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[54] PRODUCTION OF PULP BY A MULTI-STAGE AMMONIUM POLYSULPHIDE PULPING PROCESS

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[51] **Int. Cl.** **D21c 3/26**
[58] **Field of Search** 162/19, 63, 68, 82; 23/48, 23/49, 134

[56] **References Cited**

UNITED STATES PATENTS

2,944,928 7/1960 Kibrick et al. ....162/82 X

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[57] **ABSTRACT**

In a process for the production of cellulosic pulp from lignocellulosic material which comprises impregnating said material in subdivided form with a polysulphide liquor containing ammonium hydroxide in an amount sufficient to maintain a pH of at least 11.5 and at a temperature below that at which substantial decomposition of the polysulphide occurs, removing excess polysulphide from the material, heating the polysulphide impregnated material in the presence of ammonia gas to stabilize the material, and subsequently cooking the material with sodium hydroxide containing cooking liquor to delignify the material.

8 Claims, 3 Drawing Figures

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3,661,698

3 Sheets-Sheet 1

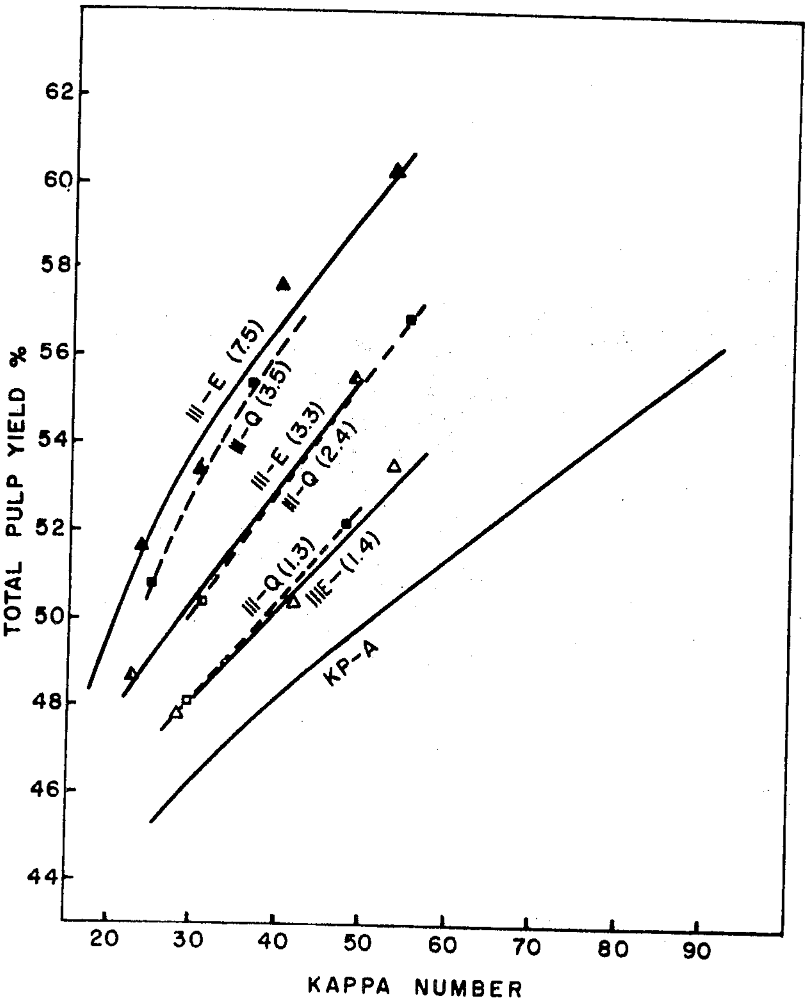

FIG. 1

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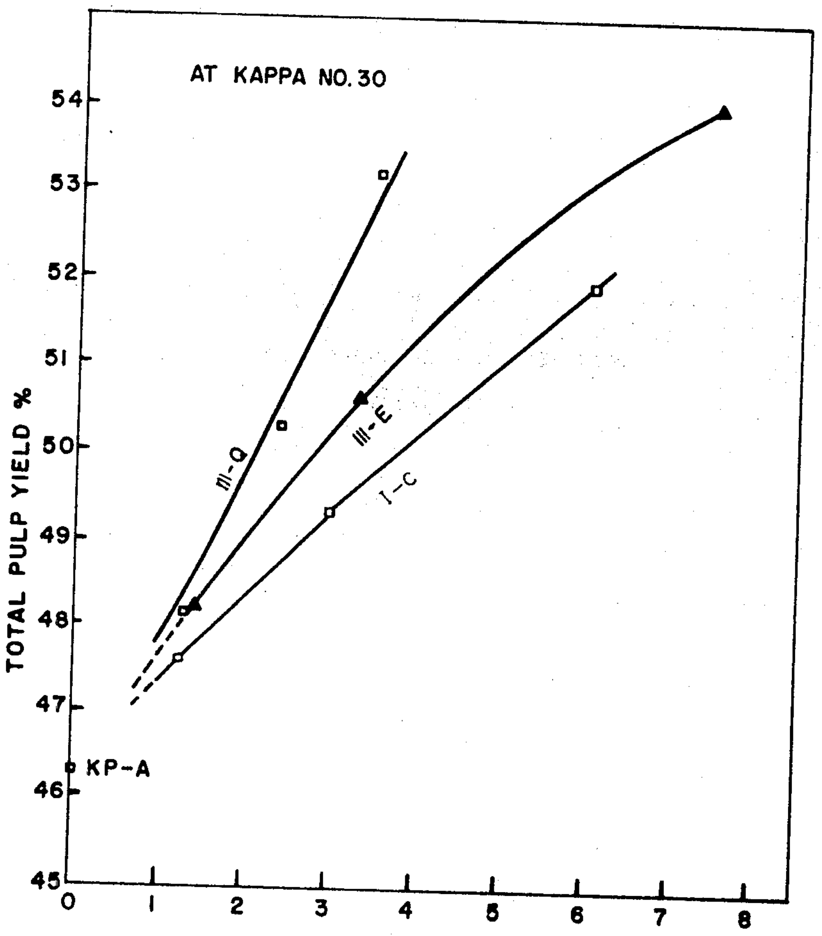
AT KAPPA NO. 30
TOTAL PULP YIELD %
54
53
52
51
50
49
48
47
46
45
0
1
2
3
4
5
6
7
8
POLYSULPHIDE CONSUMED % ON WOOD
III-Q
III-E
I-C
KP-A

