July 12, 1960 A. C. KIBRICK ET AL 2,944,928

METHOD OF PREPARING PAPER PULP

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FIG. 2

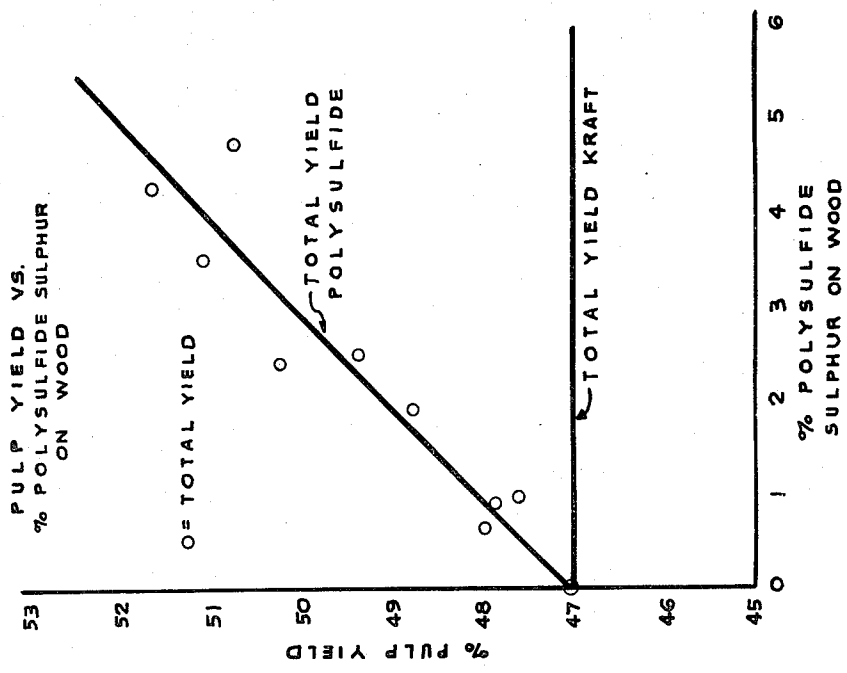
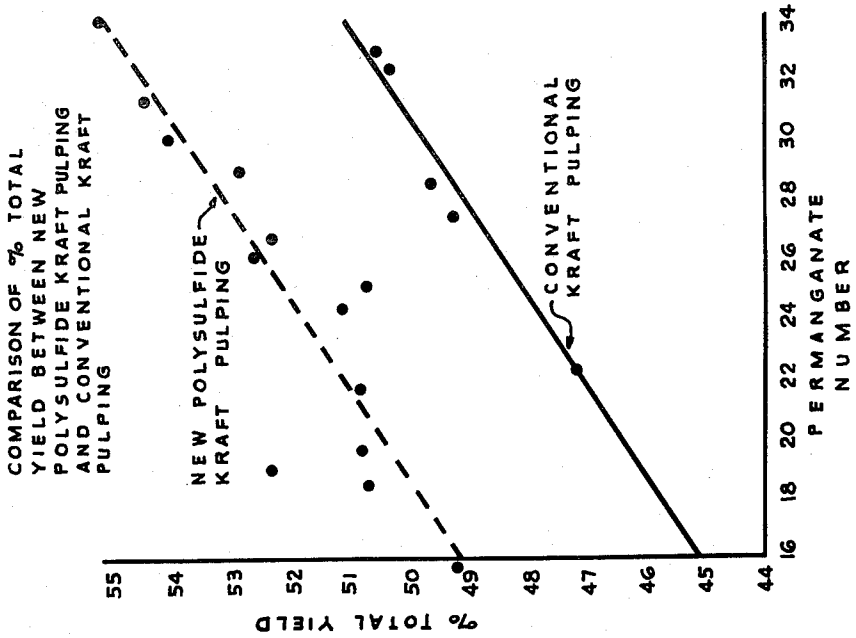



FIG. 1



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# METHOD OF PREPARING PAPER PULP

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This invention relates to the manufacture of wood pulp such as that used in paper manufacturing purposes, and in particular is concerned with improvements in the kraft or alkaline sulfate paper process.

