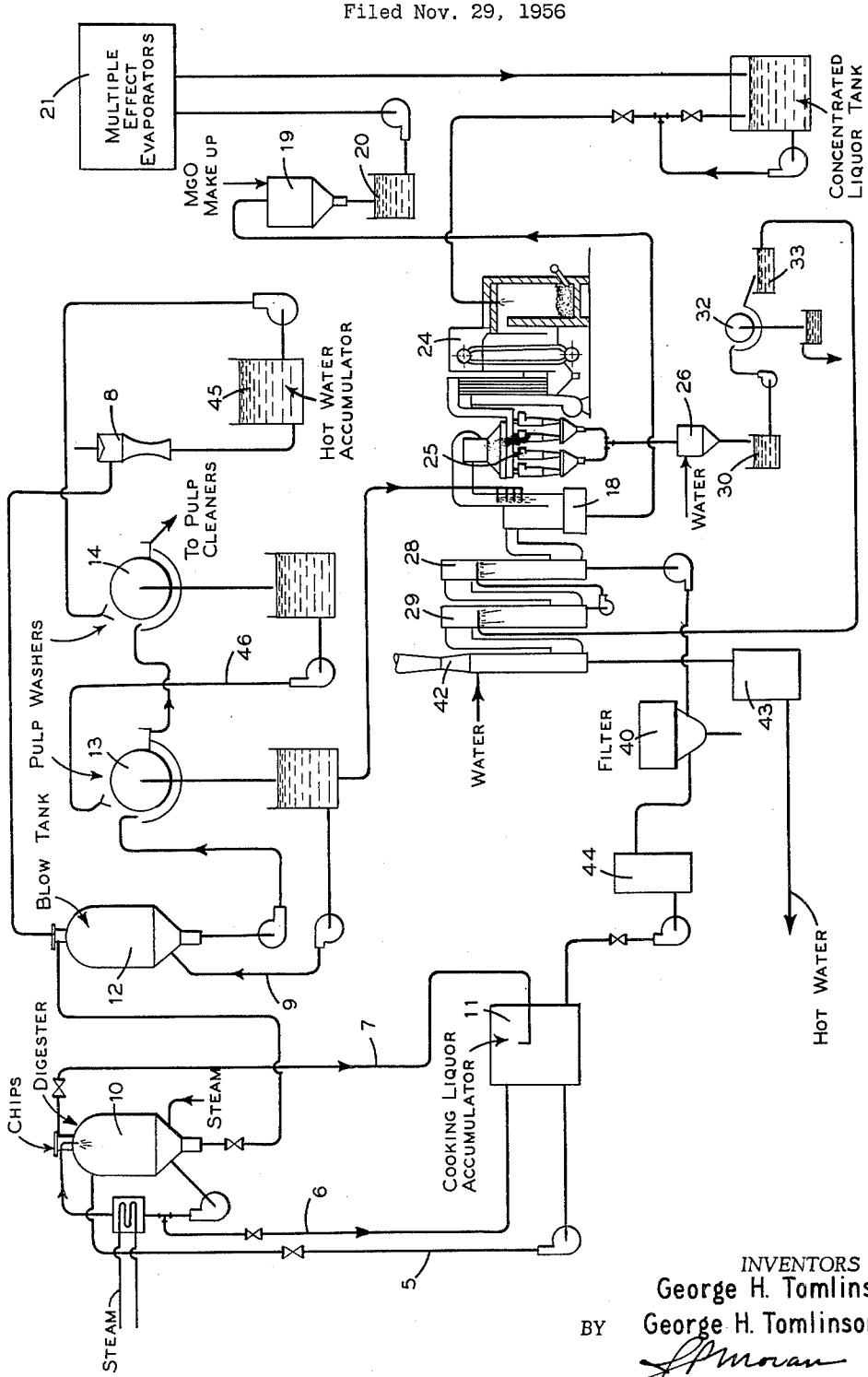
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SULPHITE PULPING PROCESS

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SULPHITE PULPING PROCESS

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The present invention relates to improvements in cyclic processes of manufacturing cellulosic pulps, and more particularly to the manufacture of pulps by an improved sulphite cooking process employing a relatively pure magnesium base cooking liquor which also permits the residual liquor to be evaporated and burned for the recovery of heat and its inorganic chemical content, the former being converted to steam and hot water and the latter being readily converted to form fresh cooking liquor. The process of this invention allows the pulping to proceed in less time and at higher temperatures than formerly employed in the production of sulphate paper pulps and, by various modifications, allows the production of pulps from a wide variety of woods or other cellulosic materials suitable for the whole range of paper making and chemical conversion. The pulps produced by this method are obtained in higher yields and have higher strength values than those obtained by the conventional sulphite process at a comparable degree of delignification. The cyclic nature of this process also results in major savings in the cost of chemicals and energy, as well as eliminating atmospheric and stream pollution.