FIG. 2

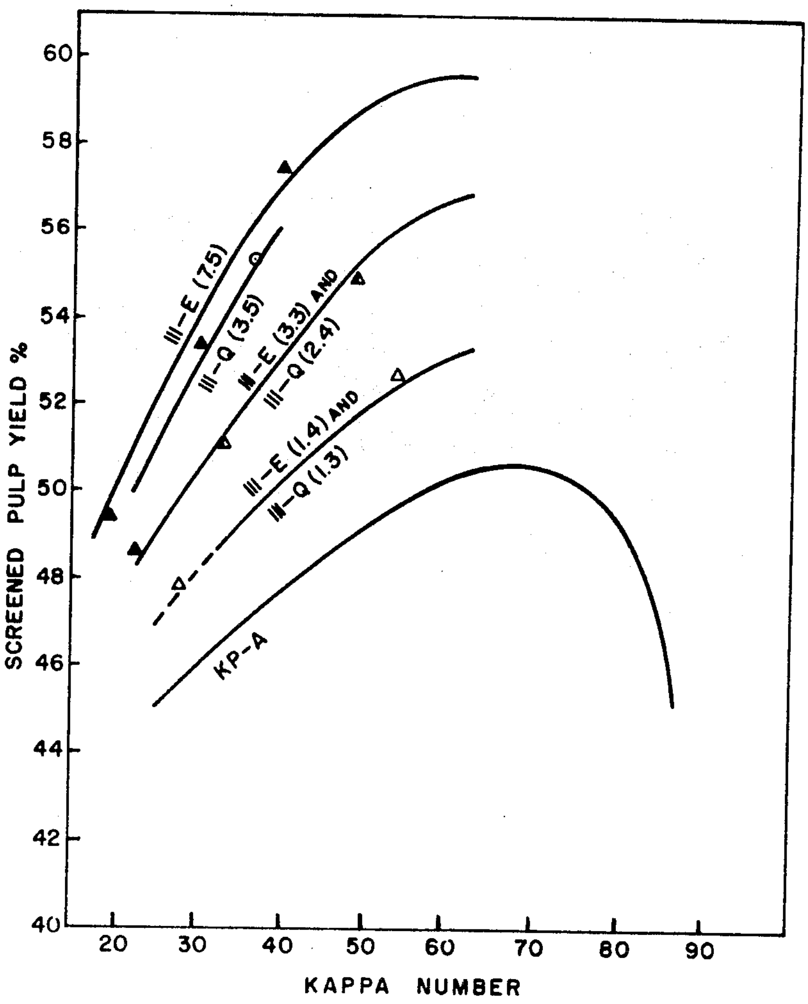
SCREENED PULP YIELD %
60
58
56
54
52
50
48
46
44
42
40
20
30
40
50
60
70
80
90
KAPPA NUMBER
III-E (7.5)
III-Q (3.5)
III-E (3.3) AND
III-Q (2.4)
III-E (1.4) AND
III-Q (1.3)
KP-A

FIG. 3

PRODUCTION OF PULP BY A MULTI-STAGE AMMONIUM POLYSULPHIDE PULPING PROCESS

The present invention relates to the production of pulp in improved yield from ligno-cellulosic materials such as wood, straws and grasses by the polysulphide process. In particular, the present invention relates to the production of cellulosic pulp in increased yield by a modification of the aforesaid polysulphide process in which the amount of polysulphide and alkali required is substantially reduced.

In the conventional kraft or sulphate process for the production of cellulosic pulp, in particular wood pulp, the subdivided wood or other ligno-cellulosic material is cooked in an aqueous solution of sodium hydroxide-sodium sulphide at a temperature of the order of 170° C. for the time required to produce a pulp in the required yield. The resulting pulp contains lignin and carbohydrate in a ratio which is determined by the specific conditions of the pulping process i.e., the temperature cycle, the time, the liquor to wood ratio and the ratio of chemical to wood. In general, the ratio of carbohydrate to lignin in the pulp from a given material at a given yield is a quantity which varies within very narrow limits being virtually fixed by the nature of the process.

