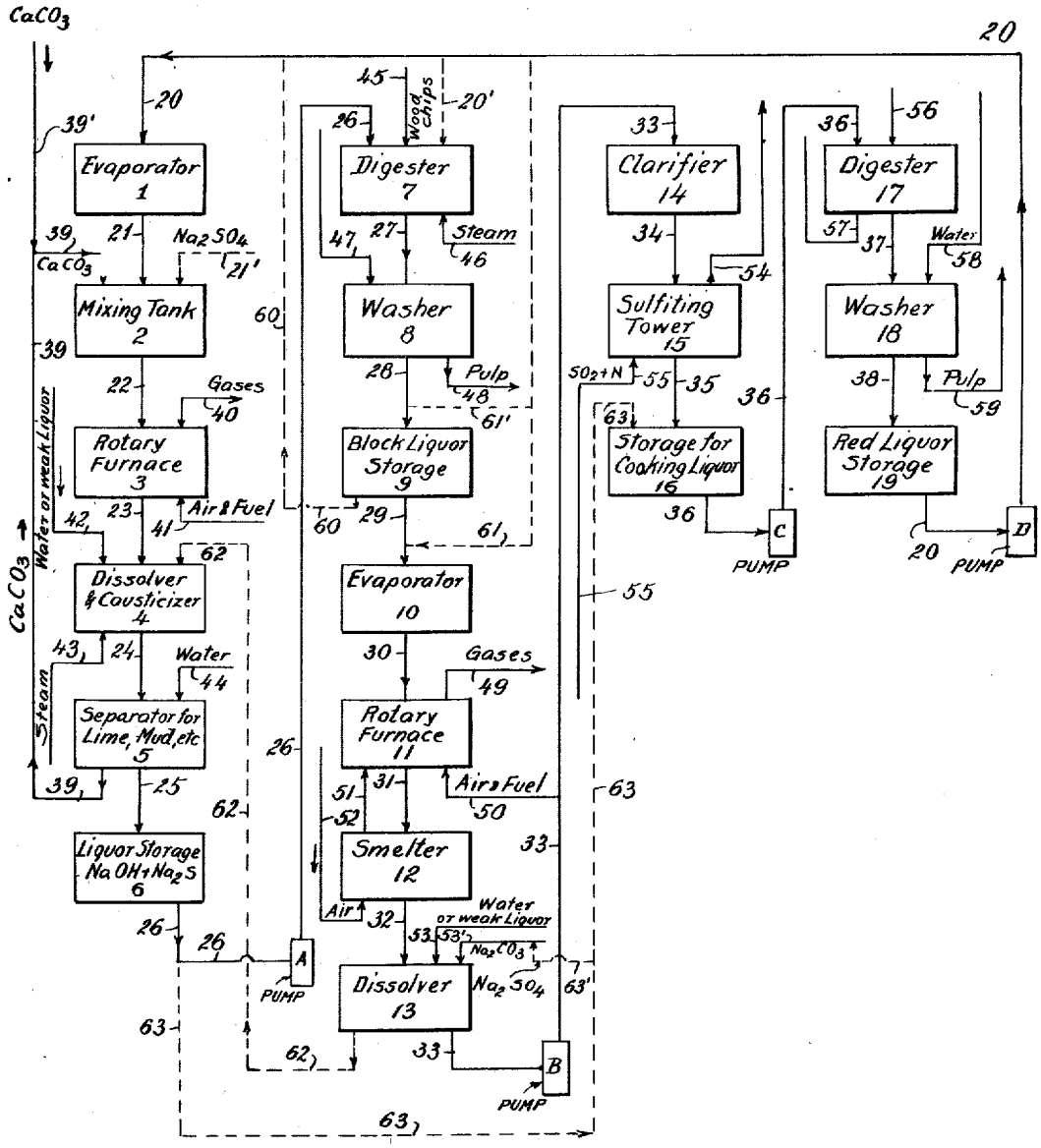
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MANUFACTURE OF PULP, ETC

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MANUFACTURE OF PULP, ETC.

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This invention relates to the treatment of residual liquors produced by digesting wood chips with cooking liquors which contain sodium-sulphur compounds as active reagents, so as to produce chemical pulp.

The present invention includes two cooking or pulp-making processes which are so combined as to be interrelated and cooperative in character. The invention includes a treatment of residual liquor from the digestion of wood with cooking liquors which contain sodium sulphite in relatively large amount and sodium thiosulphate in relatively small amount, to produce a cooking liquor which contains sodium hydroxide and sodium sulphide, and the treatment of the black liquor resulting from digesting wood with the sodium hydroxide and sodium sulphide liquor thus prepared, for the production of cooking liquor of the type which contains the sodium sulphite and sodium thiosulphate.

Among the objects of the invention are to make the process or processes cyclic in character so that the soda content of the liquors is rendered readily available for repeated use, subject to such losses of soda as may occur in any mill operated with ordinary care and economy as to reagents. Other objects will appear from the more detailed description.