Heretofore, as stated in "Pulp and Paper Manufacture," 1950 edition, vol. 1, page 303, "Essentially the sulphite process consists of the digestion of wood, in the form of chips, at temperatures from 130–150° C. in an aqueous solution containing alkaline-earth bisulphites (usually calcium bisulphite or a mixture of calcium and magnesium bisulphites) and an excess of sulphur dioxide." It is also stated that "the object of the sulphite process is to produce a maximum yield of nondegraded cellulose with substantially complete removal of the polyuronide, hemicellulose and lignin." According to "Pulp and Paper," vol. 1, J. P. Casey, 1952, "The best method of reducing attack on the cellulose and still obtain a bleachable pulp is to use strong acid, low cooking temperature, and relatively short cooking time." A typical sulphite cooking acid "generally contains about 6% total sulphur dioxide, but the trend in recent years has been toward the use of higher acid concentrations. A total sulphur dioxide content of 7 to 8% is not uncommon today, and some mills use an extreme of 10%" (p. 95). In such a cooking acid the combined CO_2 would be approximately 1%, leaving the remainder as free SO_2. It is believed by many investigators, "that the rate of delignification is directly related to the concentration of free sulphur dioxide in the liquor" (p. 97). It is generally believed that the best cooking temperature should be the lowest which gives a satisfactory degree of delignification in a reasonable time. According to Casey supra the use of too high a temperature lowers the yield, and cooking temperatures over 140° C. have a highly degrading effect on cellulose (p. 92). In general, the cooking cycles commercially employed involve a heating of the digester for approximately two hours until a temperature of 110° C. is reached and then a further heating to a maximum temperature of not more than 150° C., the total time of a cooking cycle being from 7–20 hours. The time taken to reach maximum temperature can be shortened if acids of high free sulphur dioxide are used (p. 90).

A sulphite acid cyclic pulping process employing a relatively pure magnesium base cooking liquor is disclosed

in the prior patents of G. H. Tomlinson, Nos. 2,285,876 and 2,385,955, a process now being used advantageously to produce commercial grades of sulphite pulp on an extensive scale and to eliminate stream pollution. In these prior patents of Tomlinson it is disclosed that when a magnesium base acid sulphite pulp residual liquor is evaporated and burned, an ash is obtained which consists essentially of magnesium oxide, while the sulphur content is obtained in the form of sulphur dioxide at a concentration of about 1% in the gaseous products of combustion. When this ash is separated from the gas, suspended in water, and the resultant suspension contacted with the gas, the sulphur dioxide is absorbed to form a liquor consisting of magnesium bisulphite, $Mg(HSO_3)_2$, together with a minor proportion of magnesium monosulphite, $MgSO_3$. Such liquor shows only slight, if any, partial pressure of SO_2 and the absorption of the sulphur dioxide from the low concentration furnace gas can be carried out without cooling if desired. In this case the temperature of the solution, which runs at about 70–75° C., results from the normal equilibrium established by the water vapor pressure of the furnace gas. The liquor, which now has a pH of about 4.5 and an analysis of about 2.2% "combined" SO_2 and 2.0% "free" SO_2, is cooled to about 20° C., using refrigeration if necessary, and is then saturated with a cooled gas containing about 16% SO_2 such as is obtained from a sulphur burner. An additional quantity of sulphur dioxide is then added by absorption of cooled relief gas consisting of nearly pure SO_2 as obtained by recycling relief gas from a pulp digester during the latter part of a previous digestion prior to the blow. The quantity of SO_2 thus recycled from one digester to the next is substantial, being about 2.5 times the amount obtained from the furnace gas, this relief operation requiring about 1.0 to 2 hours at the end of each digestion. The acid cooking liquor thus produced has a "combined" SO_2 content of about 1.0%, a "free" SO_2 of about 5% to 6.5% and a pH of about 1.5. The terms "free" SO_2 and "combined" SO_2 are used herein as currently defined by the Technical Section, Canadian Pulp and Paper Association (Data Sheet C–00c, June 1955), i.e., "Total SO_2" is the total amount of sulphur dioxide present in a bisulphite liquor, expressed as a percentage;

"Free SO_2" is the amount of free sulphur dioxide present in bisulphite liquor and equal to the sum of the "true free" SO_2 plus one-half the SO_2 present in the bisulphite;

"Combined SO_2" is the difference between the total SO_2 and the free SO_2 and representing one-half the SO_2 actually combined with calcium or magnesium bisulphite.

It can therefore be seen that:

When the combined SO_2 is equal to the free SO_2, then magnesium bisulphite only is present.

When the combined SO_2 is greater than the free SO_2, then the combined SO_2 minus the free SO_2 equals the true monosulphite.

When the free SO_2 is greater than the combined SO_2, then the free SO_2 minus the combined SO_2 equals the true sulphurous acid or the "excess" SO_2.

This cooking acid corresponds to a solution containing 2% SO_2 as magnesium bisulphite expressed as SO_2 plus 4% to 5.5% excess sulphurous acid expressed as SO_2. The use of this liquor in digesting the wood in existing magnesia base pulp mills has followed the techniques described supra.

Bleached pulps suitable for use in bond and other fine papers can be produced from certain woods, such as spruce, balsam, and hemlock, at lower cost by the acid sulphite process than by the sulphate process, and this is particularly true when the aforesaid cyclic magnesium base system is employed, because of the economic gain resulting from the recovery of heat and chemicals. However, in spite of this obvious economic advantage, the

aforesaid magnesia process installations have been limited to certain areas where stands having a very large wood volume per acre of such species still occur. Furthermore, the restricted development of the acid sulphite process which has occurred during recent years regardless of the base or recovery of chemicals, is also due to the fact that many important wood species such as pine and Douglas fir cannot be satisfactorily pulped by this process, and even in the case of wood species that can be pulped, the pulps obtained are materially weaker than those obtained from the same species using the sulphate process. In fact, when the short-fibered hardwoods are so pulped, the resultant sulphite pulp strength is so weak that such pulp can only be used as a minor constituent of a paper sheet. The need, which has developed in recent years, for effecting the economic harvesting and utilization of a mixed forest has, therefore, ruled out the use of the acid sulphite process and indicated instead the installation of the sulphate process for conifers and the neutral sodium sulphite semi-chemical process for hardwoods. The latter process allows the production of hardwood pulps in higher yield than can be obtained from the sulphate process but has not proved to be commercially suited to the production of pulps from softwoods. The use of this process has been restricted, since no self-contained cyclic recovery process for dealing with the residual liquor has as yet been commercially established.