In the polysulphide process the aforesaid cooking is effected in the presence of polysulphide ion, suitably effected by adding sodium polysulphide or elemental sulfur to the cooking liquor and the pulping operation is carried out under appropriately modified conditions which are well known to those skilled in the art. The polysulphide pulps which are obtained have a higher ratio of carbohydrate to lignin than the pulps obtained in the kraft or sulphate process at the same yield, due to the stabilization of the wood polysaccharides against alkaline degradation by the polysulphide ion. Thus in the conventional polysulphide pulping process it is believed that there are at least two reactions occurring which compete for the polysulphide ion including, firstly, the reaction of the polysulphide ion with the reducing end groups of the wood polysaccharides to yield oxidized polysaccharides which are more stable to hot alkali than the original polysaccharides and thus, in the polysulphide process the carbohydrate portion of the wood is not degraded to the same extent as in the kraft process during the time required to produce pulp of a similar lignin content. The "peeling reaction" which normally occurs in alkaline pulping which results in a loss of carbohydrate is avoided to a great extent in the polysulphide process and this is one of the main purposes of the use of polysulphide in the cooking process. Secondly, there is the reaction of the polysulphide ion with hydroxyl ions in the cooking liquor to produce hydrosulphide and thiosulphate ions. This is an undesirable side reaction because it destroys the polysulphide ion without any benefit to the pulping operation and alkali is consumed in the decomposition of the polysulphide ion and thus, more alkali must be added in order to make up the loss to achieve the required degree of delignification in the pulp.

Thus, while the pulp products of the aforesaid polysulphide process compare favorably with the pulps obtained in the conventional kraft or sulphate process and, in particular, pulps having the same Kappa number produced by the polysulphide process are usually darker in color, have easier beatability, have higher strength in burst and tensile, slightly lower strength in double fold and tear and have similar bleachability, the conventional single stage polysulphide process is subject to several problems. Thus, as the polysulphide sulfur charge is increased a much higher alkali charge is required for the required delignification because hydroxyl ions are consumed by the decomposition of the polysulphide ion to hydrosulphide and thiosulphate ions. Further, the rate of decomposition of the polysulphide ion increases with the temperature and becomes appreciable above 100° C. in the presence of hydroxyl ions and in a typical liquid phase pulping cycle most of the polysulphide is destroyed before the maximum temperature is reached. Whereas it is obvious that the polysulphide charge can be better used by lowering the maximum temperature the practical minimum in a single stage process is about 160° C. below which the delignification rate is too slow to be of commercial use.

In order to overcome the aforesaid problem of the decomposition of the polysulphide ion and reduce the requirements for more alkali in the single stage polysulphide process, it has been proposed in Japanese Pat. No. 7501 (1963) to effect the process in two stages in which the polysulphide is separated from the alkali to reduce the decomposition of the polysulphide. Thus, in the process of the Japanese patent the treatment with polysulphide to stabilize the polysaccharides against degradation in the ligno-cellulosic material is effected in the absence of alkali and at a temperature of about 130° C. over a period of about an hour and subsequently, the excess of polysulphide liquor is withdrawn and as it contains residual polysulphide ion can be re-used in the process. The stabilized ligno-cellulosic material is then cooked at about 170° C. for about an hour with sodium hydroxide or kraft liquor with a 15 percent sulphidity to obtain the required pulp. It is found in the two-stage process of this Japanese Patent, that pulp yield increases of 5–7 percent based on wood were obtained when compared with kraft pulps of the same Lignin content. However, the two-stage process of the Japanese Patent, although an improvement upon the single stage conventional polysulphide pulping procedure, still has the disadvantage that a substantial quantity of the polysulphide is destroyed in the stabilization stage without it reacting with the polysaccharides in the ligno-cellulosic materials. This is due to the relatively high temperature of 130° C. used in the stabilization and, although polysulphide decomposes more slowly at lower temperatures, it still decomposes fairly rapidly at 130° C. and if lower temperatures were used in the stabilization stage of the process of the Japanese Patent the reaction between the polysulphide and the polysaccharides would proceed too slowly to achieve maximum carbohydrate yield. As will be realized the decomposition of the polysulphide means a direct loss of chemical to the process and necessitates the installation of an expensive recovery system to regenerate the polysulphide for reuse in the stabilization of fresh ligno-cellulosic material and thus adds considerably to the cost of the pulp.

In our copending U.S. application Ser. No. 665,710 filed Sept. 6, 1967, there is disclosed a process for the production of pulp from ligno-cellulosic materials by the polysulphide process which is effected in three stages and in which the decomposition of the polysulphide during the impregnation of the polysaccharides in the ligno-cellulosic material is substantially reduced and at the same time, an increase in pulp yield is obtained at essentially the same Kappa number over that obtained by the conventional kraft or single stage polysulphide process.

Thus it was found according to the invention of U.S. application Ser. No. 665,710 that when the ligno-cellulosic material in subdivided form is subjected to impregnation in a separate stage from the stabilization stage and in The impregnation stage, the temperature is maintained so that essentially no polysulphide ion is decomposed and the excess polysulphide liquor containing no added sodium hydroxide is removed from the material between the impregnation and stabilization stages, it is possible to effect both the impregnation stages and the stabilization stages under conditions which are optimum for impregnation and stabilization and thus avoid the problem which has occurred heretofore, particularly in the process of the Japanese Patent namely, that the conditions for stabilization are directly opposed to the conditions desirable for impregnation.

