This invention relates to additives for oil well drilling muds, and more particularly relates to an improved form of quebracho extract characterized by improved storage properties and by improved efficiency when used as a treating agent or additive in oil well drilling muds.

Quebracho extract comprises the tannin-containing extract of the quebracho tree, which grows principally in Argentina and Paraguay, in South America. The normal commercial handling of the material includes the extraction with water or the like of the valuable constituents of the hardwood of the tree at substantially the site of cutting the tree, and the shipping of the hardened extract in solid form to grinding mills in this country. As received, the extract comprises substantially 80% to 85% solids, the remainder being occluded water. Of the solids, from 70% to all of the solids, based upon the entire extract, may be soluble in water and between 65% and 72% of the composition may be tannins. Non-tannin materials, such as lignins, waxes, gums, cellulose, sugars, and starches, comprise the remainder of the soluble constituents and the water-insoluble portion of the extract. Since the extract is a natural product often produced under relatively primitive conditions, no absolute quantitative analysis is available; in fact, the composition is variable but generally remains within the limits set forth above.

Where the quebracho extract as imported is to be diverted to well drilling uses, the same is ground and packaged by the recipient in the country to prepare the extract for use in drilling mud treatment. While no great criticality characterizes the grinding with respect to ultimate particle size, it is in general preferable and the practice in the art to grind to at least an extent that all of the material will pass a 10 or 12 mesh to the inch screen, such as a U.S. standard No. 14 screen. Finer grinding is sometimes resorted to but coarser grinds are in general not used since ultimate speed of solution is adversely modified.

After being ground and packaged, the quebracho extract is normally stored in the grinder's warehouse until purchased by drilling mud chemical distributors or sellers who maintain storage warehouses adjacent to well drilling operations. The quebracho extract is then stored in the retail distributors' warehouses until purchased by drilling operators, who dissolve the ground extract for treatment of the oil well drilling mud at the well site.

A difficulty arises in this chain of processing, however, which difficulty appears after the grinding operation of the extract in that especially in humid climates and in the warm humid summer months, but to a considerable extent the year-round, the quebracho extract after grinding has a tendency to return to solid form to an extent that the ground material may set up in solid, substantially insoluble form in a period of time as short as two weeks. Since normal marketing practice in the drilling industry does not ordinarily permit movement of ground quebracho extract to the driller in times even approaching such short periods, amounts of extract from 10% to 50% of the total received at the drilling site are commonly discarded as insoluble lumps in the course of attempting to dissolve the same. This discarding of material at the well site is normally dictated by the prohibitive expense of returning the lumped, insoluble material to the grinder for retreatment and by the immediate necessities of the activities at the well site. Particularly in view of the relatively large quantities of quebracho extract which may be employed at one time in a single drilling operation, a saving of any fraction of this discarded material is significant. For example, a drilling mud system for a single well wherein the constituents of the mud may vary widely but will in general depend upon the location of the well and usually include, as is well understood in the art, natural or artificial clay suspensions, which may or may not be weighted with barytes and a variety of other materials, may consist of as much as 650 to 4,000 or more 42-gallon barrels of mud, depending upon the nature of the drilling operation and the character of the formation being drilled. While a great number of factors well understood in the drilling art influence the amount of quebracho extract which will be incorporated in such a system, in general from 0.5 to 20 pounds of extract per barrel of mud, to give an average of usually not over ten pounds of extract per barrel of mud, the discarding of quebracho extract to caustic may vary over wide ranges in accordance with conditions met by the driller but, in general, between one-third and one and one-half parts of caustic to one part of quebracho extract are employed, a particularly suitable range being one-half part to one part of caustic to one part of the extract.

Accordingly, in order to incorporate the quebracho extract and alkaline agent, such as caustic soda, with the mud, solidifying the quebracho extract as received is necessary and where insolubles are found in the material as received up to 50% thereof, a tremendous wastage and loss of this relatively difficulty obtained commodity has heretofore obtained. Moreover, even in the rare cases where return to the grader of the solidified material is possible from an economic standpoint, a loss in weight, probably due to loss in moisture, of up to 5% occurs, which loss is an economic waste as transportation costs must be paid thereon.

The present invention has as its principal object the provision of a simple, inexpensive method for obviating the recaking of the ground quebracho extract and the provision of a composition comprising quebracho extract which remains in small particle size, soluble conditions for indefinite periods of time.

A further object of the invention is to provide a quebracho-containing material suitable for use in well drilling operations in the manner of the quebracho extract as now used in well drilling operations but having improved properties thereover and possessing the principally important property of not caking after grinding.

A further object of the invention is to provide a composition comprising quebracho extract which shall be substantially completely soluble in a relatively short time in either hot or cold water, whereby the same may be used under the extremely rugged conditions which not uncommonly exist at well sites where the material is used in drilling operations.

Further objects and advantages of the invention will
appear more fully hereinafter in the course of a detailed description of the same.