The magnesia base cannot be substituted for the sodium base for use in the neutral sulphite process because its sparing solubility is not sufficient to permit of cooking liquors of adequate concentration being prepared.

We have now found that by employing the magnesia base at the bisulphite stage, i.e. a liquor containing mainly magnesium bisulphite and only minor amounts of the monosulphite on the one hand or of excess sulphurous acid on the other, it is possible to obtain solutions of adequate concentration for digestion of the wood. With such a cooking liquor we have been able to produce a whole family of pulps including semi-chemical pulps from both hardwoods and softwoods, and chemical pulps having qualities markedly superior to those of the sulphite pulps produced with the sulphur-dioxide-fortified magnesia base sulphite liquor disclosed in said patents. It should be noted that refractory species such as pine and Douglas fir can be pulped with this liquor. We have discovered also, that the resulting residual liquor can be advantageously treated in a cyclic process for the recovery of heat and inorganic chemicals. This cyclic process, however, differs radically from the one disclosed in the prior patents in that the new type of cooking liquor used in the present invention can be obtained directly at a temperature of about 70° C. from the primary absorption towers disclosed in said prior patents. This cooking liquor has but negligible SO_2 vapor pressure, which greatly simplifies its processing. For example, considerable saving in equipment and steam is possible, since cooling of the liquor to permit of its acidification with large quantities of sulphur dioxide, followed by subsequent heating under pressure of the thus fortified liquor, is no longer needed. Furthermore, the stripping of the large quantity of SO_2 from the digester, which involved from one to two hours of digester time, is no longer required, and finally, the cooking liquor can be stored at elevated temperatures up to 100° C. in open tanks instead of in the pressure accumulators normally employed for acid sulphite liquors. However, when an accumulator designed for say 40 p.s.i.g. operating pressure is used, it is possible to store the liquor at 140° C. instead of at about 65° C., which would be the maximum temperature that could be used in such a vessel with the conventional liquor. A further advantage of this process is the fact that, inasmuch as it eliminates the handling of the large volumes of concentrated sulphur dioxide gas involved in the conventional acid sulphite process, the risk of atmospheric pollution from gas escape does not exist.

As stated supra it has heretofore been considered desirable, and in fact essential, in making sulfite pulp, that the initial cooking liquor have a "free" SO_2 considerably greater than the "combined" SO_2, that is, that a large excess of sulphurous acid be present, and that a slow temperature rise and relatively low temperatures be used. For example, sulphurous acid 400–500%, or even more, in excess of the combined SO_2, a temperature rise to 110° C. in about two hours, and a maximum cooking temperature of 150° C. or less, are normally considered to be essential. We have now discovered that, starting with a magnesium bisulphite liquor either free of or containing but a small amount of excess sulphurous acid, a very rapid rise to much higher temperatures, i.e. temperatures materially above 150° C., may be employed. We have also found that under these conditions, the pulping can be accelerated by the presence of the very small amounts of sulphurous acid resulting from reaction between the magnesium bisulphite and the acids formed from the wood as the result of the action of heat during the digestion. Furthermore we have now found that by controlling the relationship between the pressure in the digester and its temperature, it is also possible to control the quantity of excess sulphurous acid present during the cook. Thus if the pressure is not allowed to build up above the vapor pressure of steam, sulphur dioxide will be stripped off as formed, and cooled samples of the liquor taken during the cook will have a pH of 4.5 to 5.0. Whereas the wood can be pulped under these conditions it is preferred to allow the pressure to build up slightly above that which would be established by the water vapor pressure alone. Thus when cooking at 166° C. we normally employ a pressure of 96 p.s.i.g. to 100 p.s.i.g. instead of 90 p.s.i.g. which is the pressure of saturated steam at that temperature. Under these conditions the pH of a cooled sample of the cooking liquor when withdrawn during the cook will have a pH of 3.0 to 4.0, this being the pH condition we normally prefer to establish and maintain during the cook. Inasmuch as acids are formed from the wood during the cook, and SO_2 can be stripped from the digester, it is therefore possible to start with a liquor having an initial pH of 4.5 to 5.0 on the one hand or of 2.5 to 3.0 on the other and still maintain a pH of 3.0 to 4.0 during the cook, this pH depending upon the extent to which the SO_2 is retained or relieved from the digester.

An essential feature of our invention is that the cooking liquor must be relatively free of excess sulphurous acid at the start and during the early stages of the cook. However it is also possible and sometimes desirable, after the initial sulphonation reaction at digestion temperature has occurred, to add sulphur dioxide so as to carry pressures substantially greater than would be obtained from the sulphur dioxide generated in the digester. In carrying out such a two-stage cook, the temperature of the digester may be reduced before adding the sulphur dioxide although such temperature reduction is not essential.