According to the present invention, we utilize a so-called sulphate-process mill operation, with or without modifications, to produce a recovered soda product which contains considerably more sodium carbonate than sodium sulphide which may be employed in an advantageous manner for the production of a suitable sodium sulphite cooking liquor by sulphiting methods; and we utilize such sulphited liquors for the pulping of wood and the production of a residual liquor which can be advantageously employed for the production of a soda product which contains a considerable amount of sodium sulphide as well as some sodium carbonate and which upon causticization readily yields a solution of sodium hydroxide and sodium sulphide suitable for digesting wood chips.

According to the process of the present invention, which may be readily carried out as a cyclic operation, two types of digesting or pulp-making are employed.

One type employs a cooking liquor which contains a considerable amount of sodium sulphite, in which a small amount of sodium thiosulphate is usually present, and which may contain other reagents, e. g. sodium sulphide, sodium hydroxide, sodium carbonate, or mixtures of two or more of these. The residual liquor from such digesting process is herein termed red liquor.

The other type of cooking liquor employs both sodium hydroxide and sodium sulphide, with which may be present sodium carbonate, sodium sulphite, sodium thiosulphate, or mixtures of two or more of these, etc. The residual liquor from the digesting step with the latter type of cooking liquor is herein termed black liquor.

Each of these residual liquors is utilized for the production of the cooking liquor for the other type of digesting treatment. The red liquor is treated to remove water, decompose organic compounds and obtain a recovered soda product which contains sodium carbonate and a rather large amount of sodium sulphide, the sodium compounds are dissolved to produce a solution of requisite strength, the solution is causticized by treatment with lime, the solution is separated from the lime mud, and the cooking liquor thus prepared is employed for digesting wood chips to produce chemical pulp and yield a black liquor which contains only a small amount, if any, of free sodium hydroxide. The recovered soda obtained therefrom generally contains considerably more sodium carbonate than sodium sulphide, and a solution prepared from such recovered soda can be readily sulphited to give a cooking liquor for the sulphite cooking step which has the desired preponderance of sodium sulphite over the sodium thiosulphate.

The process is capable of a number of modifications without departing from the spirit of the invention.

Some of these modifications which illustrate the invention, are indicated on the drawings which is in the nature of a flow sheet, showing the arrangement and sequence and

inter-relation of the various processes, and steps thereof.

One of the steps used in the process is that of causticizing a regenerated solution containing sodium carbonate and sulfide with lime to convert sodium carbonate into caustic soda. This causticizing treatment results in the production of so-called lime mud made up largely of calcium carbonate which may be admixed with some unused lime, with carbon, etc. This lime mud may be washed and then discarded or it may be reburned in any suitable way to produce lime for use in the causticizing step. But the lime mud is advantageously returned to the process and admixed with residual liquor from one of the processes, before such residual liquor is subjected to the furnacing treatment, so that calcium carbonate of the lime mud will be converted into lime during the furnacing operation, thereby giving a self-causticizing furnace product. In the diagram or flow sheet shown in the drawing, this utilization of the lime mud is included, and the flow sheet and process will be more particularly described in connection therewith. This process of treating residual liquors in which lime mud is added before the furnacing operation to give a self-causticizing furnace product is described in our prior application Serial No. 96,665, filed March 22, 1926, patented January 7, 1930, No. 1,743,080.

In the flow sheet, the so-called red liquor, which is the residual liquor from the sodium sulphite cooking operation, is shown as being introduced through the line 20 into the multiple effect evaporator 1, provided with the usual facilities including steam for heating, a condenser, etc. The weak red liquor is concentrated in this evaporator to about 30 to 40° Bé., then passed through the line 21 into a mixing tank 2 in which it may be admixed with calcium carbonate, which, as indicated by the line 39, may be lime mud from the causticizing step or which may be calcium carbonate from some other source, as indicated by the line 39'. Where the finely divided washed lime mud is not sufficient, additional finely divided calcium carbonate may be supplied to make up for losses or to supply the deficiencies.

The amount of calcium carbonate admixed with the liquor in the mixer 2 is advantageously sufficient to furnish sufficient calcium oxide during the subsequent furnace operation to causticize the sodium carbonate to the desired extent. When a high causticity is desired, a considerable excess of calcium carbonate over that theoretically required should be used, e. g. about 40% or more in excess.

The mixture of calcium carbonate and strong red liquor passes through the line 22 into a calcining furnace 3, such as a rotary calcining furnace. In this furnace the water is evaporated and the organic compounds are decomposed and calcium carbonate also is decomposed. The furnace gases leaving through line 40 contain water vapor, carbon dioxide, some sulphur compounds, etc. Air, as well as additional fuel, may be added as indicated at 41.

The black ash produced in the calcining furnace and which contains calcium oxide, sodium carbonate, sodium sulphide, carbon, etc., passes through the line 23 into a combined dissolver and causticizer 4 of any suitable construction such as an iron tank provided with suitable agitator. Sufficient water or weak liquor may be introduced through the line 42 so that the solution is of suitable strength when the charge of black ash and lime mixture has been added. A steam line is indicated at 43 for introducing steam into the dissolving tank 4 if needed. Where the black ash is added hot to the tank, and with the heat of reaction of the calcium oxide and water, and with water or weak liquor of the temperature available, the charge in the tank 4 may reach a sufficient temperature to effect the desired dissolving and causticizing without requiring additional steam for further heating it.