In particular in U.S. application Ser. No. 665,710 there is provided a process for the production of cellulosic pulp from ligno-cellulosic materials which comprises substantially completely impregnating said materials in subdivided form with a polysulphide liquor containing no added sodium hydroxide at a temperature below that at which substantial decomposition of the polysulphide occurs, removing excess polysulphide liquor from the impregnated materials, stabilizing the impregnated materials against alkaline degradation by increasing the temperature of said materials and subsequently delignifying said stabilized materials by cooking said material in a cooking liquor containing sodium hydroxide.

The impregnation is carried out so that the required amount of polysulphide ion is uniformly taken up in the subdivided lignocellulosic material without any substantial loss by decomposition. After the excess of polysulphide liquor is withdrawn, the temperature and usually the pH of the material can be adjusted in order to effect the stabilization reaction for which optimum conditions depend upon the nature of ligno-cellulosic material, e.g. the wood species.

Thus, because the excess of polysulphide liquor is withdrawn before the stabilization reaction is effected, the conditions for stabilization are not limited by the necessity of protecting polysulphide ion from decomposition. The essence of the invention in U.S. application Ser. No. 665,710 therefore is the capability of the process for the establishment of optimum conditions for a complete and uniform impregnation of the lignocellulosic material with the least loss of polysulphide decomposition followed by the maximum possible stabilization of polysaccharides before the alkaline delignification stage.

As set forth in U.S. application Ser. No. 665,710 subsequent to the impregnation of the ligno-cellulosic material, e.g. wood chips, with polysulphide in the impregnation stage and removal of excess polysulphide from contact therewith, the impregnated ligno-cellulosic material is then subjected to stabilization which necessitates increasing the temperature above 100° C. and suitably above 120° C. in order to cause reaction to occur between the polysulphide and the ligno-cellulosic material. Further the rate at which the polysulphide stabilizes the polysaccharides in the lignocellulosic material is much lower at a low pH of about 11, than at high pH of about 14 and according to one embodiment of the invention set forth in U.S. application Ser. No. 665,710, ammonia gas is added to the stabilization stage and the impregnated cellulosic material is heated with direct steam above 130° C. Thus the pH within the ligno-cellulosic material is adjusted to a value at which the net loss of polysaccharides is at a minimum. Such a process is specifically illustrated in Example II of U.S. application Ser. No. 665,710.

In the impregnation stage in U.S. application Ser. No. 665,710 it is critical to the invention that no sodium hydroxide is added to the polysulphide solution as the presence of sodium hydroxide raises the pH of the polysulphide solution to about 13.5 causing substantial decomposition of the polysulphide into thiosulphate or hydrosulphide by reaction with hydroxyl ions thus decomposition becoming appreciable at about pH 12.5. Thus decomposition represents a loss of effective chemical, i.e. polysulphide and alkali to the process.

However, it has now been found according to the present invention that at a pH below about 11.5 the polysulphide ion in the liquor in the impregnation stage is subject to conversion into sulphur and hydrosulphide and that this conversion in the impregnation stage may be substantially reduced by the addition of ammonium hydroxide to the impregnation stage which tends to buffer the polysulphide solution to a pH in the range of about 12. The stabilization stage of the process of the present invention then involves raising of the temperature of the impregnated ligno-cellulosic material suitably by steaming with the addition if necessary of further ammonia to provide optimum stabilization conditions therein and the delignification stage involves addition of sodium hydroxide of Kraft liquor in a similar manner as in U.S. application Ser. No. 665,710.

According to the present invention therefore there is provided in a process for the production of cellulosic pulp from ligno-cellulosic materials which comprises substantially completely impregnating said material in subdivided form with a polysulphide liquor containing no added sodium hydroxide at a pH below 12.5 and at a temperature below that at which substantial decomposition occurs; removing excess polysulphide from the impregnated material; stabilizing the impregnated material against alkaline degradation by increasing the temperature of said material and subsequently de-lignifying the stabilized material by cooking said material in a cooking liquor containing sodium hydroxide, the improvement which comprises effecting impregnation of said material with a polysulphide liquor containing ammonium hydroxide in an amount sufficient to maintain a pH of at least about 11.5 and effecting stabilization by heating the impregnated material in the presence of ammonia gas under superatmospheric pressure.

While the present invention has application to any ligno-cellulosic material, particularly those in the production of paper products, it has particular application to the treatment of wood such as softwood and thus, the present invention will be further described with reference to wood as the ligno-cellulosic material and, in particular, to wood chips representing the ligno-cellulosic material in subdivided form. However, it is pointed out that the present invention is not limited to the treatment of wood chips.

The impregnation of the wood chips with the polysulphide liquor is according to the present invention effected at a temperature below that at which substantial decomposition of the polysulphide ion takes place in the polysulphide liquor. It has been found experimentally that the polysulphide ion, particularly when in contact with wood decomposes to a substantial extent at temperatures above 110° C. and it is, therefore, according to the present invention suitable to effect the impregnation at temperatures below 110° C. and suitably below 100° C. in order to maintain any excess applied pressure required to maintain the ammonium hydroxide in solution at a minimum and, further, to avoid any insignificant decomposition of the polysulphide ion. In a preferred embodiment of the present invention the temperature is suitably in the range 70°–90° C. and, more preferably in the range 80°–90° C. which allows the impregnation to be effected at pressures less than about **20** psig and the impregnation time is suitably 30 to 60 minutes.