We have found that in carrying out the digestion a very rapid temperature rise to temperatures of the order of 160–190° C. can be employed, an operation which can be facilitated by withdrawing a considerable portion, or possibly even all, of the surplus cooking liquor from the chips following their impregnation. By this procedure low liquor to wood ratios that may be of the order of 1.5:1 to 2.5:1 can be successfully employed owing to the fact that the character of the cooking liquor of the present invention allows the use of solutions of a concentration sufficiently great that the relatively small volume of liquor that is retained in the chips is adequate for the pulping reaction. At the same time the magnesium bisulphite reagent is sufficiently mild in its action on cellulose that the increased concentration in the liquor required at this low liquor to wood ratio does not adversely affect strength or yield of pulp, and under certain conditions it may actually result in increased yield and greater strength. This low liquor ratio when employed, results

in a reduced steam requirement for digestion, and also, because of the high solids content of the residual liquor under these conditions, a low steam requirement for subsequent evaporation of the residual liquor.

In general, the process of the present invention, when used for the production of pulp from wood, comprises first displacing the air from the wood chips in the digester and then impregnating the chips with the new type of magnesium bisulphite cooking liquor. The impregnated chips are then heated to a predetermined temperature in the range of about preferably 160–190° C. This elevated temperature is held for a predetermined period of time depending upon the temperature and pressure employed. At 160° C. this may be of the order of 3 to 4 hours, and at 190° C. may be as short as 10 to 20 minutes, when the digester pressure is maintained about 5–15 p.s.i. above the vapor pressure of pure water at the digestion temperature, to give a chemical pulp having the desired quality and yield. The digester pressure may then be lowered to atmospheric, and the liquor washed from the pulp either before or after the pulp is removed from the digester. The residual liquor thus obtained is evaporated to a solids concentration suitable for self-sustaining combustion and burned, a major portion of the liberated heat being converted to steam. The magnesium oxide and sulphur dioxide formed on combustion of the liquor are subsequently combined in aqueous solution to form fresh cooking liquor. The make-up for losses in chemical is added either in the form of magnesium sulphate to the residual liquor before its combustion or as purchased magnesium oxide to the fresh cooking liquor.

In the attached drawing we have illustrated a flow diagram of a pulp mill of the type shown in Patent No. 2,385,955, modified to be operable in accordance with the present invention. The following operating stages are involved:

(1) The chips are added to the digester **10** and steamed to displace air.

(2) Magnesium bisulphite solution, as prepared in stage (14), to be described later, and preheated in accumulator tank **11** to the desired temperature, is pumped to digester **10** through line **5** until the digester is full, the pumping being continued to build up a hydrostatic pressure of about 5 to 6 atmospheres or more to aid penetration of the chips.

(3) Surplus liquor is then drained from the digester **10** to give the desired liquor to wood ratio and returned through line **6** to the accumulator tank **11** from which it was initially withdrawn.

(4) The temperature of the contents of the digester is rapidly increased until it is brought to the value desired for cooking, for example 166° C., where it is held for the desired time, for example 2¼ hours, the pressure meanwhile being held at a value slightly greater, say about 6 p.s.i., than that for the vapor pressure of pure water at the digester temperature which is 90 p.s.i.g. at 166° C.

(5) The pressure of the digester is then rapidly reduced, the initial portion of steam, if desired, passing through line **7** to liquor accumulator **11**, where liquor for the next cook can be heated to temperatures up to 100° C. if the accumulator is at atmospheric pressure or up to higher temperatures, e.g. 120° C. or greater, if the accumulator is built for superatmospheric pressures. The small amount of SO_2 carried in the relief gases from stages (4) and (5) is absorbed in liquor accumulator **11**, this giving the final adjustment to the pH of the cooking liquor.

(6) The contents of the digester are then discharged to blow tank **12**, leaving the digester available for another cook at stage (1), the steam released being condensed with fresh water in direct condenser **8** which discharges to hot water accumulator **45**.

(7) The pulp in blow tank **12** is next suspended in a portion of the residual liquor recycled through line **9** from rotary washer **13** to which the thus diluted stock is

delivered and where it is washed with a dilute liquor obtained from secondary rotary washer **14** through line **46**, the pulp passing to stage (8) and the remaining portion of residual liquor to stage (9).

(8) The partially washed pulp from washer **13** passes to washer **14** where it is washed with hot water obtained from tank **45** using directly the water condensed from, and heated by, the blow, the washed pulp being screened, cleaned, and/or bleached and converted to sheeted pulp, or to paper.

(9) Hot residual liquor as obtained from operation (7) is sprayed into a direct contact evaporator **18** where it is contacted with hot flue gases as they leave the magnesia separating cyclones **25** of a chemical recovery furnace unit **24**, stage (12). This simultaneously cools the gas to a temperature approximating its dew-point, about 70° C., and at the same time partially evaporates the liquor.

(10) The partially concentrated liquor is then brought to pH 6 or 7 at mixer **19** with make-up or recovered MgO and is then transferred from tank **20** to multiple-effect evaporator **21** where it is concentrated to a concentration in the range of 45 to 70% solids.

(11) The evaporated liquor is then fired in recovery furnace **24** of the general type described in U.S. Patent 2,385,955 where the organic portion of the liquor is burned for the recovery of heat and the production of steam while the inorganic portion is broken down into magnesium oxide and sulphur dioxide.

(12) After passing through the heat exchange zones of the furnace and its auxiliary equipment, the magnesium oxide is separated from the gas by means of the dry cyclones **25**.

(13) The magnesium oxide is slurried in water at **26**, collected in tank **30**, and filtered at a wash filter **32**, so that soluble alkali salts, calcium sulphate, etc. which originate in the water or the wood may be removed from the cycle, and the filter cake is then reslurried and slaked at tank **33**.