The causticized mixture produced in the tank 4 and containing sodium hydroxide, sodium sulphide, sodium carbonate, calcium carbonate, carbon, etc., together with water in regulated amount, passes through the line 24 into a separating appliance of suitable construction 5 for separating the lime mud and carbon from the solution and for washing the remaining lime mud to the desired degree. From this separating appliance the liquor and the desired amount of wash water are withdrawn through the line 25 to the liquor storage tank 6.

It is advantageous to have the liquor recovered in the storage tank 6 at a concentration slightly above that required for use in the digester or as much stronger as is suitable for the digesting operation since it can readily be diluted by admixing more or less residual liquor from the same or different process in making up the cooking liquor. A line for introducing water for washing the lime mud is indicated at 44. By regulating the amount of water used in washing and adding the wash water to the storage tank 6, the strength of the cooking liquor can be regulated.

The washed lime mud and carbon is withdrawn as indicated by line 39 and may be returned to the mixer 2 to be mixed with more strong red liquor. In case any of this mixture of lime mud and carbon is to be discarded, this can be done at this point in the cycle. In case an excessive accumulation of carbon takes place in the cycle or in the lime mud, a sufficient amount of the admixed lime mud and carbon can be discarded or can be

separately treated to reduce the carbon content, e. g., by suitable burning operations. Any deficiency in lime mud required in the mixing tank 2 can be supplied by finely divided calcium carbonate from some other source introduced through the line 39'.

The cooking liquor in the storage tank 6 is clarified or partially clarified. Further clarification may be effected in this tank in any suitable manner, for example, by settling. The clarified liquor of proper strength is withdrawn from the tank 6 through the line 26 and pumped by the pump A to one or more of a series of digesters indicated at 7, which is charged with wood chips through the line 45. Some red liquor may also be added to the digester in making up the charge of cooking liquor, as indicated by the dotted line 20'. Steam for heating the digester is indicated by the line 46.

In the digester, the cooking operation is carried out under conditions similar to those used in the so-called sulphate process of cooking wood and with the production of wood pulp and of a residual liquor which is herein referred to as black liquor.

At the end of the digestion period, the mixture of fibrous material and black liquor is discharged through the line 27 to a suitable washing device indicated at 8. The black liquor is separated from the pulp and the pulp is washed and the washings added to the black liquor, the resulting mixture being known as weak black liquor which passes through the line 28 into a storage tank 9. Water for washing may enter through the line indicated at 47 and the washed pulp leaves as indicated at 48.

From the storage tank 9 the weak black liquor passes through the line 29 to a multiple-effect evaporator 10 of any suitable type, wherein it is concentrated to form a strong black liquor, for example, around 30 to 40° Bé., and from the evaporator it then passes through the line 30 to a rotary calcining furnace 11 wherein a further concentration takes place and organic matter is decomposed, the gases leaving at 49 and air with additional fuel if required entering at 50. The escaping gases carry water vapor, some carbon dioxide, sulphur compounds, etc. Hot gases from the smelting furnace 12 may enter through the line 51 and assist in the heating of the rotary calcining furnace. From the rotary furnace the green ash, or mixture of black ash and residue of the black liquor pass through the line 31 to the smelting furnace 12, which may be of the type used in the ordinary sulphate process mill. An air line for the furnace is indicated at 52. The molten material from the smelter passes through the line 32 into a dissolver 13, into which water or weak alkaline liquor enters through the line 53 in the desired amount. The dissolver is provided with an agitator so that a solution of suitable strength can be made by the regulation of the amount of liquor and of melted product and by thorough agitation of the mixture.

Sodium carbonate is advantageously added to the cycle at this point, for example, through the line 53' in sufficient amount to replace the soda lost or rendered unavailable in the cycle of operations. The solution will be made up mainly of sodium carbonate, but may contain varying amounts of sodium sulphide, although the amounts will usually be moderate. The solution passes from the dissolver 13 through line 33 and is pumped by pump B into a clarifier 14 wherein the liquor is separated from objectionable suspended matter and then passes through the line 34 into a sulphiting tower 15.

In the sulphiting tower 15 the liquor comes into contact with a mixture of gases containing sulphur dioxide and nitrogen, such as may be obtained by burning sulphur with air. The alkaline solution absorbs the sulphur dioxide and a solution which contains sodium sulphite is thus obtained, while the nitrogen escapes, together with some hydrogen sulphide, carbon dioxide, etc., through the line 54.

Where the solution thus sulphited is free, or nearly free from sodium sulphide, the amount of hydrogen sulphide, if any, produced will be small. The amount of carbon dioxide given off when sulphiting a hot solution which contains a large amount of sodium carbonate and only a small amount of sodium sulphide, aids in preventing the formation of sodium thiosulphate, inasmuch as the carbon dioxide aids in the removal of hydrogen sulphide by reacting with sodium sulphide to form hydrogen sulphide and sodium carbonate. The current of nitrogen also seems to be of assistance in removing hydrogen sulphide and in preventing the formation of large amounts of sodium thiosulphate in the resulting solution. The sulphiting gases containing sulphur dioxide and nitrogen are shown as entering at 55. By carrying out the sulphiting operation with hot liquor in the manner above described, a sodium sulphite cooking liquor can be produced with only a moderate amount at most of sodium thiosulphate.