The polysulphide liquor may be a sodium polysulphide liquor as in the process of U.S. application Ser. No. 665,710. in a preferred embodiment of the present invention the polysulphide liquor is an ammonium polysulphide liquor $(NH_4)_2S$which it is found promotes the impregnation of the wood chips particularly when in admixture with ammonium hydroxide in accordance with the present invention.

The impregnation of the chips with the liquor can be effected on either dry chips or water saturated chips, the latter being the preferred procedure as in U.S. application Ser. No. 665,710. If the chips are dry, impregnation can be brought about by forcing liquid into the empty capillaries in the fibers, carrying the chemicals with it, this being referred to as penetration. If the chips are moisture saturated no further entry of liquid is possible and ions must enter by diffusion after the liquid has enveloped the chips. In intermediate moisture contents both mechanisms contribute to the impregnation.

While it might have been expected that the diffusion rate would be much lower than the penetration rate it was, in actual fact, found that the diffusion rate of the liquid into wet chips was comparatively rapid and thus while dry chips took up a substantial amount of sulfur at 450 psig after one hour, with diffusion presumably contributing little to the uptake, after the same time at atmospheric pressure wet chips took up a comparable amount of sulfur with diffusion supplying the sole driving force. Further, with wet chips, i.e., chips having a moisture content in excess of 100 percent based on dry wood, the results were reproducible whereas with dry chips the minimum pressure required to impregnate the liquor fully into the dry chips varied from 50 to 400 pounds per square inch from one sample to another of the same wood species. It is, therefore, preferred according to the present invention that the impregnation of the polysulphide be effected upon wet chips of moisture content in excess of 100 percent based on dry wood and this high moisture content is preferably produced, when the moisture content of the chips is initially too low, by soaking the chips in warm water for some time. The impregnation of wet chips with the polysulphide can, of course, be effected at substantially atmospheric pressure whereas in using pressure in combination with dry chips it is necessary to use complicated apparatus involving pressure vessels, which, of course, is from a commercial point of view to be avoided. While it is obvious that as high a chip moisture content as possible is preferable, moisture contents in excess of 170 percent give difficulties in operating a continuous process unless expensive equipment to condense the excess of withdrawn liquor is installed and for practical purposes a moisture content in the range 100–160percent is preferred for impregnation under mild conditions. The impregnation of the wet chips is suitably effected for a period of the order of ½ hour to 1 hour as it is found that in this range of times the wet chips can be impregnated with two-thirds of the quantity of the chemicals which can be introduced after four days. Further, after one-half hour, the unimpregnated area in wet chips disappeared in the cross section thereof. Accordingly, when a sufficient amount of chemicals can be introduced within a short time by means of a high concentration the size of the impregnation vessel can be reduced because the throughput is higher.

The concentration of the polysulphide sulphur in the liquor is suitably in the range of 5–40 grams per liter for below 5 grams per liter impregnation with polysulphide ions is not generally sufficient for the process of the present invention and above 40 grams per liter there is no substantial advantage to be gained. Thus, the amounts of sodium and total polysulphide sulfur introduced into moisture saturated chips within a given time at 85° C. and at atmospheric pressure are proportional to the concentrations because the rate of diffusion is dependent upon the concentration gradient.

The liquor-to-wood ratio in the impregnation stage is suitably in the range of 2.5:1 to 4:1 as above the ratio of 4:1 an "infinite bath" effect is approached where a two-fold increase in the ratio leads only to a 10 percent increase in impregnation under the same conditions. A high liquor volume places a great load on the circulation system and inherently exposes a large quantity of polysulphide to the risk of decomposition in a given time. Accordingly, to obtain efficient impregnation it is preferable to keep the liquor-to-wood ratio as low as possible and to increase the polysulphide concentration. A desirable impregnation is from 2 to 4 percent polysulphide on oven dry (o.d.) wood which gives optimum increases in yield of pulp over the process of Example III of U.S. application Ser. No. 665,710.

Subsequent to the impregnation of the wood chips which, from a practical point of view, must be as complete and uniform as possible, in order to produce a useful pulp, the excess of liquor is removed from contact with the chips and may be recycled for further use in impregnation of fresh chips. The impregnated chips are then subjected to stabilization which necessitates increasing the temperature above 100° C., suitably above 120° C. and desirably in the range 170° C. to 175° C. in order to cause reaction to occur between the polysulphide and the chips.

The stabilization may be effected by heating the impregnated chips under pressure after withdrawal of the excess of polysulphide liquor with direct steam to a temperature of at least 170° C. and preferably 170°–175° C. for the time necessary to stabilize the chips, and suitably for a period of from 30 to 45 minutes, desirably at a pressure in the range 120–150 psig. Alternatively, after withdrawal of the excess polysulphide liquor from the impregnated chips ammonia gas may be added and the impregnated chips are heated with direct steam in the presence of the ammonia gas under the above conditions.