(14) The gas after leaving the dry cyclones **25** and passing through the direct contact evaporator **18** where it is saturated with water as described for stage (9), passes to the primary absorption towers **28** and **29** where it is contacted with a slurry containing the washed recovered magnesium hydroxide, as obtained from slaking tank **33**. The sulphur dioxide from the gas is absorbed, thus forming magnesium bisulphite together with a small amount of magnesium monosulphite.

(15) The resultant magnesium bisulphite liquor is filtered at **40** to remove silicates, etc. and run from storage tank **44** to the accumulator **11** for return to the cycle at stage (2).

(16) The effluent gas from stage (14) which has been stripped of magnesium oxide and sulphur dioxide is cooled by countercurrent contact with water in a condensing tower **42**, the hot water thus produced being available at tank **43** for use in bleaching the pulp and for other purposes.

Small percentages of the magnesia and sulphur dioxide are lost from the system, either with the pulp, or through other mechanical loss. These losses can be made up by addition of magnesium sulphate to the concentrated liquor before incineration at stage (11). Alternatively, magnesia losses can be made up by adding purchased magnesia or magnesium hydroxide to the slurry going to the absorption equipment of stage (14). Fresh sulphur dioxide can be added to the gas at stage (14), or alternatively and to avoid dilution of the gas, it can be added to the filtered liquor in the accumulator **11**, where the liquor can be held at the desired magnesium bisulphite composition.

In addition to the recovery of heat as steam in the recovery furnace, the recovery of hot water at stages (6) and (16) adds materially to the economy of the process. Because of the low SO_2 vapor pressure in the

digester, the hot water recovered at stage (6) can be used directly for the washing of the pulp. A corresponding condensate from the conventional acid sulphite process is saturated with SO_2 making its direct use impossible and the recovery of its SO_2 content a troublesome operation.

Whereas the above description has been related to batch digestion; it is obvious that continuous digesting equipment can be used. Certain other of the enumerated stages described above can also be modified or even eliminated without departing from the major advantage of the cyclic system of the present invention. Of special importance is the flexibility of the operation such that high quality pulps of different types and yield and using materially differing fibrous raw material can now be produced with a single cooking liquor and a single heat and chemical recovery system. When a semichemical pulp is to be produced, milder cooking conditions, such as shown in Examples Nos. 6 and 8 below, are employed, and provision must be made for mechanical disintegration of the softened chips.

As indicative of the types of pulp which can be produced, the following laboratory pilot plant examples may be cited:

Example No. 1

4235 g. moisture-free weight of spruce chips having 31.7% moisture content were placed in a digester and steamed at atmospheric pressure for 30 minutes to displace the air. A magnesium bisulphite liquor at a temperature of 90° C. having a pH of 3.32 containing 1.97% "free" SO_2 and 1.93% "combined" SO_2 (the excess sulphurous acid, expressed as SO_2 being only 0.04%) was added to cover the chips; a hydrostatic pressure of 90 p.s.i.g. was applied for 30 minutes, and then surplus liquor was withdrawn to an accumulator to leave a residual liquor to wood ratio of 4.75:1.0. The temperature was brought to 166° C. in 40 minutes, heating indirectly by means of a circulating system, and the temperature was held at 166° C. for 2.25 hours, the digester then being allowed to relieve at 96 p.s.i.g. During the heating period the pH values of cooled samples of the liquor increased to 4.25 after 30 minutes when the temperature reached 155° C., this resulting from the transfer of SO_2 from the liquor to the vapor space of the digester. However, as a result of acids formed, the pH value decreased to 4.12 after 40 minutes when the digester reached 166° C., decreasing further to 3.55 at 2 hours, with an average value of about 3.7 during the cook. Following the desired cooking period the pressure was decreased to atmospheric pressure and the resultant pulp was washed and screened.

The screened yield was 54.0%, the screened rejects 0.12%, the Roe chlorine number 10.2 and the G.E. brightness value 63.0. This pulp, before drying, was beaten in a Standard TAPPI Valley beater using a weight of 4.5 kg. on the bed-plate. Standard hand sheets were prepared from the pulp at various beating times and tested in accordance with TAPPI Standards—T205 and T220. The following data were obtained on the pulp before beating and after beating to 300 cc. Canadian freeness.

Beating Time, Minutes	Canadian Freeness, cc.	TAPPI Bulk, cc./g.	TAPPI Burst	TAPPI Tear	Burst +½ Tear	Tensile Breaking Length, Meters
0	683	1.41	65	106	118	8,800
50	302	1.16	89	86	132	13,200

Example No. 2

In this digestion a similar cooking liquor and wood were used as in Example 1 and similar techniques were employed. However, the liquor was preheated to 140° C. before it was added to the chips, and following an impregnation period of 30 minutes, only 15 minutes were employed to bring the temperature to 166° C. where the temperature was held for 3 hours with the maximum pressure being 96 p.s.i.g.

In this case the screened yield was 50.3%, the screened rejects 0.06%, the Roe chlorine number 6.4 and the G.E. brightness 60.0. This pulp showed the following strength characteristics when tested as indicated above:

Beating Time, Minutes	Canadian Freeness, cc.	TAPPI Bulk, cc./g.	TAPPI Burst	TAPPI Tear	Burst +½ Tear	Tensile Breaking Length, Meters
0	683	1.42	60	91	106	8,700
38	300	1.27	79	74	116	11,300

Example No. 3

In this case a similar cooking liquor and wood were used as before, the impregnation temperature was 90° C., and the digestion temperature was brought to 180° C. in 55 minutes and held at that temperature for 30 minutes. The maximum pressure was allowed to rise to 140 p.s.i.g. (10 p.s.i. higher than the vapor pressure of water at 180° C.) and the pH value of the liquor was 3.35 during the cook.