When the solution has been sulfited to the desired degree, which may be when substantially all of the sodium carbonate has been transformed into a sodium sulphur compound, the solution passes from the sulphiting tower, or tank, through line 35 into cooking liquor storage tank 16, from which it is drawn as required through line 36 and pump C into digester 17, which is charged with wood chips through line 56. Steam is shown entering digester 17 through line 57. When the digestion operation has been completed, the mixture of fibrous material and residual

liquor, known as red liquor, passes through line 37 and into a suitable washer 18, wherein the red liquor is separated from the pulp and the pulp is washed by water in regulated amount, so as to avoid excessive dilution of the red liquor. The water is shown entering through line 58 and is preferably used in the warm or hot condition. The washed pulp passes through line 59 to any desired point. The weak red liquor, together with a regulated amount of washings, passes through 38 into weak red liquor storage tank 19, from which it passes through line 20 and pump D to the multiple-effect evaporator shown at 1, thus completing the cycle.

Line 60 shows how some of the black liquor may be used for mixing with some of the red liquor passing to evaporator 1. The amount thus diverted may be varied and this diversion used for regulating the composition of the cooking liquor used in digester 7, as well as the amount thereof. Lines 61 and 61′ show how some red liquor may be diverted and mixed with black liquor which enters evaporator 10. The amount so diverted, if any, preferably is small, so as to avoid the production of a recovered material which contains a large proportion of sodium sulphide. A small amount thus diverted seems to be of assistance in the evaporator and in the modification of odors in the mill.

Line 62 shows how some of the solution of sodium carbonate and moderate sodium sulphide content may be diverted and added to the soda which enters the dissolver and causticizer 4, in which case a further amount of lime may be added to 4 to causticize the additional sodium carbonate, if not enough lime is already present, e. g. a sufficient excess coming from 3 through 23 along with the soda in the black ash. This step is of value for various reasons, for example, in controlling the proportion of carbon returned with the lime mud to mixer 2.

Line 63 shows how some of the causticized liquor may be diverted and introduced into tank 16 and therein be admixed with the sulphited liquor which comes from the sulphiting tower 15. The amount thus diverted may be controlled and used if desired for neutralizing any acidity contained in the sulphited liquor, and may even be used to form a sulphited liquor which also contains some caustic soda, or some sodium sulphide or a mixture of sodium sulphite, sodium hydroxide and sodium sulphide in regulated amount, and such solutions be used in digester 17, thus securing the combined advantages of these reagents. The liquor thus used may also contain a moderate amount of sodium thiosulphate and of sodium carbonate.

As illustrated in the flow sheet, provision is made for returning the lime mud from the causticizing step of the process and admixing it with the red liquor from the multiple-effect evaporator, or with a mixture of red liquor and black liquor. The resulting mixture of concentrated liquor and lime mud is thereafter subjected to a heat treatment to remove water, decompose organic matter and the calcium carbonate, so as to produce a self-causticizing mixture. It is advantageous to use more lime mud than calculations show to be theoretically required, so that the amount of calcium oxide produced will be sufficient to convert the sodium carbonate into caustic soda to the desired extent. If only the theoretical amount of lime mud is admixed with the red liquor, difficulty is had in obtaining a self-causticizing mixture which will readily causticize and give a high percentage of sodium hydroxide from the sodium carbonate, and melting also readily occurs in the furnace. However, by admixing with the strong liquor an amount of lime mud considerably in excess of the theoretical amount required, various advantages are obtained. For example, if the amount of lime mud thus added is such that an excess of about 40 to 50% over the theoretical amount is employed, the tendency to melt is less, the intumescence is less objectionable, and a self-causticizing mix is obtained which can readily causticize a high percentage of sodium carbonate.

The carbon dioxide liberated from the calcium carbonate seems to aid in eliminating some of the carbon from the product formed in the rotary incinerating furnace, due to the reaction between the carbon dioxide and incandescent carbon to form carbonmonoxide, which very shortly thereafter is burned to form carbon dioxide. Also, the reactions in the furnace seem to promote the elimination of some of the sulphur so that the amount of sodium sulphide and of sodium polysulphide is below an objectionable point.

The returning of the lime mud and carbon in a cyclic process should be so regulated, together with the other steps, that the amount of carbon thus returned is kept below a prohibitive amount. By treating enough of the black liquor so as to decompose organic compounds and to burn a large amount of the resulting carbon, e. g. by treatment in a suitable smelting type of furnace with a blast of air through tuyères or blow-pipes, and adding enough of the resulting sodium carbonate and sodium sulphide to the material which is to be causticized, the amount of carbon which is returned with the lime mud, in case the lime mud is so returned, can be kept below an objectionable amount.

The excess of lime mud thus prepared is then ready for return and in this way advantage is taken of the combined steps to provide the desired excess of lime mud for the incinerating furnace and the excess of the calcium oxide thus produced is employed

to a considerable extent, at least, in the causticizing step.