The present invention contemplates a combination with quebracho extract in the course of grinding, or the mechanical combination with ground quebracho extract immediately subsequent to grinding, of alkali metal lignosulfonates in amounts ranging between 5% and 25% by weight of the quebracho extract and most suitably about 10%. The particle size of the ground material may be as disclosed above. When quebracho extract is so treated, either during the grinding or immediately subsequent thereto, the extract no longer sets up into a cake following its grinding, even under the most severe humidity conditions. As a result of the present invention, the quebracho extract comes to the drilling rig in a very readily soluble form, as it is still substantially as finely ground as it was at the grinding operation and is found to be more readily soluble in both cold and hot water than untreated quebracho extract, whether finely ground or not.

Where the expression "alkali metal lignosulfonate" is used, it will be understood that any alkali metal lignosulfonate, such as lithium, sodium, potassium, rubidium, and cesium, may be employed and it will moreover be understood that, particularly since the sodium lignosulfonate is normally recovered from paper manufacturing operations, a sodium compound in general will be preferred both for simplicity in use and for economic reasons. Highly refined alkali metal lignosulfonates may be used but since they appear to add nothing to the efficient operation of the invention, relatively crude lignosulfonates are in general preferred. Thus, the sodium lignosulfonate may be recovered from weak solutions in paper manufacturing operations; a particularly satisfactory material for the purpose of the present invention has been found to be spray-dried or drum-dried sodium lignosulfonate recovered from such solutions.

A particular advantage arising from the employment of the combination of this invention lies in the speed with which the material will dissolve in cold water, as compared to the speed with which quebracho extract alone dissolves in cold water. It is apparent that the sodium lignosulfonate addition to the quebracho acts as a solubilizer for the quebracho extract itself; most or all of the insolubles normally present in the quebracho extract become soluble and available for treating of the drilling mud.

As pointed out hereinafore in connection with the quebracho extract itself, the combination of this invention may also be combined with an alkaline material, such as those mentioned and particularly caustic soda, for application to the mud. The same proportions mentioned hereinafore are also applicable, viz. one-third part to one and one-half parts of caustic to one part of the composition of this invention, the range, i.e. one-half to one part of caustic to one part of the composition, of this invention being in general preferred. The action of alkaline materials in the systems under discussion is well-understood and since such action forms no part of the present invention it need not be further adverted to.

It is a feature of the present invention that the combination of quebracho extract and alkali metal lignosulfonate results in a mud treating material having somewhat more advantageous properties with respect to viscosity, initial gel strength, ten-minute or delayed gel strength, and particularly water loss than quebracho extract itself.

The property of the quebracho extract solution when used in treating the mud, of reducing the viscosity of the mud, in order that cuttings and other foreign matter may settle out of the mud in settling pits, is enhanced by the addition to the quebracho extract of between 5% and 25% of sodium lignosulfonate, by a factor of the order of 5%. Though apparently a relatively slight improvement obtains in the efficiency of the material of this invention over quebracho extract itself, it will be appreciated that present in the composition of this invention is only between 75% and 95% of quebracho extract as compared to 100% in the pure quebracho extract and that therefore, less of the quebracho extract plus the alkali metal lignosulfonate is doing a somewhat better job with respect to reducing the viscosity of the mud than is done by the quebracho extract itself. This advantage of the material over quebracho extract itself is, of course, additive to the important advantage of the combination which is the non-foaming character of the combination and its easy solubility, as pointed out above. An additional significance of the viscosity reduction by the use of the combination of this invention lies in the reduction of fluid friction in the drill pipe and the improved washing or cleansing action on the drill bit that a lower viscosity fluid will have.

Furthermore, the combination of between 5% and 25% of alkali metal lignosulfonate, such as sodium lignosulfonate, with ground quebracho extract has the added advantage of providing low initial gel strength in the mud when the material is added to the mud in quantities ranging between 0.2 pound/bbl and 20 pounds/bbl. of the material of this invention to mud. The low initial gel strength, of course, is understood to be desirable in order that the mud remain as free as possible of sticking action on the drill bit. Moreover, it is the characteristic of muds used for this purpose that they shall have higher gel strength at periods following their initial use in order that they may adequately pick up and remove high specific gravity solids in the well, suspend high specific gravity solids in the bore hole while the mud is quiescent, and remove the same from the bore hole and deposit them in the settling beds. It is, of course, undesirable to have the subsequent gel strength of the mud go so high as to prevent its being pumped from the well or to cause dangerous "swabbing of the hole." It has been found that when quebracho extract itself, after suitable grinding and solubilizing, is added to mud on a basis to provide an ultimate ratio of between 0.5 pound/bbl. and 10 pounds/bbl. of mud that the subsequent ten-minute or delayed gel strength of the mixture is reasonably satisfactory. The material of the present invention, when substituted for straight quebracho extract, is similar in properties to quebracho extract itself with respect to gel strength, it being understood that thereby a 5% to 25% saving in the amount of the extract necessary for treatment of the mud is effected, and the extract thus saved is replaced by a material which is less expensive, is entirely domestic, and contributes to the easy solubility of the extract in accordance with the present invention.

Finally, it is found that the third significant property desired by drilling experts to be found in a treated drilling mud, i.e. low water loss, where water loss has reference to the seepage of water through the mud cake or filter zones in the bore hole, is present to a significantly greater extent in the material of the present invention comprising a combination of alkali metal lignosulfonate and quebracho extract than in quebracho extract itself. Thus, where hereofore quebracho extract alone resulted in a water loss over a given period of time of the order of 5 and 10 units, the combination of between 5% and 25% of sodium lignosulfonate with the quebracho extract prior to solution and the use of such combination in mud in a ratio of between 0.2 pound/bbl. and 10 pounds/bbl. of mud results in water loss in the order of 3 to 7 units based on the same scale of measurement.

As pointed out above, that this lower water loss is achieved while using between 5% and 25% less of the quebracho extract.

Further advantages of the present invention are the absolute avoidance of regrinding and consequent loss of weight referred to above and more significantly the fact that by combining quebracho extract with alkali metal
lignosulfonates, such as sodium lignosulfonate, in the course of grinding the solubilizing effect upon the insolubles of prior art quebracho extract to an extent that insolubles of a tannin character, as referred to above, are substantially eliminated and substantially all of the soluble material is therefore available as tannins for their well-known influence on the mud. Thus, a typical quebracho extract ground with 10% of sodium lignosulfonate contains 84.7% of total solids, 78.6% of which is soluble and all of which is tannins and is thus made available in the mud. The effective increase in solubility, both by avoiding recaking and by making available more of the tannins present in the extract, is an important feature of this invention.

In order that those skilled in the art may more fully be informed of the invention, the following examples are offered:

**Example I**

Quebracho extract, as imported from the Argentine, is ground by a conventional grinding apparatus with one part by weight of sodium lignosulfonate in powdered form being added to each nine parts of quebracho extract ground. Subsequently the material is stored in ground condition for a period of two and one-half months and thereafter is unpacked and found to be in a free-flowing state. This material is dissoluted to make a solution comprising 12% thereof and 12% caustic soda. A natural drilling mud obtained from a drilling well was treated with the solution in the proportion of one part of solution to ninety parts of mud. For comparison, ground quebracho extract containing no lignosulfonate was put in identical aqueous solution comprising 12% quebracho extract and 12% NaOH and the same natural drilling mud was treated with the solution in the proportion of one part of solution to ninety parts of mud. The tests showed the quebracho-lignosulfonate compound produced a reduction of viscosity in the mud slightly greater than the 100% quebracho extract solution alone; the reduction of gel strength was substantially the same with both solutions; and the water loss in the case of the quebracho-lignosulfonate composition was approximately 7.5% less.

The quebracho-sodium lignosulfonate composition was used to treat the drilling mud in the above-mentioned well until completion of drilling operations.

**Example II**

Quebracho extract, as received from import, is ground in a conventional manner and subsequent to grinding, 10% of sodium lignosulfonate in dry powdered form is intimately mechanically mixed therewith. Thereafter, the material is stored for a period of three months, after which it is removed from storage and found to be in a free-flowing condition and ready for use in drilling mud treatment. This material was placed in solution and tests conducted on a natural drilling mud in comparison with identical ratio solutions containing 100% quebracho extract. It is found that in accordance with standard tests of such treating materials, the resultant reduction of viscosity is comparable, as are the resultant reductions of gel strengths, while the water loss is improved by a factor of about 10% over 100% quebracho extract.

While there have been described various embodiments of the invention, the methods and products described are not intended to be understood as limiting the scope of the invention as it is realized that changes therewithin are possible and it is further intended that each element recited in any of the following claims is to be understood as referring to an equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A dry, free-flowing, non-caking additive for drilling muds comprising a mechanical mixture of dry ground quebracho extract and between 5% and 25% by weight thereof of alkali metal lignosulfonate.

2. A composition as claimed in claim 1 wherein the alkali metal lignosulfonate is sodium lignosulfonate.

3. A dry, free-flowing, non-caking additive for drilling muds comprising a mechanical mixture of dry ground quebracho extract and 10% by weight thereof of sodium lignosulfonate.

4. The method of improving the solubility of quebracho extract and preventing its caking after grinding, which includes grinding solid quebracho extract and substantially simultaneously mechanically mixing dry alkali metal lignosulfonate with said dry extract at least prior to resolidification of said extract after grinding.

5. The method of claim 4 wherein the alkali metal lignosulfonate is sodium lignosulfonate.

6. The method of claim 4 wherein said alkali metal lignosulfonate is sodium lignosulfonate recovered from paper-making operations.

7. The method of claim 4 wherein between 5% and 25% by weight of said sodium lignosulfonate is employed.

8. The method of claim 4 wherein 10% by weight of said sodium lignosulfonate is employed.

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