The screened yield was 50.1%, the screened rejects 0.11%, the Roe chlorine number 9.5 and the G.E. brightness 60.3. Strength characteristics were as follows:

Beating Time, Minutes	Canadian Freeness, cc.	TAPPI Bulk, cc./g.	TAPPI Burst	TAPPI Tear	Burst +½ Tear	Tensile Breaking Length, Meters
0	682	1.47	64	119	124	8,800
40	300	1.18	87	90	132	12,300

Example No. 4

In this case the cooking liquor had an initial pH of 3.50 and contained 4.22% "free" SO_2 and 4.51% "combined" SO_2. Following the impregnation of the chips at 90° C. all of the free liquor was withdrawn, and the temperature was brought to 166° C. in 28 minutes using direct steam and held at that temperature for 1½ hours. The pressure was maintained at 100 p.s.i.g.

The screened yield of pulp was 56.7%, the screened rejects 0.14%, the Roe chlorine number 12.9 and, the G.E. brightness value 57.1. This pulp showed the following strength characteristics.

Beating Time, Minutes	Canadian Freeness, cc.	TAPPI Bulk, cc./g.	TAPPI Burst	TAPPI Tear	Burst +½ Tear	Tensile Breaking Length, Meters
0	670	1.39	72	95	120	10,500
43	300	1.19	94	74	131	12,700

Example No. 5

In this case the magnesium bisulphite solution, having a pH of 4.60 and containing 3.54% "combined" SO_2, was added at a temperature of 100° C. and the digester was heated to 160° C. in 60 minutes, after which all surplus liquor was withdrawn. This temperature was held at 160° C. and the pressure at 75 p.s.i.g. for 2 hours and the temperature was then rapidly dropped to 153° C. by relieving the digester. Pure sulphur dioxide was then added to bring the pressure to 90 p.s.i.g., where it was held for 30 minutes, after which the pressure was reduced to atmospheric.

The screened yield was 56.9%, the screened rejects 0.2%, the Roe chlorine number 11.3 and the G.E. bright-

ness 57.2. The pulp had the following strength characteristics:

Beating Time, Minutes	Canadian Freeness, cc.	TAPPI Bulk, cc./g.	TAPPI Burst	TAPPI Tear	Burst +½ Tear	Tensile Breaking Length, Meters
0	673	1.45	74	79	109	11,600
19	300	1.23	91	65	124	14,000

The above examples in which spruce wood was cooked indicate the extraordinary nature of the results that may be obtained. With conventional sulphite pulping the screened yield of pulp is normally in the range of about 46 to 49%. In Example No. 4 above, the screened yield was 56.7% with only 0.14% rejects. It has been observed that these pulps not only show extremely small quantities of screenable rejects but they are also remarkably free of the small shive and bark dirt that pass through the screens and which are characteristic of the conventional acid sulphite pulps. The low shive content results from the remarkably uniform pulping obtained with these liquors while the low bark content results from the fact that the inner bark is pulped, which is certainly not the case when the conventional low pH liquors are used.

The strength values of these pulps are also exceptional, both at the unbleached stage, as reported above and after bleaching where the corresponding values are normally as great or even greater. With the conventional acid sulphite process, the strongest pulps are normally prepared by the Mitscherlich method where the maximum temperature is kept below 125° C. or 130° C. and the cooking time is 16 to 18 hours. A commercial Mitscherlich pulp showed the following strength values when tested by the same methods reported above:

Beating Time, Minutes	Canadian Freeness, cc.	TAPPI Bulk, cc./g.	TAPPI Burst	TAPPI Tear	Burst +½ Tear	Tensile Breaking Length, Meters
0	667	1.4	26	117	85	4,320
30	300	1.17	62	60	92	9,200

It is apparent that all of the pulps of the present invention described above are materially stronger than the Mitscherlich pulp, the burst+½ tear value being in some cases 40% greater.

Example No. 6

This digestion with spruce chips was carried out in such a manner as to produce a semi-chemical pulp. Following the pressure impregnation with a magnesium bisulphite liquor having a pH of 4.75 and containing 2.86% "free" SO_2 and 3.3% "combined" SO_2, all surplus liquor was drained back to the accumulator. The ratio of the net liquor added to the dry weight of the wood was 1.66:1. The temperature was brought to 160° C. in 1 hour with direct steam and held at that temperature for 2 hours; the pressure being 75 p.s.i.g. The washed semi-cooked pulp was refined in a disc refiner and the resultant pulp was found to give a yield of 69.5% based on the weight of wood, a brightness of 54.6 G.E. and a Roe chlorine number of 23.5. The pulp had the following strength characteristics:

Beating Time, Minutes	Canadian Freeness, cc.	TAPPI Bulk, cc./g.	TAPPI Burst	TAPPI Tear	Burst +½ Tear	Tensile Breaking Length, Meters
0	658	1.66	68	77	103	10,100
49	300	1.35	85	54	112	14,000

Both the burst and tensile values are markedly higher than those of the Mitscherlich pulp, and, although the tear values are slightly lower, the overall strength, as measured by the burst+½ tear value can be considered quite remarkable for a pulp at the very high yield of 69.5%.