It is not necessary that the calcium carbonate be thus returned, but it is an advantageous improvement on the main cycle of the invention. The carbon dioxide thus liberated in close proximity to the soda compounds in the incinerating furnace appears to effect the elimination of sulphur and thus modifies the treatment of the red liquor.

In case it is desired to eliminate more sulphur than that eliminated in one treatment, the recirculation of soda compounds through the sulphate-process portion of the cycle may be relied upon to eliminate a further amount of sulphur, and thus control the composition of the solution of sodium carbonate and sodium sulphide which is to be sulphited, e. g. by a mixture of sulphur dioxide and nitrogen which may be readily obtained by burning sulphur with air in any suitable burner.

Lines 21′ and 63′, respectively, show the introduction of sodium sulphate as make-up, in case this material is to be the source of soda for replacing that lost in operation, and the addition of some of the sodium-hydroxide and sodium sulphide solution to the liquor which is to be sulphited.

In the event that the lime mud is not to be returned for mixing with the red liquor, it may be discarded from the cycle, and reburned in any suitable manner and the lime thus produced used for causticizing in any suitable way. Or it may be discarded and not again reused.

The lime mud may, on the other hand, be admixed with black liquor and these two given a heat treatment to decompose organic matter, eliminate some sulphur and form a self-causticizing mix, the lime mud being separated from the liquor and the solution of sodium hydroxide with moderate amount of sodium sulphide may be the solution which is sulphited in the tower 15. The lime mud may be returned for mixing with more black liquor. By proceeding in this manner, the sulphited liquor may be obtained by the sulphiting step, leaving any unchanged sodium sulphide in the liquor, if desired. Some thiosulphate may be formed due to reaction between the sulphur dioxide and the sodium sulphide in the liquor, but the amount can be kept low, especially when the liquor to be sulphited contains but a small amount of sodium sulphide relative to the sodium hydroxide and the sodium carbonate.

From one point of view, the organic matter dissolved by the digesting step with the sodium hydroxide-sodium sulphide liquor is employed for the elimination of some sulphur so as to facilitate the production of a cooking liquor containing sodium sulphite which is free from an objectionable amount of thiosulphate (e. g. an excessive amount), and the sodium sulphite cooking step is relied upon to yield a red liquor which furnishes sodium-sulphur compounds to the sulphate-process type of cooking operation; and this provides an advantageous cooperative treatment whereby both are cyclic.

The process of the present invention is, as heretofore described, advantageously carried out with utilization of the lime mud from the causticizing step by returning it for admixture with concentrated residual liquor and subjecting calcium carbonate to decomposition while admixed with the resulting soda compounds so that a self-causticizing furnace product is produced. When the lime mud is thus returned admixed with residual liquor, either red liquor, or black liquor, or a mixture of both, and when it is present in a considerable excess over that theoretically required to form enough calcium oxide for the sodium carbonate, certain important advantages are obtained. For instance, the material appears to melt less readily in the furnace, the swelling or intumescence of the organic compounds appears to be very materially reduced, the soda seems to be recovered more readily and the clarification of the causticized liquor seems to be materially improved. Owing to the raising of the melting point, the furnace can be operated more readily with less danger of ringing up, the carbon is readily kept low enough in amount owing to the promotion of its elimination due to the physical condition of the solids, and the removal of carbon by carbon dioxide in the manner hereinbefore described. The porous condition and the accompanying gases appear to have a marked influence upon the elimination of sulphur.

Some of the highly concentrated residual liquor, instead of being added to the furnace charge, may be utilized separately, free from lime mud, and atomized into the hot calcining furnace in which the lime mud is being treated, and the resulting heat of its combustion made use of in the treatment of the mixture of lime mud and residual liquor. The large excess of lime tends to prevent objectionable fusion of the product and is otherwise advantageous.

The smaller the amount of the sodium thiosulphate in proportion to the sodium sulphite in the cooking liquor of this type which is charged into each digester, the less the amount of sulphur which has to be eliminated from the soda in the residual liquor therefrom, and the smaller the amount of sodium sulphide in the mixture of sodium carbonate and sodium sulphide, the more readily can cooking liquors be prepared which are high in sodium sulphite and low in thiosulphate.

In the so-called sulphate process, cooking liquors which contain about 60 parts of NaOH for every 40 parts of Na_2S are desir-

able. High quality pulp can easily be produced and the amount of lime required for causticizing is low. The amount of the lime mud being relatively small, strong cooking liquors can be prepared readily, thus permitting the charging of a considerable volume of black liquor into the digesters in admixture with the cooking liquor and thus effect a saving in the evaporation step. Cooking liquors which are rather high in sodium sulphide, such as in the above example, or a liquor which contains 70 parts of NaOH for every 30 parts of Na2S, and those which contain 50 or more parts Na2S for each 50 parts NaOH, are, as stated, advantageous in the pulp-making operation. However, it is also advantageous to recover a high percentage of the soda and thus economize in chemicals.

