a water solution consisting preponderantly of sodium bisulfite at a temperature of about 150° to about 175° C., and maintaining some sulfurous acid salt in the reaction mixture until a portion of the insoluble part of the bark is converted to water-soluble hydroxy aromatic compounds, separating from the bark residue the bark derivative containing water-soluble hydroxy aromatic compounds which are practically free of saponified matter, and alkalizing the solution by the addition of a sodium compound.

7. A water-soluble product comprising alkali metal sulfonic acid salts of aromatic hydroxy polymeric compounds and inorganic alkali metal salts resulting from digesting a bark of the group consisting of Douglas fir, Amabilis fir, and southern pine in an acid water solution at a pH below 7.0 of a salt of sulfurous acid of the group consisting of sodium bisulfite, and sodium sulfite at a temperature of from 105° C. to 200° C. until a portion of the insoluble part of the bark is converted to water-soluble hydroxy aromatic alkali sulfonate compounds, separating from the bark residue the water-soluble composition which is practically free of saponified matter, and alkalizing the solution by the addition of a sodium compound.

8. A water-soluble product as defined in claim 7 in which the composition is formed by digesting the bark in a water solution of a mixture of sodium sulfite and sodium bisulfite consisting of at least 50% of sodium bisulfite at a pH of from 4.5 to 6.

9. A water-soluble product as defined in claim 8 containing added alkali to give the solution thereof a pH of about 8.5.

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