The delignification of the stabilized chips is suitably carried out by adding soda or kraft liquor to the stabilized chips and cooking the chips at a temperature of 160° C. or higher. A minimum temperature of 160° as aforesaid is usually required for the delignification but suitably this is from 170° C. to 175° C. in the liquid phase, the pressure suitably being from 100–120 psig and the time suitably being from 40 to 70 minutes.

The present invention will be further illustrated by way of the following examples.

EXAMPLE

Black spruce guillotine chips with a size of 1 inch by ¾inch (grain direction) by 1/6 inch thick were prepared from black spruce logs. The chips were dried in the atmosphere to a moisture content of 10 percent based on dry wood were separated in aliquots of 326 gms (oven dry weight) and each aliquot was saturated with moisture in a pressure vessel by two steam purges at 30 psig for 2 minutes each and forced impregnation of water at 70° C. under a pressure of nitrogen gas at 100 psig for one hour. Following this, the chips were sealed in a polyethylene bag and were stored in a cold room at 3° to 5° C. for from 2 to 5 weeks. Before being subjected to cooking any free water was drained away by keeping the wet chips in a wire mesh basket (60 mesh) for 1 hour. While the surface of the chips was tending to dry the moisture content of the chips was 179 ± 3 percent based on dry wood which approached the saturation point for spruce wood of 190 to 200 percent.

In a first series of cooks according to the present invention a number of these aliquots were subjected in an impregnation stage to heating with 1305 ml. of an aqueous ammonium polysulphide plus ammonium hydroxide at a pH of about 12 and a liquor to wood ratio of 4:1. The impregnated chips were in each case heated to 90° C. over a period of 15 minutes in a 2.5 liter bomb and maintained under superatmospheric pressure for 60 minutes. Cooks S 246 and S 244 referred to in Table I were impregnated at a pressure of about 20 psig and the other cooks at a pressure of about 10 psig.

The excess polysulphide liquor was then removed leaving an impregnated charge containing polysulphide sulfur equivalent to a percentage set forth in Table I, based on oven dried wood.

A volume of 25 percent ammonium hydroxide solution was then added to the volume for cooks S 246 and S 244 being 100 ml. and for the remainder 250 ml. and the temperature raised by steaming over a period of 25 minutes to 175° C. where it was maintained for a period of 45 minutes, the pressure being raised to 150 psig for the stabilization stage.

In the third or delignifying stage Kraft liquor with a charge of effective alkali set forth in Table I and at a sulphidity set forth in Table I was fed into the bomb the temperature being raised from 155° C. to 170° C. in 15 minutes where it is maintained at a pressure of 120 psig for a period of 60–75 minutes.

The ammonium polysulphide solution used in the impregnation stage was prepared by injecting hydrogen sulphide gas into 2N ammonium hydroxide solution and then dissolving the required amount of elemental sulphur in this solution at 90° C. The composition of the solution is set forth in Table I.

After separating the cooking liquor, disintegrating and screening the pulp through a vibrating flat screen with 0.001 inch slits, the weights of the screen rejects and of the screened pulp were determined. These are summed up as the total pulp yield.

The conditions and results are given in Table I.

TABLE I

Cook No.	Chip moisture percent on dry wood	1st stage			P S		2nd stage, ammonia charge NH_3 percent
		Liquor to wood ratio	Chemical's conc.		Initial charge	Consumed	
			$(NH_4)_2S_3$	NH_4OH			
III-Q(1.3)-1 S-189	180	4/1	12 g./l. as S	6 g./l. as NH_3	4.8	1.3	15→
III-Q(1.3)-2 S-190	180	4/1	12 g./l. as S	6 g./l. as NH_3	4.8	1.3	15→
III-Q(2.4)-1 S-187	180	4/1	22 g./l. as S	12 g./l. as NH_3	8.8	2.4	15→
III-Q(2.4)-2 S-188	180	4/1	22 g./l. as S	12 g./l. as NN_3	8.8	2.4	15→
III-Q(3.5)-1 S-246	180	4/1	35 g./l. as S	45 g./l. as NH_3	14.0	3.5	6—
III-Q(3.5)-2 S-244	180	4/1	35 g./l. as S	45 g./l. as NH_3	14.0	3.5	6→

Table I—Continued

Cook No.	3rd stage Effective alkali	Sulphidity	Active alkali	Time at max. temp. (min)	Yield percent Screened	Rejects	Total	Kappa No. in scr. P.	Brightness
III-Q(1.3)-1 S-189	16	10	16.9	70	51.6	0.6	52.2	47.5	22.4
III-Q(1.3)-2 S-190	25	15	27.1	75	48.0	0.1	48.1	29.3	27.3
III-Q(2.4)-1 S-187	12	5	12.3	60	56.2	0.7	56.9	54.8	21.0
III-Q(2.4)-2 S-188	20	10	21.1	65	50.3	0.1	50.4	30.5	26.6
III-Q(3.5)-1 S-246	14	10	14.7	75	55.3	0.1	55.4	36.1	22.4
III-Q(3.5)-2 S-244	19	10	20.0	75	50.8	0.0	50.8	24.8	26.5

For comparison purposes a further series of cooks was effected on further aliquots of the chips in which the impregnation liquor was a sodium polysulphide liquor within the scope of U.S. application Ser. No. 665,710.

In this series of cooks the impregnation stage was at atmospheric pressure. The first six cooks given in Table II below were effected in the same way as in the previous cooks except the temperature of 90° C. was held in the impregnation stage for 45 minutes, the temperature of 170° C. in the delignification stage was held for periods ranging from 20 to 70 minutes and the heating to 170° C. after addition of the Kraft liquor was given 20 minutes. In the last six cooks the heating from 80° to 175° C. for the stabilization stage was rapid and the delignification stage temperature of 170° C. was held for periods ranging from 50–70 minutes. The conditions and results are given in Table II.

For further comparison purposes a conventional polysulphide Kraft pulping at a sulphidity of 30 percent was effected with aliquots of dry chips weighing 326 grams and a further aliquot of said saturated chips, the cook being heated over a period of 90 minutes to 170° C. where it was maintained for periods ranging from 60 to 75 minutes.

The conditions and results obtained are given in Table III below.

TABLE II

Cook No.	Chip moisture percent on dry wood	1st stage Liquor to wood ratio	Chemical's conc. Na_2S_4, g./l.	P S initial charge	consumed	2nd stage, ammonia charge NH_3, percent
III-E(1.4)-1 S-199	180	4/1	15	6.0	1.4	15 →
III-E(1.4)-2 S-200	180	4/1	15	6.0	----------	15
III-E(1.4)-3 S-201	180	4/1	15	6.0	----------	15
III-E(3.3)-1 S-185	180	4/1	35	14.0	3.3	15 →
III-E(3.3)-2 S-186	180	4/1	35	14.0	3.3	15
III-E(3.3)-3 S-156	180	4/1	35	14.0	3.3	15
III-E(7.5)-1 S-183	180	4/1	70	28.0	7.5	15 →
III-E(7.5)-2 S-184	180	4/1	70	28.0	7.5	15
III-E(7.5)-3 S-152	180	4/1	70	28.0	7.5	15
III-E(7.5)-4 S-153	180	4/1	70	28.0	7.5	15
III-E(7.5)-5 S-154	180	4/1	70	28.0	7.5	15
III-E(7.5)-6 S-155	180	4/1	70	28.0	7.5	15

Cook No.	3rd stage Effective alkali	Sulphidity	Active alkali	Time at max. temp. (min.)	Yield percent Screened	Rejects	Total	Kappa No. in scr. P	Brightness
III-E(1.4)-1 S-199	15	20	16.6	65	52.7	0.8	53.5	53.0	22.6
III-E(1.4)-2 S-200	19	20	21.1	70	50.0	0.4	50.4	41.4	24.9
III-E(1.4)-3 S-201	26	25	29.7	75	47.8	0.0	47.8	28.0	28.8
III-E(3.3)-1 S-185	12	10	12.7	65	54.9	0.6	55.5	48.2	21.5
III-E(3.3)-2 S-186	18	10	19.0	70	51.1	0.1	51.2	32.8	25.0
III-E(3.3)-3 S-156	24.5	15	26.5	70	48.6	0.0	48.6	22.6	28.4
III-E(7.5)-1 S-183	5	0	5.0	20	19.7	52.9	72.6	94.6	10.3
III-E(7.5)-2 S-184	10	5	10.3	60	58.9	1.3	60.3	52.5	14.6
III-E(7.5)-3 S-152	12	5	12.3	50	57.5	0.1	57.6	39.4	18.7
III-E(7.5)-4 S-153	16	5	16.4	55	53.4	0.0	53.4	30.1	21.9
III-E(7.5)-5 S-154	20	10	21.1	60	51.6	0.0	51.6	23.7	23.2
III-E(7.5)-6 S-155	26	10	27.3	65	49.4	0.0	49.4	19.8	24.1

TABLE III

Cook No.	Chip moisture before presteaming, percent on drywood	Liquor to wood ratio	Effective alkali as Na_2O, percent on w.	Sulphidity	Na_2S as Na_2O, percent on w.	Time at 170°	Yield percent Screened pulp	Rejects	Total pulp	Kappa No. in scr. pulp	Brightness
KP-A-1 S-93	10	4/1	13	30	4.6	60	45.3	10.0	55.3	78.5	20.7
KP-A-2 S-33	10	4/1	14	30	4.9	60	50.7	3.1	53.8	69.2	23.1
KP-A-3 S-34	10	4/1	16	30	5.7	65	48.4	1.5	49.9	49.4	27.2
KP-A-4 S-35	10	4/1	18	30	6.4	70	47.4	0.3	47.7	36.6	30.9
KP-A-5 S-36	10	4/1	20	30	7.1	75	45.1	0.4	45.5	26.3	34.5
KP-A-6 S-242	180	3/1	16.5	30	5.8	70	48.6	0.1	48.17	46.6	28.4

The concentration of polysulphide in the fresh and withdrawn liquors was determined by the acidimetric method proposed by Johnsen K., (Norsk Skogind 20, No. 3: 91–95 March 1966) and improved by Ahlgren, P., (Svensk Papperstidn. 21, No. 15; 730–733, November 15, 1967). For the sulphide ion in ammonium polysulphide the mercury chloride method of Bilberg, E. (Norsk Skogind 12, No. 11; 470–478 November 1958) was used.