Where the sulphate-process is ordinarily practiced as a cyclic operation and sodium sulphate is employed for replacing the soda lost, it is very difficult to have a high percentage soda recovery and at the same time have a cooking liquor which is relatively high in sodium sulphide. The two are difficult to obtain at one time. With the process of the present invention, however, each type of cooking liquor does for the other that which it cannot so well do by itself alone. Thus they cooperate as a cycle. A considerable part of the sulphur which is used for preparing the sulphited liquor, is recovered and employed as sodium sulphide in the NaOH—Na2S cooking liquor. And since sodium sulpho-organic compounds eliminate sulphur more readily than does sodium sulphite, the red liquor advantageously may contain a fair amount of sodium sulphite, e. g. more than would be present if the ordinary acid sulphite process were employed with the usual low amount of base. This facilitates the production of sodium sulphide.

The furnace treatments should be so regulated that at most only a moderate amount of sodium polysulphide is present in the liquor which is to be sulphited, owing to the readiness with which sodium thiosulphate may be produced from liquors which contain polysulphides. When residual liquors, which contain large amounts of sodium thiosulphate, are treated to remove water and decompose organic compounds, the heat treatment should be conducted at sufficiently high temperature and for a sufficient period of time to drive off most of the loosely combined sulphur which might otherwise appear as a polysulphide in the solution prepared from the recovered ash. Therefore the steps of the process should be so regulated as to avoid the presence in the liquor to be sulphited of any large amount of sodium polysulphide. This can be done by controlling the number of times the soda compounds are utilized in the sulphate-process steps of the cycle, and by controlling the heat treatment so as to eliminate most of the loosely combined sulphite.

We claim:

1. The method of producing wood pulp from wood, which comprises cooking wood in a sodium monosulphite cooking liquor containing sodium thiosulphate, cooking wood in an alkaline cooking liquor comprising sodium sulphide, and recovering sodium compounds from the residual liquor resulting from each cooking operation and using the same in the formation of the cooking liquor for the other cooking operation.

2. The method of producing wood pulp from wood, which comprises cooking wood in a sodium monosulphite cooking liquor containing sodium thiosulphate, subjecting the residual liquor from such cooking operation to a carbonizing and reducing treatment with resulting production of a product containing sodium carbonate and sodium sulphide, and treating such product for the production of a cooking liquor comprising caustic soda and sodium sulphide, said treatment including a causticizing treatment to convert sodium carbonate into caustic soda.

3. The method of producing wood pulp from wood, which comprises cooking wood with an alkaline cooking liquor containing caustic soda and sodium sulphide, treating the residual liquor by a concentrating and carbonizing treatment to give a furnace product containing the sodium salts mainly as sodium carbonate and treating this product to produce sodium monosulphite and sodium thiosulphate therefrom, said treatment including a sulphiting treatment, and cooking wood with the resulting sodium monosulphite solution containing sodium thiosulphate.

4. The improvement in the treatment of residual liquors from a sodium monosulphite cooking process in which the cooking liquor contains a preponderating amount of sodium monosulphite and a smaller amount of sodium thiosulphate which comprises concentrating the liquor, then subjecting the same to a carbonizing and reducing treatment, with resulting production of a product comprising sodium carbonate and sodium sulfide, dissolving the soluble sodium salts and causticizing the same to produce a cooking liquor comprising caustic soda and sodium sulfide.

5. The improvement in the treatment of residual liquors from an alkaline cooking process in which caustic soda and sodium sulphide are the principal reagents, which comprises concentrating the residual liquor and subjecting the same to a furnacing treatment under reducing conditions to give a product containing the sodium salts mainly as sodium carbonate and sodium sulphide, dissolving these soluble sodium salts and sulphiting the same to produce a sodium monosulphite cooking liquor containing thiosulphate, and cooking cellulose-bearing material with

liquor containing the sodium compounds thereby produced.

6. In the art of producing chemical pulp from wood, the cyclic process which includes the following steps: (*a*) digesting wood chips with a cooking liquor which comprises a relatively large amount of sodium monosulphite and a smaller amount of sodium thiosulphate; (*b*) separating residual liquor from the pulp thus produced; (*c*) removing water from such residual liquor; (*d*) decomposing sodium organic compounds by heat treatment; (*e*) treating the recovered sodium compounds in the presence of water with lime whereby the causticized liquor comprises a solution of sodium hydroxide and a lesser amount of sodium sulphide; (*g*) separating the causticized liquor from the lime mud; (*h*) digesting wood with such cooking liquor; (*i*) separating residual liquor from the pulp thus produced; (*j*) removing water from such residual liquor; (*k*) furnacing sodium compounds under reducing conditions to form a product containing the sodium salts mainly as sodium carbonate and sodium sulfid; (*l*) preparing a solution of the resulting soda compounds; (*m*) sulphiting a solution comprising the sodium compounds thus obtained, whereby a suitable cooking liquor is produced comprising a relatively large amount of sodium monosulphite and a smaller amount of sodium thiosulphate; and repeating the cycle one or more times.

7. In the art of producing chemical pulp, the cyclic process which includes the following steps:—(*a*) digesting fibre-bearing material with a cooking liquor which comprises a substantial amount of sodium monosulphite and a lesser amount of sodium thiosulphate; (*b*) separating residual liquor from the pulp thus produced; (*c*) removing water from such residual liquor; (*d*) decomposing sodium organic compounds by heat treatment in the presence of hot gases whereby some sulphur is eliminated and some sodium carbonate is formed; (*e*) treating the recovered sodium compounds with lime in the presence of water to form a causticized liquor comprising more sodium hydroxide than sodium sulphide; (*g*) separating the causticized liquor from the lime mud; (*h*) digesting fibre-bearing material with such causticized liquor; (*i*) separating residual liquor from the pulp thus produced; (*j*) removing water from such residual liquor; (*k*) decomposing organic compounds by heat treatment in the presence of hot gases whereby a relatively large amount of the soda is obtained as an alkaline compound which contains no sulphur; (*l*) preparing a solution of the resulting soda compounds; (*m*) sulphiting a solution comprising the sodium compounds thus obtained, whereby a suitable cooking liquor is produced monosulphite and a lesser amount of sodium thiosulphate; and repeating the cycle one or more times.

8. In the art of producing chemical pulp, the cyclic process which includes the following steps:—(*a*) digesting fibre-bearing material with a cooking liquor which comprises a preponderating amount of sodium monosulphite and a lesser amount of sodium thiosulphate; (*b*) separating residual liquor from the pulp thus produced; (*c*) removing water from such residual liquor; (*d*) decomposing sodium organic compounds by heat treatment in the presence of a current of hot gases whereby a substantial amount of sulphur is eliminated and the resulting ash contains more sodium carbonate than sodium sulphide; (*e*) treating the recovered sodium compounds in the presence of water with lime to form a causticized liquor comprising more sodium hydroxide than sodium sulphide; (*g*) separating the causticized liquor from the lime mud; (*h*) digesting fibre-bearing material with such cooking liquor; (*i*) separating residual liquor from the pulp thus produced; (*j*) removing water from such residual liquor; (*k*) decomposing sodium organic compounds by a reducing heat treatment in the presence of a current of hot gases whereby some sulphur is eliminated and the resulting ash contains its sodium compounds principally as sodium carbonate and sodium sulphide; (*l*) preparing a solution of the resulting sodium compounds; (*m*) sulphiting a solution which contains more such recovered sodium carbonate than sodium sulphide so as to produce a cooking liquor which comprises a preponderating amount of sodium monosulphite and a lesser amount of sodium thiosulphate; and repeating the cycle one or more times.

9. In the art of producing chemical pulp, the steps which include:— (*a*) removing water from residual liquor resulting from digesting fibre-bearing cellulosic material with a cooking liquor containing as its principal chemical ingredient sodium monosulphite; (*b*) decomposing sodium organic compounds by heat in the presence of a current of hot gases whereby the resulting ash comprises sodium carbonate and sodium sulphide; (*c*) treating the recovered sodium compounds in the presence of water with lime thereby producing a causticized liquor comprising a preponderating amount of the soda in the form of sodium hydroxide and a substantial amount of sodium sulphide; (*e*) separating such causticized liquor from the lime mud; and (*f*) employing such causticized liquor for digesting fibre-bearing cellulosic material.

10. In the art of producing chemical pulp from raw fibre-bearing cellulosic material, the steps which include:—(*a*) removing water from residual liquor resulting from the digestion of fibre-bearing cellulosic material with a cooking liquor which comprises a pre-

ponderating portion of its soda in the form of sodium hydroxide and a lesser portion in the form of sodium sulphide; (*b*) decomposing sodium organic compounds by a reducing heat treatment in the presence of hot gases whereby an ash is formed comprising a preponderating portion of the sodium compounds in the form of sodium carbonate, and a lesser portion in the form of sodium sulphide; (*c*) preparing a solution of such sodium compounds; (*d*) sulphiting such solution whereby a cooking liquor is produced comprising a considerable amount of sodium monosulphite and a lesser amount of sodium thiosulphate; and (*e*) digesting fibre-bearing cellulosic material therewith.

11. In the art of producing chemical pulp, the cyclic process which includes the following steps:—(*a*) digesting cellulosic fibre-bearing material with a cooking liquor comprising essentially sodium monosulphite and a lesser amount of sodium thiosulphate in aqueous solution; (*b*) digesting cellulosic fibre-bearing material with a cooking liquor containing as its principal reagents sodium hydroxide and sodium sulphide; (*c*) mixing residual liquor resulting from (*a*) with residual liquor resulting from (*b*); (*d*) removing water from the mixed residual liquors; (*e*) decomposing sodium organic compounds by heat in the presence of a current of hot gases to form sodium carbonate and sodium sulfid; (*f*) causticizing a portion of the recovered sodium carbonate to form a cooking liquor containing sodium hydroxide and sodium sulfid; (*g*) sulfiting a portion of the recovered sodium carbonate and sodium sulfid to form a cooking liquor containing sodium monosulfite and sodium thiosulfate; and repeating the cycle.

12. In the art of producing chemical pulp, the steps which include:—(*a*) digesting wood chips with a cooking liquor which comprises sodium monosulphite, sodium bisulphite and an amount of sodium thiosulphate which is less than the amount of sodium monosulphite, in aqueous solution; (*b*) separating residual liquor from the pulp thus produced; (*c*) adding to the residual liquor a sodium compound, which is alkaline to litmus, in sufficient amount to produce a liquor which is alkaline to litmus; (*d*) removing water from such alkaline liquor; (*e*) decomposing sodium organic compounds by heat treatment in the presence of a current of hot gases containing nitrogen and CO_2, whereby a considerable elimination of sulphur occurs; (*f*) treating some of the recovered sodium compounds in the presence of water with sufficient lime to produce a solution which contains more sodium hydroxide than sodium sulphide; (*h*) separating the causticized liquor from the lime mud; and (*i*) digesting wood chips therewith.

13. In the art of producing chemical pulp from wood, the steps which include digesting wood with a cooking liquor which includes or comprises residual liquor resulting from the use of a cooking liquor which contains as a principal reagent sodium monosulphite in an aqueous solution for the digesting of wood chips, and a sufficient amount of sodium hydroxide and of sodium sulphide to effect the desired degree of digestion; the sodium hydroxide being present in the cooking liquor in greater amount than that of the sodium sulphide at the starting of the digestion step.

14. In the art of producing chemical pulp, the cyclic process which comprises digesting fiber bearing material in a cooking liquor comprising a sulfite of sodium, digesting fiber-bearing material in a cooking liquor comprising sodium hydroxide and sodium sulfide, separating residual liquor from each of such digesting processes and treating each residual liquor to produce a cooking liquor suitable for use in the other digesting process, the treatment of the residual liquor from the sulfite digesting process including mixing therewith calcium carbonate produced by the causticizing step of the process, furnacing solid constituents of the mixture under conditions to convert sodium constituents thereof into sodium carbonate and a lesser amount of sodium sulfid and to convert the calcium carbonate at least in part into caustic lime, treating the resulting mixture in water whereby sodium carbonate thereof is causticized by the caustic lime and separating the resulting solution for use in the sodium hydroxide sodium sulfid digesting process and the calcium carbonate for mixing with more residual liquor from the sulfite digesting process.

15. In the process of claim 8 adding calcium carbonate separated in step (*g*) to the residual liquor obtained in step (*b*) and conducting the heat treating step (*d*) at a temperature and for a time adapted to convert at least a part of the calcium carbonate in the mixture into caustic lime required for step (*e*).

16. In the art of producing chemical pulp the steps which include: (*a*) digesting fiber bearing material with a cooking liquor which comprises sodium monosulfite, sodium bisulfite and an amount of sodium thiosulfate which is less than the amount of sodium monosulfite; (*b*) separating residual liquor from the pulp thus produced; (*c*) adding to the residual liquor calcium carbonate from step (*g*); (*d*) removing water from such mixture; (*e*) decomposing calcium compounds of such mixture by heat treatment in the presence of a current of hot gases under conditions including temperature and time adapted to convert a substantial amount of calcium carbonate of such mixture into calcium oxide; (*f*) mixing the resulting furnace

product with water; (*g*) treating the mixture thus prepared under conditions adapted to convert sodium carbonate into sodium hydroxide and calcium oxide into calcium carbonate; (*h*) separating the causticized liquor from the lime mud; and (*i*) digesting fiber bearing material with the liquor thus formed.

17. In the art of producing chemical pulp the cyclic process which comprises digesting fiber bearing material in a cooking liquor comprising a sulfite of sodium, separating residual liquor from resulting fibrous material and subjecting solid constituents of such residual liquor to a reducing furnacing treatment adapted to drive off some of the sulfur originally combined in the cooking liquor, dissolving sodium compounds from the furnace product and causticizing the resulting solution so as to form a cooking liquor containing sodium hydroxide and sodium sulfide, digesting fiber bearing material with the cooking liquor so formed, separating residual liquor from the resulting fibrous material, subjecting solid constituents of this residual liquor to a reducing furnacing treatment, dissolving resulting sodium compounds composed principally of sodium carbonate and sodium sulfid, sulfiting sodium carbonate of the solution so as to form a cooking liquor containing more sodium sulfite than sodium thiosulfate, and cooking wood with cooking liquor thereby obtained.

In testimony whereof we affix our signatures.

LINN BRADLEY.
EDWARD P. McKEEFE.

CERTIFICATE OF CORRECTION.

Patent No. 1,860,570. **May 31, 1932.**

LINN BRADLEY ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 7, line 64, claim 7, before the word "monosulphite" insert the words comprising a substantial amount of sodium; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 5th day of July, A. D. 1932.

M. J. Moore,
Acting Commissioner of Patents.

(Seal)

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17. In the art of producing chemical pulp the cyclic process which comprises digesting fiber bearing material in a cooking liquor comprising a sulfite of sodium, separating residual liquor from resulting fibrous material and subjecting solid constituents of such residual liquor to a reducing furnacing treatment adapted to drive off some of the sulfur originally combined in the cooking liquor, dissolving sodium compounds from the furnace product and causticizing the resulting solution so as to form a cooking liquor containing sodium hydroxide and sodium sulfide, digesting fiber bearing material with the cooking liquor so formed, separating residual liquor from the resulting fibrous material, subjecting solid constituents of this residual liquor to a reducing furnacing treatment, dissolving resulting sodium compounds composed principally of sodium carbonate and sodium sulfid, sulfiting sodium carbonate of the solution so as to form a cooking liquor containing more sodium sulfite than sodium thiosulfate, and cooking wood with cooking liquor thereby obtained.

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