Hitherto, in the preparation of wood pulp for paper production, wood, in the form of finely divided pieces, is subjected to a cooking process in the presence of sodium sulfides and minor amounts of sodium sulfates. It is, for example, customary to treat raw wood chips, such as may be obtained from southern yellow pine, notably mixtures of loblolly, longleaf and shortleaf pine, and also from jackpine and from various species of spruce, fir, hemlock, larch and aspen, with a liquor prepared from sodium hydroxide and sodium sulfide. These agents are combined in such amounts as to provide a solution having a predetermined alkalinity and sulfidity, and are charged into a digester together with an appropriate quantity of raw wood chips. The cooking or digesting step is accomplished at moderately elevated temperature and pressure. At the end of this step the cooked wood pulp together with the accompanying residual liquors is introduced into a separator where by means of filtering and other known means the digested wood pulp, comprising chiefly cellulose, is isolated. The liquors are recycled back to the digestion stage after various treatments involving elimination of the lignin, and adjustment of the alkali and sulfidity factors. The separated wood pulp may be washed, screened, bleached, dried and ultimately employed in the fabrication of paper products.

The wood used in the process is usually first debarked, and cut and chipped to appropriate size. The types used vary considerably but generally show properties falling within the ranges shown in the following table:

TABLE I

| | minimum | maximum |
|---|---|---|
| Specific gravity | 0.31 | 0.56 |
| Shrinkage | 7.9 | 14.1 |
| Bark | 7.5 | 18.9 |
| Cellulose | 54.4 | 63.0 |
| Lignin | 25.9 | 34.1 |

The types of pulps prepared using the sulfate process may vary considerably. Usually these fall within those classifiable as three basic types, at least insofar as those produced in large tonnage are concerned. These types are designated as types A, B and C in the following table, which gives for each, the approximate permanganate number which constitutes a measure of the ease of bleaching, and also the approximate yields and typical end uses for pulps of these types.



TABLE II

| Type | $KMnO_4$ Number | Approximate Yield | End Use |
|---|---|---|---|
| A | 18 | 46 | Bleached bags and writing, wrapping and printing papers. |
| B | 24 | 48 | Unbleached heavy papers for bags, wrappings, etc. |
| C | 34+ | 50+ | Unbleached corrugated and solid-fiber board. |

In the digestion of the prepared wood the factors entering into consideration are the species and quality of the wood and the characteristics desired in the final product. Time and temperature of the digestion step, sulfidity of the cooking liquor, the ratio of the cooking chemical to the wood used (on a moisture free basis), and the concentration of the cooking chemical in the liquor may vary widely. It is known that the process may be carried out either in batch or in continuous digestion systems. It is further known that the black liquor may be discarded or recycled back into the process. These and other factors understood by those skilled in the art are related to the ultimate characteristics of the pulp.

Upon completion of the digestion step the liquors and solids are recovered and the solids are leached with water. The pulp is separated and subjected to further processing. The weak black liquor may be concentrated and/or recycled back to the digestion process where it may be reinforced with make-up chemicals. Hydrogen sulfide is partially removed in the evaporators as a result of the following reaction:

$$NaHS+H_2O \rightleftharpoons NaOH+H_2S$$

In the direct heat evaporators hydrogen sulfide is readily evolved, but not completely in most operations, as a result of the carbonation reaction which occurs as a result of the direct contact with the flue gases. The resulting strong black liquors are decomposed in the recovery furnace, where make-up salt cake also may be added, and the resulting smelt dissolves to produce the so-called green liquors. Upon causticizing and clarifying this liquor a so-called white liquor is recovered which may be used to digest incoming wood chips, thus completing the conventional recycle operation.