Example No. 7

Whereas chips from mature pine logs cannot normally be pulped by the acid sulphite process, we have found that satisfactory results can be obtained by the present methods. This digestion was essentially a duplicate of Example No. 1 with the exceptions that chips cut from mature jack pine and having 52.2% moisture content were used and that the digestion time was 3 hours. The yield was 51.4%, the screened rejects 1.9%, the Roe chlorine number 9.0 and the G.E. brightness 55.5. The following strength characteristics were obtained:

Beating Time, Minutes	Canadian Freeness, cc.	TAPPI Bulk, cc./g.	TAPPI Burst	TAPPI Tear	Burst +½ Tear	Tensile Breaking Length, Meters
0	708	1.68	40	113	97	4,100
50	308	1.26	61	89	106	7,900

Example No. 8

The above techniques can also be applied to the hardwoods which are characterized by short fibre length.

This digestion was essentially a duplicate of Example No. 1, with the exception that chips cut from aspen and having 30.5% moisture content were used, and the digestion time was only 30 minutes. The washed semi-cooked pulp was refined in a disc refiner, and the resultant pulp was found to give a yield of 69.7% based on the weight of wood and a Roe chlorine number of 16.0. The pulp had the following strength characteristics:

Beating Time, Minutes	Canadian Freeness, cc.	TAPPI Bulk, cc./g.	TAPPI Burst	TAPPI Tear	Burst +½ Tear	Tensile Breaking Length, Meters
0	599	1.42	37	58	66	6,900
27	300	1.22	56	50	81	9,700

The above pulp is quite similar in strength characteristics to a conventional neutral sodium sulphite semichemical pulp.

Whereas the percentage, based on wood, of total sulphur dioxide used in the above cooks is materially less than that used in producing conventional acid sulphite pulp, the combined sulphur dioxide is normally somewhat greater. However, because of the cyclic nature of the present process the increased quantity of combined sulphur dioxide required for optimum results is not of great significance, since only the cost of make-up for losses of this extra chemical is involved on account of the cyclic nature of the process.

This application is a continuation-in-part of our prior copending application Serial No. 558,918, filed January 13, 1956, now abandoned.

While in accordance with the provisions of the statutes we have disclosed herein preferred embodiments of the invention, those skilled in the art will understand that changes may be made in the method of operation and form of the apparatus disclosed without departing from the spirit of the invention covered by the claims, and that certain feaures of the invention may sometimes be used to advantage without a corresponding use of other features.

What is claimed is:

1. The method of preparing a chemical pulp from cellulosic raw material comprising impregnating the material in a digester with a magnesium bisulphite solution essentially free of excess sulphurous acid and initially in the range of 2.5–5.0 pH, draining solution from the digester to establish a predetermined solution-material ratio in the digester, rapidly heating the impregnated material

to a maximum cooking temperature between 160 and 190° C., and maintaining the pH of the solution as measured at room temperature at a value between 3.0 and 4.0 at said cooking temperature during the period when the major sulphonation of the lignin and dissolution from the cellulose takes place, to form a defibred pulp without mechanical refining.

2. The method of preparing a chemical pulp from cellulosic raw material comprising digesting the material with a magnesium bisulphite solution essentially free of excess sulphurous acid and at a pH value when measured at room temperature in the range of 3.0 to 4.0 during the period when the major sulphonation of the lignin and dissolution from the cellulose takes place, to form a defibred pulp without mechanical refining.

3. The method of preparing a chemical pulp from cellulosic raw material comprising impregnating the material with a magnesium bisulphite solution initially in the range of 2.5–5.0 pH as measured at room temperature, and digesting the impregnated material with said magnesium bisulphite solution essentially free of excess sulphurous acid at a temperature between 160 and 190° C., and maintaining the solution during a major portion of the period when the major sulphonation of the lignin and dissolution from the cellulose takes place at a pH between 3.0 and 4.0 as measured at room temperature, to form a defibred pulp without mechanical refining.

4. The method of preparing a chemical pulp from cellulosic raw material comprising impregnating the material with a magnesium bisulphite solution initially in the range of 2.5–5.0 pH as measured at room temperature, digesting the impregnated material at a temperature between 160 and 190° C., and maintaining the pH of the solution during a major portion of the digestion period between 3.0 and 4.0 as measured at room temperature by regulating the digesting pressure to retain a portion of the sulphurous acid liberated during the digestion, to form a defibred pulp without mechanical refining.

5. A process for preparing a pulp from a cellulosic raw material which comprises impregnating the raw material with a solution of magnesium bisulphite essentially free of excess sulphurous acid, digesting the impregnated material under conditions such that the pH of the solution as measured at room temperature is between 3.0 and 4.0 and the digestion temperature is between 160 and 190° C. for a predetermined period of time varying between approximately four hours if at the lower temperature and approximately thirty minutes if at the high temperature and when the major sulphonation of the lignin and dissolution from the cellulose takes place, lowering the temperature of the solution, and separating the pulp from the residual liquor.

6. A method of preparing a chemical pulp from a cellulosic raw material which comprises impregnating chips of the cellulosic material in a digester with a cooking liquor consisting of a hot magnesium bisulphite solution essentially free of excess sulphurous acid and having a pH of 2.5 to 5.0, rapidly heating the digester contents to a cooking temperature in the range of 160–190° C., holding the digester at said cooking temperature for a predetermined period varying between approximately ten minutes and four hours, the lower the temperature the longer the time, and vice versa, while maintaining the digester pressure at a value slightly greater than the vapor pressure of pure water at the digester temperature to maintain the pH of the solution as measured at room temperature at a value between 3.0 and 4.0 during the period when the major sulphonation of the lignin and dissolution from the cellulose takes place, relieving the digester by reducing the pressure therein, and separating the residual liquor from the pulp.