From the above results graphs were plotted as shown in the accompanying drawings in which:

FIG. 1 is a plot of Kappa numbers against total percent yield at different polysulphide consumptions shown in parentheses for the three different processes;

FIG. 2 is a plot of total percent pulp yield against polysulphide consumption at Kappa number 30, and

FIG. 3 is a plot similar to FIG. 1 of screened percentage pulp yield against Kappa number for different polysulphide consumption.

It will be seen from the graphs that the three stage polysulphide process of the present invention involving the use of ammonium hydroxide in the impregnation stage (III-Q) gives better yields both of the screened and unscreened pulp of similar Kappa number for the same polysulphide consumption than that in which the ammonium hydroxide is only present during the stabilization stage (III-E). Further both of these three stage processes are superior to the single stage polysulphide process for which a graph of pulp yield vs. polysulphide sulphur consumption is shown as I-C in FIG. 2.

In the single stage polysulphide process represented by the graph I-C a series of cooks on drying spruce wood chips containing 10 percent water based upon dry wood was effected under the conditions set forth in the following Table IV at polysulphide consumptions of 1.5, 3.0 and 6.0 percent on wood.

In the process the chips were steam-purged at 120° C twice for periods of three minutes, admixed with the polysulphide liquor at 20° C at a pressure of 100 psig for 60 minutes at a liquor to wood ratio at 5 to 1 and the temperature was then raised over 90 minutes to 170° C and maintained at that temperature for a period of 55 to 70 minutes. The cooking conditions and the results obtained are shown in the following Table IV from which graph I-C was obtained.

We claim:

1. In a process for the production of cellulosic pulp from lignocellulosic materials which comprises substantial completely impregnating said materials in subdivided form with a polysulphide liquor at a pH below about 12.5 and at a temperature below that at which substantially decomposition of the polysulphide occurs, and for a time sufficient for substantially complete impregnation of said lignocellulosic material, removing excess polysulphide from the lignocellulosic material, heating the lignocellulosic material impregnated with said polysulphide liquor to a higher temperature of at least about 130° C. in the presence of ammonia gas under superatmospheric pressure to cause complete reaction between the polysulphide liquor and the cellulosic materials without substantial delignification of the material and to prevent degradation of the material, which stabilizes the material and subsequently adding cooking liquor containing sodium hydroxide to the material and cooking the material for a time sufficient to delignify said material, the improvement wherein said impregnation of lignocellulosic material is with a polysulphide liquor containing ammonium hydroxide in an amount sufficient to maintain a pH of at least about 11.5.

2. A process as claimed in claim 1 in which the polysulphide is present in the impregnating liquor as ammonium polysulphide.

3. A process as claimed in claim 1 in which the impregnating temperature is in the range 80° to 90° C.

4. A process as claimed in claim 1 in which the impregnation occurs at a pressure which does not exceed 20 psig.

5. A process as claimed in claim 1 in which the stabilization temperature is in the range 170°to 175° C.

6. A process as claimed in claim 1 in which the stabilization pressure is in the range 120 to 150 psig.

TABLE IV

Cook No.	Chip moisture before presteaming, percent on dry wood	Liquor to wood ratio	Effective alkali as Na_2O, percent on w.	Sulphidity	Na_2S as Na_2O, percent on w.	Na_2S_4 charge as S, percent on w.	Consumed PS as S, percent on w.	Time at 170°	Yield percent			Kappa No. in scr. pulp	Brightness
									Screened pulp	Rejects	Total pulp		
I-C(1.5)-1 S-158	40	5/1	15	10	1.6	1.5	1.5	55	52.3	3.5	55.8	76.9	22.2
I-C(1.5)-2 S-159	40	5/1	17	15	2.8	1.5	1.5	60	51.4	1.1	52.5	56.7	26.8
I-C(1.5)-3 S-181	40	5/1	20	15	3.2	1.5	1.5	65	49.0	0.1	49.1	36.9	31.0
I-C(1.5)-4 S-182	40	5/1	24	20	5.3	1.5	1.5	70	46.4	0.1	46.5	24.2	35.4
I-C(3.0)-1 S-126	40	5/1	15	10	1.6	3.0	3.0	45	44.9	15.5	60.2	80.4	20.5
I-C(3.0)-2 S-157	40	5/1	16	10	1.7	3.0	3.0	50	54.5	0.9	55.4	60.3	24.4
I-C(3.0)-3 S-179	40	5/1	20	10	2.1	3.0	3.0	55	51.4	0.5	51.9	44.0	28.4
I-C(3.0)-4 S-180	40	5/1	24	10	2.5	3.0	3.0	60	48.7	0.1	48.8	27.6	33.4
I-C(6.0)-1 S-127	40	5/1	16	0	0	6.0	5.9	50	56.0	2.2	58.5	57.4	24.2
I-C(6.0)-2 S-128	40	5/1	21	0	0	6.0	5.9	55	52.9	0.4	53.3	34.8	30.8
I-C(6.0)-3 S-129	40	5/1	27	5	1.4	6.0	5.9	60	49.3	0.0	49.3	21.9	35.1
I-C(6.0)-4 S-130	40	5/1	33	10	3.5	6.0	5.9	65	41.7	0.0	41.7	15.9	38.3

7. A process as claimed in claim 1 in which ammonia is added to the stabilization stage.

8. A process as claimed in claim 1 in which the material impregnated with polysulphide is heated by steaming to raise the temperature thereof for stabilization.

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