By reason of the nature of the process, there are present in the white liquors which are employed to digest the wood certain constituents, namely, sodium compounds of mono- and hydrogen sulfides, sulfates, oxygen-sulfur intermediates such as thiosulfates, and carbonates, these compounds being present to varying degree. It is generally held however, that the main constituent responsible for the superior features of the sulfate process over the alkaline process where no sulfur is present, is the sodium hydrogen sulfide which is formed in the following reaction:

$$Na_2S+H_2O \rightleftharpoons NaHS+NaOH$$

Plants operating on the sulfate process normally find that a relatively well-defined equilibrium of composition and sulfidity can be established. The source of sulfur make-up is through the use of salt-cake. While from one pulp mill to another wide variations may exist, it may be stated generally that sodium monosulfide and sodium hydrogen sulfide are the agents predominantly responsible for the success of the process.

Figures 1 and 2 demonstrate the advantages of the polysulfide pulping process.

Hitherto the yield of wood pulp obtained in the sulfate process has been within the range of about 46% to 50% when producing pulps having permanganate values between about 18 and 34 respectively. We now have found that the yield of wood pulp may be significantly increased as hereinafter described:

As originally conceived our studies were directed to establishing the effect of polysulfides with reference to the cellulose and lignins in wood. In this view it was found that difficulties were encountered in obtaining sodium polysulfides, and therefore sulfurated potash was substituted on the theory that the potassium ion would in general constitute the equivalent of sodium. We found however, to our considerable surprise, that the substitution gave an unexpected increase in the pulp yield ranging from 1 to 15% over and above the amount secured in control runs employing conventional sodium monosulfide or sulfate systems. This unusual result was first ascribed to the presence of the potassium ion. However, further investigation indicated that the yield increase was to a considerable extent attributable to the presence of alkali polysulfides. However, we do not wish to be bound by any theoretical explanation.

Our process contemplates the introduction of chemicals to the body of raw wood chips in ratio of about 4 to 1, based on the amount of cooking liquor and dry basis wood chips, and carrying out the digestion of the wood under elevated temperature and pressure. This digestion is carried out in a pressure vessel or autoclave preferably, with circulation of the cooking liquors, at a temperature ranging from about 160° C. to 180° C. under autogenous pressure which may normally range from about 100 to 140 p.s.i. The chemicals and the wood chips being admixed the vessel after suitable venting may be closed and the temperature raised to about 170° C., or normal operating temperature, the period of time for such increase in temperature consuming about 0.5 hours to 5 hours, about 1.75 hours being considered normal. After the charge has attained the desired temperature, it may be held at about that temperature for 0.5 to 3.0 hours, preferably about 1.0 to 1.5 hours. As is understood by those skilled in the art, an increase in temperature normally shortens the period of time required to produce a pulp of given characteristics.

We have found that by carrying out the digestion process under conditions herein disclosed the wood pulp product of given permanganate number may be obtained in higher yield. We believe that the cause of this higher yield can be ascribed to the action of the chemicals involved in the digestion process, specifically, in that the attack thereof on the wood material, especially the cellulose component, is less severe. It therefore becomes possible pursuant to our invention to modify the concepts of optimum operating conditions that have hitherto prevailed. It may, for example, be desired to obtain a given yield in shorter time by operating at higher temperatures, or the process may be operated commercially at lower temperatures and shorter times to give a yield equal to that now produced in conventional sulfate operations. Depending upon the amount of delignification obtained, our improved process makes possible yield increases ranging from about 1 to 15%, normally between about 4% and about 10% in comparison with conventional systems, these yield increases being equated to a base of 100%. In general we find that the yield increase in the case of severe cooking, such as may be used to produce bleachable grades, is notably higher than hitherto, and that in methods using less severe cooking, the observed improvement in yield generally becomes even more pronounced.

In carrying out the cooking operation the amount of active alkali expressed as $Na_2O$ may vary between about 15 to about 35 percent based on the charge of wood



used. Good results may be obtained using about 20 to 25 percent. Sulfidity which is normally expressed as a percentage of the active alkali used, may be established by introducing into the so-called white liquors, containing $Na_2S$, alkali polysulfides such as $Na_2S_2$, $Na_2S_3$, $Na_2S_4$, $Na_2S_5$, or possibly higher polymers, and mixtures thereof, these agents being generally referred to as $Na_2S_x$. The employment of the sodium system has some advantage from the standpoint of cost. However, assuming equal cost, operations employing sulfurated potash or sulfide polymers of potassium are preferred.

Since the atomic weight of potassium exceeds that of sodium it would be expected that the effective amount of active alkali as $K_2O$ would be proportionately higher than $Na_2O$. It was found, however, that when equal weights are compared, for example, using an active alkali weight percent of about 25 percent, of KOH, and when using sulfurated potash, as against NaOH, the potassium system gave the higher yield of pulp.

In preparing the polysulfides, elemental sulfur as in the form of flowers of sulfur may be reacted with the alkali in the form of the carbonate, hydroxide or monosulfide. Commercially available sulfurated potash is produced by reaction of $K_2CO_3$ with elemental sulfur at a temperature of about 350° C. Although some oxygen-sulfur intermediate compounds exist in the commercial material it is undoubtedly the polysulfides or sulfide polymers that constitute the active agents in the pulp yield increase. Various methods of preparing sulfide polymers of the type suitable in our process are known to the art. The presence of the polymers may be visually observed by noting a darker color of the solution, approaching red-brown. In the practice of the process the prepared liquors for digestion of the wood normally contain in addition to the sulfide polymers, intermediate compounds having an oxygen content, such as the thiosulfates. Polysulfide solutions in the absence of air are relatively stable at room temperatures, and at higher temperatures, especially above 150° C., undergo a degree of decomposition. The sulfidity of the treating liquor may be regulated within the range of 10 to 30, 19 percent being considered preferable using sulfurated potash. In this respect it should be noted the sulfidity figures are based on the conventional iodine-thiosulfate titration, and that other analytical methods may give values somewhat at variance, as will be understood by those skilled in the art.

Upon completion of the digestion in the manner set forth the digestion mass is discharged into a blow tank where disintegration of the cooked wood chips and the solids recovered therefrom takes place. These solids upon leaching and screening are refined and then processed into paper products, following a bleaching operation when bleached pulps are desirable. Pulps prepared according to our preferred process make possible the use of a less severe bleach and the use of less severe bleaching chemical, such as calcium hypochlorite.

The liquor separated from the wood pulp, known as weak black liquor, is subjected to evaporation whereby there are removed water and sulfides. Hydrogen sulfide evolved from these and the blowdown operations may either be discarded or converted to sulfur available for recycling to prepare additional treating liquor containing polysulfides or sulfide polymers. The concentrated black liquor, which may contain 50 to 70 percent solids may be admixed with additions of alkali sulfates, such as $Na_2SO_4$ and/or $K_2SO_4$ to make up lost alkali, and decomposed in a furnace at a temperature of about 1000° C. or higher. Carbonaceous material resulting from this treatment may be recovered and used as a fuel or as a reducing agent for the alkali sulfate. While $K_2SO_4$ has a higher decomposition temperature than $Na_2SO_4$ it is found that under reducing conditions a temperature of about 1000° C. is suitable in most cases. Further, since $K_2SO_4$ has a higher decomposition temperature than $Na_2SO_4$, less $K_2O$ loss may occur in the smelting operations than in the case of the sodium compounds.

The smelt from the furnace containing predominantly alkali sulfide, carbonate and unreduced sulfur compounds, is cooled with water and dissolved. Preferably a portion or all of the cooled smelt may be treated with sulfur for formation of alkali polysulfides. Part or all of the polysulfides prepared may be dissolved and clarified prior to use for digestion with fresh wood. The polysulfides may be combined in any desired proportion with the treating liquor or so-called white liquor containing monosulfides. As above noted, sulfide polymers also may be prepared by treating a portion or all of the white or green liquors with elemental sulfur, and if desired the polysulfide content may be further raised by additional sulfur. Sulfur also may be mixed or slurried with the white liquors prior to or during the reaction with the wood chips.

In further illustration of the invention the following specific examples are given:

*Example I*

To 100 pounds (moisture free basis) of wood chips, composed of approximately equal amounts by weight of loblolly, shortleaf and longleaf southern pine, there was added sufficient alkali, alkali polysulfides and water to provide a ratio of water to wood (moisture free basis) of 4, an active alkali content of 28.0 percent, expressed as the hydroxide, and a sulfidity of 20.5 as determined using the iodine-thiosulfate titration method. All of the sulfur was added in the form of a solution prepared by dissolving the previously prepared alkali sulfide polymers. The materials, having been introduced into a pressure vessel, the later was closed, and with intimate mixing of the solid and liquid phases, the mixture was gradually heated over a period of 100 minutes to 172° C. This temperature was maintained at autogenous pressure for an additional period of 100 minutes, at the end of which time the contents of the pressure vessel were discharged to a collection device at atmospheric pressure. The solids were removed and recovered by filtration and then washed by repulping and mixing with three 300 gallon portions of water at a temperature of about 35° C. Solids from the last leaching were recovered and weighed with a product weight of 52.0 pounds (moisture free basis) unscreened yield. Chemical analysis of the product revealed the $KMnO_4$ number to have a value of 24.6. The product was subjected to conventional refining treatments and provided a paper material having physical properties comparable to those of conventional sulfate pulp.

*Example II*

Following the general details of procedure of Example I, sulfurated potash was used. The active alkali content was controlled to 28 percent, the sulfidity to 20.5 percent, and the temperature of digestion to 178° C. The product weight was found to be 49.1 percent (moisture free basis) unscreened yield, and 48.7 percent screened yield. The $KMnO_4$ number was 17.95.

*Example III*

The same general details of procedure were followed as in the foregoing examples. The active alkali value was controlled to 28 percent KOH, the sulfidity to 20.5 percent. The temperature was raised to a maximum of 168° C. during a period of 70 minutes and thereafter maintained at that point for an additional 70 minutes. There resulted an unscreened yield of 58.6 percent of a product having a $KMnO_4$ number of 88.6.



*Example IV*

The procedural details hitherto set forth were carried out, except that a conventional sulfate system with 25 percent NaOH active alkali was used. Sulfidity was controlled to 20 percent. The temperature of the reaction mass was brought over a period of 100 minutes to a temperature of 172° C., and so maintained for an additional 100 minutes. The unscreened yield was 46.9 percent, the screened yield, 46.2 percent. The $KMnO_4$ number of the product was 18.2.

*Example V*

In this case the process described in the above examples was modified in that a 34 percent KOH active alkali system was established, at 20 percent sulfidity. The digestion was effected during 100 minutes to 172° C. and a further 100 minutes, temperature held substantially constant at 172° C. The unscreened yield of product was 47.0 percent; the screened yield 46.6 percent. The $KMnO_4$ number was 18.4.

From the foregoing description and illustrations further details within the scope of the present invention will be apparent to those skilled in the art. We claim and desire to protect by Letters Patent:

1. In the method of producing wood pulp according to a pulping process, the improvement comprising cooking the raw wood in solutions of alkali polysulfides with a sulfidity of 10% to 30% maintained by alkali polysulfides.

2. In the method of producing wood pulp according to a pulping process, the improvement comprising cooking the raw wood in solutions predominately of alkali polysulfides.

3. In the method of producing wood pulp according to a pulping process, the improvement comprising cooking the raw wood in solutions predominately of alkali polysulfides, with the sulfidity of 10% to 30% maintained in whole or in part with alkali polysulfides.

4. In the method of producing wood pulp according to a pulping process, the improvement comprising cooking the raw wood in solutions of predominately alkali polysulfides with the sulfidity of 10% to 30% maintained with a combination of alkali polysulfides and the conventional sodium monosulfide.

5. In the method of producing wood pulp according to a pulping process, the improvement comprising the introduction into a spent cooking liquor containing $Na_2S$, alkali polysulfides including $Na_2S_2$, $Na_2S_3$, $Na_2S_4$, $Na_2S_5$, and higher polysulfides and mixtures thereof, these agents generally referred to as $Na_2S_x$, to maintain the sulfidity of 10% to 30% with these polysulfides, and cooking the pulps with the liquor high in alkali polysulfides content.

6. In the method of producing wood pulp in the pulping process, the improvement comprising the adding of concentrated alkali polysulfides to a spent liquor to produce a sulfidity of 10% to 30% and pulping with the mixture.

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