7. A method of preparing a chemical pulp from chips of cellulosic material in a digester which comprises charging the digester with the chips, impregnating the chips with a hot magnesium bisulphite soluton essentially free of excess sulphurous acid and having a pH of 2.5 to 5.0, heating the impregnated chips to a temperature between 160 and 190° C. and with the solution at a pH between 3.0 and 4.0 as measured at room temperature during the period when the major sulphonation of the lignin takes place, and adding sulphur dioxide to the digester until the pressure is raised to a predetermined value and for a predetermined time such that the sulphurous acid formed in the chips effects a hydrolysis of sulphonated lignin and its subsequent solution at a temperature in excess of 140° C.

8. The method of preparing pulp from chips of cellulosic material in a digester which comprises charging the digester with the chips, impregnating the chips by flooding with a hot magnesium bisulphite solution essentially free of excess sulphurous acid and having a pH of 2.5 to 5.0, separating the impregnated chips from the surplus liquor, heating the impregnated chips to a temperature between 160 and 190° C. and at a pH between 3.0 and 4.0 as measured at room temperature to effect sulphonation of the lignin and for a predetermined time such that the sulphurous acid formed in the chips can effect the solution of the sulphonated lignin to the desired extent.

9. A cyclic method of preparing a pulp from a cellulosic raw material and recovering heat and chemicals from the pulp residual liquor comprising digesting the raw material with a magnesium bisulphite solution essentially free of excess sulphurous acid and at a pH of 3.0 to 4.0, separating the residual liquor from the pulp, concentrating the liquor to a concentration in the range of 45–70% solids, burning the concentrated liquor with the recovery of heat, magnesium oxide and sulphur dioxide, recombining the magnesium oxide and sulphur dioxide to form an aqueous solution of magnesium bisulphite essentially free of excess sulphurous acid, and using said reformed liquor in the digesting step while maintaining the reformed liquor essentially free of excess sulphurous acid.

10. A cyclic method of preparing a chemical pulp from a cellulosic raw material and recovering heat and chemicals from the pulp residual liquor comprising impregnating the raw material with a magnesium bisulphite solution having a pH of 2.5 to 5.0 as measured at room temperature, digesting the impregnated material at a temperature of 160–190° C. for a predetermined time and at a predetermined superatmospheric pressure, maintaining the pH of the solution as measured at room temperature at a value between 3.0 and 4.0 at said cooking temperature during the period when the major sulphonation of the lignin and dissolution from the cellulose takes place, separating the residual liquor from the pulp, concentrating the liquor to a concentration in the range of 45–70% solids, burning the concentrated liquor with the recovery of heat, magnesium oxide and sulphur dioxide, recombining the magnesium oxide and sulphur dioxide to form an aqueous solution of magnesium bisulphite essentially free of excess sulphurous acid, and using said reformed liquor in the digesting step.

11. A method of preparing a pulp from a cellulosic raw material which comprises digesting chips of the cellulosic material in a cooking liquor consisting of a hot magnesium bisulphite solution essentially free of excess sulphurous acid and at a cooking temperature in the range of 160–190° C., holding the chips at said cooking temperature for a predetermined period and with a solution pH as measured at room temperature at a value between 3.0 and 4.0 during the period when the major sulphonation of the lignin and dissolution from the cellulose takes place, separating the residual liquor from the pulp, concentrating the residual liquor to a predetermined solid concentration in the range of 45–70% solids, burning the concentrated liquor with the production of heat, magnesium oxide and gaseous products including sulphur dioxide, forming a slurry containing recovered magnesium hydroxide, contacting the gaseous products with

the magnesium hydroxide slurry to form an aqueous solution of magnesium bisulphite essentially free of excess sulphurous acid, and using said reformed liquor in the digesting step while maintaining the reformed liquor essentially free of excess sulphurous acid.

12. A method of preparing a pulp from a cellulosic raw material which comprises steaming chips of the cellulosic material in a digester to displace air, impregnating the chips with a cooking liquor consisting of a hot magnesium bisulphite solution having a pH of 2.5 to 5.0, draining the surplus cooking liquor from the digester, rapidly heating the digester contents to a cooking temperature in the range of 160–190° C., holding the digester at said cooking temperature for a predetermined period while maintaining the digester pressure at a value slightly greater than the vapor pressure of pure water at the digester temperature to maintain the pH of the solution as measured at room temperature at a value between 3.0 and 4.0 during the period when the major sulphonation of the lignin and dissolution from the cellulose takes place, relieving the digester by reducing the pressure therein, separating the residual liquor from the pulp, concentrating the residual liquor to a predetermined solids concentration suitable for self-sustaining combustion, burning the concentrated liquor with the production of heat, magnesium oxide and gaseous products including sulphur dioxide, forming a slurry containing recovered magnesium

hydroxide, contacting the gaseous products with the magnesium hydroxide slurry to form an aqueous solution of magnesium bisulphite essentially free of excess sulphurous acid, and using said reformed liquor in the digesting step while maintaining the reformed liquor essentially free of excess sulphurous acid.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,046,182 July 24, 1962

George H. Tomlinson et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 21, for "sulphate" read -- sulphite --; line 52, for "CO_2" read -- SO_2 --.

Signed and sealed this 13th day of November 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents