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HIGH YIELDS BISULPHITE PULPING PROCESS

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2 Sheets-Sheet 1

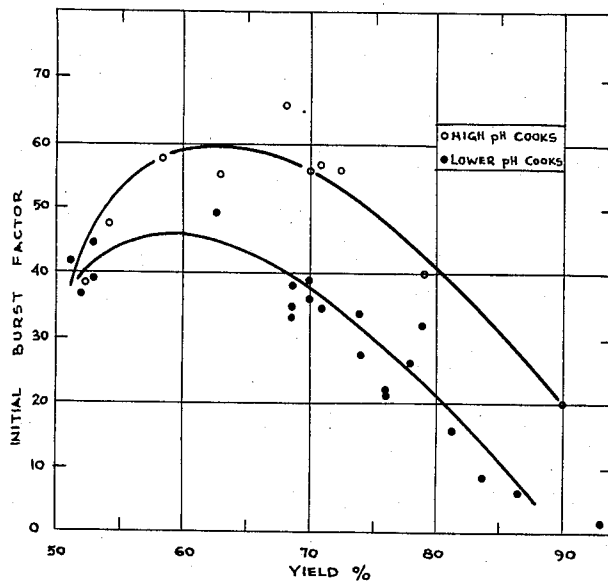


Fig. 1.

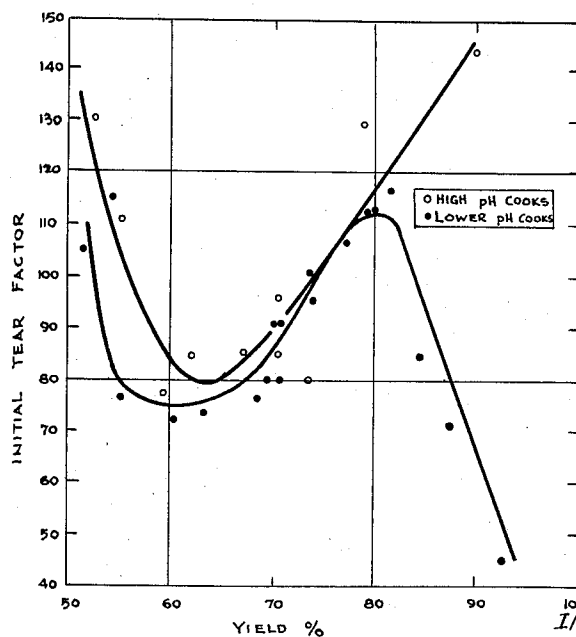


Fig. 2.

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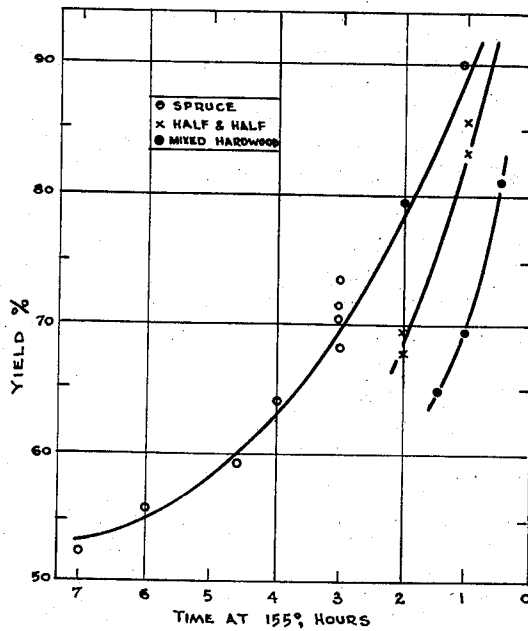


Fig. 3.

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HIGH YIELDS BISULPHITE PULPING PROCESS

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Claims priority, application Canada July 13, 1953

6 Claims. (Cl. 162—83)

This invention relates to a process for pulping wood chips and more particularly to a semi-chemical process in which the pulping liquor is a bisulphite solution.

Semi-chemical pulping processes involve an initial chemical treatment of the wood chips to soften and partially remove the bonding material of the middle lamella followed by a mechanical refining step to separate the fibers. Semi-chemical processes are commercially attractive because it is possible to obtain an increased yield accompanied by low chemical consumption. The lignin is extracted more selectively than with conventional pulping processes and a far higher proportion of the hemicelluloses is retained. Alkaline cooking liquors are generally unsuitable for semi-chemical pulping as a dark coloured pulp is produced which cannot be bleached. Neutral sulphite semi-chemical processes which are carried out at a high temperature and under neutral or slightly alkaline conditions give good yields of bright, bleachable pulp where hardwoods are treated but in the case of softwoods or mixed hardwoods and softwoods the process is unsatisfactory as a pulp is produced having poor strength, bad colour, and high resistance to bleaching. In addition the chemical consumption is high. Acid sulphite processes are unsatisfactory as giving low strength pulps of poor brightness and bleachability. Acid sulphite processes using decreased quantities of chemicals and in particular less free sulphur dioxide than in conventional processes have been investigated. An example of a process of this nature is Belgian Patent 496,841 which issued July 31, 1950, on an application filed by Azienda Brevetti Industriali. The pulp produced by this process does not provide adequate strength and brightness in a reasonable pulping period.

The object of this invention is in general to provide an improved semi-chemical pulping process, capable of providing, even in the case of softwoods or mixed softwoods and hardwoods a high yield of pulp possessing good strength and brightness, and requiring low refining power.

It has been found in accordance with this invention that a pulp having desirable properties can be produced by cooking wood chips with a solution of a bisulphite of a substance selected from the group consisting of sodium, potassium, and ammonium. The cooking liquor used in accordance with this invention contains substantially no true free sulphur dioxide. The chemical step is followed by a mechanical refining treatment to separate the fibers.

The nature of the cooking liquor used in accordance with this invention, and the essential distinction between

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it and cooking liquor previously used for semi-chemical processes will be apparent from the explanation which follows. In the case of conventional sulphite processes the sulphur dioxide content is reported in terms of "free SO_2 " and "combined SO_2 ." In fact the amount of sulphur dioxide reported as combined is the amount theoretically combining with the base as monosulphite. The amount of sulphur dioxide reported as "free SO_2 " will include a percentage of sulphur dioxide which is actually in combination to form the bisulphite and some true free sulphur dioxide. The amount of the free sulphur dioxide which is in combination to form the bisulphite will be equal to the sulphur dioxide reported as combined and the true free sulphur dioxide can be calculated by subtracting the value for combined sulphur dioxide from the value for free sulphur dioxide. For example a solution reported as having 1% combined SO_2 and 5% free SO_2 will actually include 2% of bisulphite and 4% of true free SO_2 . It is contemplated in accordance with this invention that the solution contain equal proportions of combined SO_2 and free SO_2 as ordinarily reported. This means that all of the SO_2 will actually be in combination with the base as bisulphite and there will be substantially no true free sulphur dioxide. It is emphasized that the bisulphite process of this invention must be distinguished from the processes commonly referred to as "bisulphite" processes and which involve the use of sulphur dioxide in excess of the amount theoretically necessary to combine with the base of bisulphite. "Bisulphite" is sometimes used as a synonym for the sulphite process.

The process of this invention is characterized by an initial pH of between 4 and 5. During pulping organic acids are released from the wood and these cause the pH to fall to about 3.5, but in no case does the pH decrease below 3. This may be contrasted with sulphite acid solutions which normally have a pH of about 1.5 and which are strongly buffered, the pH changing little over a considerable range of compositions and concentrations.

It is necessary that the base used in the process of this invention be capable of forming a soluble monosulphite. Thus calcium is unsuitable as in the absence of excess sulphur dioxide there would be precipitation of the base. Sodium, potassium and ammonium form soluble sulphites and it is therefore possible to use solutions free of excess sulphur dioxide.

One of the advantages of the process of this invention in comparison with processes such as the acid sulphite process is that it is possible to raise the temperature to as high as 155°C . without producing a burned pulp. As a consequence the reaction proceeds at several times the rate of a similar process carried out at a maximum of, say 140°C . In the acid sulphite process it is necessary to operate within a maximum of about 135°C . to avoid excessive degradation of the cellulose. This possibility of using an increased temperature provides compensation for the reduced rate of reaction due to the absence of true free sulphur dioxide.

It might be expected that at a temperature of 155°C . there would be an excessive attack on the hemicelluloses. In fact it has been found that there is an unexpected decrease in the extent to which hemicelluloses are attacked in comparison with a sulphite process carried out at a

lower temperature and having a comparable yield. It is believed that this is due to decreased hydrolysis of the hemicelluloses with the higher pH employed in accordance with this invention.

A further advantage of the process of this invention is that sulfur losses on blowing the cook are reduced. In the conventional acid sulphite process about 30 lbs. of sulphur per ton of pulp is released. In the process of this invention substantially all of the sulphur dioxide being present as a definite chemical compound, will remain in the liquor phase from whence it can be recovered by conventional methods. In addition the retention of the cooking chemical in the waste liquor resulting from the process of this invention makes it feasible to reuse the waste liquor.

Another advantage partially dependent on the factors which have been discussed and probably due partially to other causes which have not yet been fully investigated is the empirical fact that the general properties of the pulp produced in accordance with this invention are highly desirable. The pulp has good strength and brightness at high yields and requires lower refining power than pulps produced by the sulphite process at comparable yields. A soft chip is produced at a high yield. Microscopic examination of the pulp together with fiber classification has shown that the pulp after refining had been fully defibred with little cutting or breaking of the tracheids. The fibers were cylindrical rather than the usual flat form of pulp fibers. The refined pulp exhibited a remarkably fast drainage rate.

The properties of the pulp will depend to a certain extent on the yield. It is preferred that cooking be continued to a yield of 65 to 75% which is about 20% higher than a comparable complete chemical cook. This range may be extended within the ambit of this invention to give special qualities to the pulp. In Example 1 an example is given of a cook in accordance with this invention.

EXAMPLE 1

The digester was charged with 1 part by weight of spruce chips and 5 parts by weight of a liquor formed by dissolving sufficient sodium metabisulphite in water to provide a total SO_2 content of 2.5%. The chips were digested under pressure at a temperature which was raised to 110° C. during a 2 hour period. The temperature was raised further to 155° C. during a 2½ hour period and the temperature was maintained at this figure for a further period of 1½ hours. The initial pH was 4.7 and the final pH 3.5. The yield was 74%. The cook was blown and the softened chips were separated from the liquor and washed and then passed through a disc refiner which separated the fibers to form the pulp. Particulars of the properties of the pulp will be apparent from Table 1 below under the heading Cook No. 6. While the above example shows a liquor/wood ratio of 5:1, experimental results indicate that there should be no difficulty in utilizing a ratio of 3:1 corresponding to 12% NaHSO_3 B/wood. The cooking liquor can also be prepared from a solution of soda ash and sulphur dioxide gas.

The equipment and procedures used in Example 1 and in obtaining the other test results reproduced in this specification will now be briefly described. The laboratory digester is a stainless steel pressure vessel of about 2 cubic foot capacity with a bolted top and a cone bottom. It is arranged for circulation, the liquor being introduced near the top, striking a distributor and then falling by gravity over the chips, after which it is removed through a screen in the cone and a pipe near the bottom of the cone. Temperatures are measured in

the inlet and outlet pipes. The liquor is circulated by a pump through a heat exchanger, then into the top of the digester again. There is a complete turn-over of the liquor about every half-minute.

Cooking liquor is made up in glass carboys holding about 110 lbs. of liquor. Sulphite liquor is made from calcium or sodium carbonate, and SO_2 gas from a cylinder. The constituents are added by weight, then an accurate analysis made by the standard Palmrose method. For cooks in accordance with this invention the same procedure may be followed, or commercial sodium metabisulphite may be dissolved in water. The same is true for neutral sulphite cooks, but again the proportions are different. The liquor to wood ratio may be varied, but for sulphite cooks follows the usual commercial practice at 5.0. For cooks in accordance with this invention 4.0 is usually used, while for neutral sulphite 2.7 is common.

For spruce, 30 lbs. of chips are used for a charge, adjusted to 40% moisture, equivalent to exactly 18 lbs. of dry wood substance. (Moisture is determined by drying a sample at 105° C.) These chips are charged into the digester with some hand-packing, and the lid bolted on. The cold liquor is added and the pump started, then steam is admitted to the heat exchanger fast enough to bring the temperature at the inlet up at a steady rate, according to a pre-determined schedule. At moderate rates of heating, the temperature drop to the outlet is about 3°. After the maximum temperature is reached, it is maintained for the time specified; the maximum pressure is also specified, and maintained by an automatic relief valve. Then the steam is turned off, the pressure partly relieved and the 3-inch blow-valve at the bottom of the digester is opened. The softened chips are partly blown out into the blow tank—about four times the capacity of the digester—and if they are well-cooked they are largely reduced to pulp. The remainder are washed out and the whole washed with water in the blow tank.

The drained mass is then transferred to a dilution tank in the case of pulp, where the yield is determined, and the pulp is then screened to remove uncooked pieces of wood, etc. Hard chips are taken to the refiner.

Refining is conducted as follows: The high-yield or hard chips are defibred in a standard 24" Bauer double-disc refiner with plates of standard design. This is a commercial model, equipped for handling small charges of chips in the laboratory. The amount available from a cook varies, but at 70% yield using spruce, the charge to the refiner will be about 12.5 lbs. The chips are spread uniformly over a feed belt which drops them into the refiner at a constant rate. Standard conditions of plate setting, i.e. distance between the revolving plates, and refining consistency (water is added to the pulp between the plates), are used. Between refining passes the pulp consistency is increased to approximately 20% B.D. by pressing in cloth bags in a cold press. The cloth used is fine enough to retain the "fines" present in the refined stock. The number of refining passes used is determined by the appearance of the pulp examined on a "blue-glass"—it is refined until it appears "shive-free." Complete defibration may take from 2 to 4 passes, but usually not more than three, and the total power consumed, measured by an integrating watt-meter, is commonly between 10 and 20 horse-power-days per ton of pulp.

In Table 1 a comparison is made between lime base sulphite cooks, soda base sulphite cooks and a bisulphite cook in accordance with this invention. In each case the wood chips being treated were spruce and the ratio of 5:1 of liquor to wood was used.

Table 1

Cook No.-----	1	2	3	4	5	6
Type of liquor-----	Lime-base	Sulphite	Soda-base	Sulphite	Bisulphite	Bisulphite.
Free SO ₂ , percent-----	3.01	3.02	3.04	3.04	1.27	1.25.
Combined SO ₂ , percent-----	0.80	0.82	0.80	0.80	1.27	1.25.
Temp., °C-----	135	135	135	135	155	155.
Time to 110°, hrs-----	2	2	2	2	1	2.
Time to maximum, hrs-----	2	2	2	2	2.5	2.5.
Time at maximum, hrs-----	1.5	1	1	0.5	2.5	1.5.
Total time-----	5.5	5	5	4.5	6	6.
Initial pH-----	Approx.	1.5	Approx.	1.5	4.6	4.7.
Final pH-----	Approx.	1.5	Approx.	1.5	3.4	3.5.
Refiner passes-----	2	3	2	2	1	2.
H.-P. days/ton-----	9.5	14.7	7.7	11.0	4.3	11.4.
Freeness, C.S.F-----	705	710	690	710	700	710.
Yield, percent-----	63	69	63	70	67	74.
Brightness-----	42	44	48	52	57	56.
Initial burst factor-----	44	39	49	41	56	52.
Initial tear factor-----	72	78	72	79	89	104.
Pentosan-----	4.2	4.3	4.6	4.7	4.8	5.5.

¹ Using the process known as vapurge, described in United States Patent 2,640,774.

In Table 2 a comparison is made between a cook in accordance with this invention (No. 8) and a cook at the same temperature and using a slight excess of true free sulphur dioxide (No. 7). Both cooks were conducted using vapurge to assist penetration. This table emphasizes the distinction between the process of this invention and conventional sulphite processes. In particular the unsatisfactory physical properties of the product obtained using an excess of sulphur dioxide will be noted.

Table 2

Cook No.-----	7	8
Free SO ₂ -----	1.00	1.27
Combined SO ₂ -----	0.50	1.26
Maximum temperature, °C-----	155	155
Time to 110°, hours-----	1	1
Time 110°, maximum hours-----	1	0.5
Time at maximum, hours-----	0.5	2.5
Total time, hours-----	2.5	4.0
Initial pH-----	2.5	4.7
End pH-----	2.6	3.7
Yield, percent-----	74.5	68.1
Brightness-----	39	50
Lignin, percent-----	29.2	17.1
Freeness, C.S.F-----	685	670
Initial burst factor-----	11	66
Initial tear factor-----	110	85
Initial fold factor-----	4	460

In Table 3 the result of increasing the temperature with a cook in accordance with this invention is shown. It will be noted that at 155° C. a combination of desirable properties is obtained including low refining power, low cooking time and good physical properties. It is apparent that these desirable properties are retained even at a cooking temperature as high as 165° C.

Table 3

EFFECT OF TEMPERATURE

Cook No.-----	9	10	11	12	13	14	15
Free SO ₂ -----	1.26	1.26	1.22	1.22	1.22	1.27	1.27
Comb. SO ₂ -----	1.30	1.30	1.26	1.26	1.27	1.26	1.27
Max. temp., °C-----	115	125	135	145	155	155	165
To 110°, hours-----	2	2	2	2	2	1	1
110, max., hours-----	0.5	1	1.5	1.5	2	0.5	1.5
At max., hours-----	7.5	7	6.5	6.5	3	2.5	1
Total time, hours-----	10	10	10	10	7	4	3.5
Initial pH-----	4.5	4.4	4.2	4.2	4.4	4.7	4.8
End pH-----	3.5	3.3	3.2	3.1	3.4	3.7	3.7
Yield, percent-----	95.0	87.0	80.9	75.2	63.0	68.1	65.1
Brightness-----	58.3	56.5	53.3	47.5	49.2	49.8	50.2
Lignin, percent-----	24.9	23.5	20.8	15.7	13.1	17.1	15.6
Freeness, C.S.F-----	725	735	585	665	670	670	680
Init. burst factor-----	4	5	61	64	69	66	70
Init. tear factor-----	145	80	115	70	75	85	80
Fold-----	0	0	75	480	960	460	640
Refiner passes-----	4	4	3	2	2	2	2
Refiner, H.P.D./ton-----	19.8	20.2	14.5	8.0	9.4	10.6	11.1

The difference between cooks in accordance with this invention conducted at an initial pH of 4.2 to 5.0 and a final pH of 3.3 to 4.5 and cooks conducted in accordance with conventional procedures at an initial pH of about 1.5 to 2.5 is further illustrated in Figure 1 which shows

yield plotted against initial burst factor. The cooks in accordance with this invention are designated as "high pH" and conventional cooks as "low pH." The results providing the basis for Figure 1 were obtained with spruce pulps. It will be noted from Figure 1 that throughout the range of high yield pulps the process of this invention gives an initial burst factor higher by about 15 points.

It is appreciated that full length cooks have previously been conducted on an experimental basis using a solution of sodium bisulphite. In each case however the properties of the pulp were found to be unsatisfactory and no further investigation appears to have been made. The present invention is to be distinguished from such processes as the advantages obtained in accordance with this invention are fully achieved only in the case of a semi-chemical cook in which an initial chemical treatment is followed by a mechanical refining treatment. Thus it will be noted from Figure 1 that with a decreased yield the advantage in initial burst factor presented by the process of this invention decreases until a point is reached at about 52% yield where it presents no advantage over a conventional cook. A full length cook at a high pH is also unattractive as a cooking time of about 9 hours is required for 52% yield as compared with a total time of about 4 hours for an 80% yield.

Figure 2 is a similar plot of tear factor against yield. It is well known in the pulp industry that burst and tear are to some extent inverse; that is, when pulp is subjected to a treatment such as beating, the burst commonly rises while the tear declines. It will be seen from Figure 2 that this inverse relationship holds with both types of pulp over most of the range, but the pulps produced in accordance with this invention are generally higher in tear, rather than lower as might have been expected from their higher burst. In other words an enhancement has been obtained in the opposed properties of burst and tear. These results point to the unique nature of the pulp produced in accordance with this invention. The fibres appear to be softer than those obtained at a lower pH but no satisfactory measurement of this quality has yet been developed which would properly express this property.

Figure 3 shows a plot of pulp yield against cooking time for cooks conducted in accordance with this invention.

We claim:

1. A semi-chemical process for forming pulp consisting essentially of the steps of cooking submerged wood chips for about 2½ to 7 hours to weaken the inter-fiber bonding with a solution of a bisulphite of a substance selected from the group consisting of sodium, potassium and ammonium and having an initial pH of not less than 5, the pH being not less than 3 during said cooking, said solution having substantially no sulphur dioxide in excess of the stoichiometric amount necessary to form said

bisulphite, the middle lamellae of said wood chips being softened and partially dissolved to enable the fibers readily to be mechanically separated but said fibers being coherent during the blowing of the cook, followed by mechanically refining the softened wood chips to separate the fibers.

2. A semi-chemical process for forming pulp consisting essentially of the steps of cooking submerged wood chips for about 2½ to 7 hours to weaken the inter-fiber bonding at a temperature rising to about 155° C. with a solution of a bisulphite of a substance selected from the group consisting of sodium, potassium and ammonium, said solution having substantially no sulphur dioxide in excess of the stoichiometric amount necessary to form said bisulphite, the middle lamellae of said wood chips being softened and partially dissolved to enable the fibers readily to be mechanically separated but said fibers being coherent during the blowing of the cook, followed by mechanically refining the softened wood chips to separate the fibers.

3. A semi-chemical process for forming pulp consisting essentially of the steps of cooking submerged wood chips for about 2½ to 7 hours with a sodium bisulphite solution having a total sulphur dioxide content of about 2½% and a combined sulphur dioxide content of half the percentage of total sulfur dioxide and having an initial pH within the range 4 to 5, the pH being not less than 3 during said cooking, said cooking step being continued until the middle lamellae of said wood chips are softened and partially dissolved to enable the fibers readily to be mechanically separated but said fibers being coherent during the blowing of the cook, followed by mechanically refining the softened wood chips to separate the fibers.

4. A semi-chemical process for forming pulp consisting essentially of the steps of cooking submerged wood chips for about 2½ to 7 hours with a sodium bisulphite solution having a total sulphur dioxide content of about 2½% and a combined sulphur dioxide content of half the percentage of total sulphur dioxide and having an initial pH within the range 4 to 5, the pH being not less than 3 during said cooking, the cooking being conducted at a temperature rising to about 155° C. until the middle lamellae of said wood chips are sufficiently softened and partially dissolved to enable the fibers readily to be mechanically separated but said fibers being coherent during the blowing of the cook, followed by mechani-

cally refining the softened wood chips to separate the fibers.

5. A semi-chemical process for forming pulp consisting essentially of the steps of cooking submerged soft-wood chips for about 2½ to 7 hours with a sodium bisulphite solution having a combined sulphur dioxide content of half the total sulphur dioxide content and having an initial pH within the range 4 to 5, the pH being not less than 3 during said cooking, the cooking being conducted at a temperature rising to about 155° C. until the middle lamellae of said wood chips are sufficiently softened and partially dissolved to enable the fibers readily to be mechanically separated but said fibers being coherent during the blowing of the cook, followed by mechanically refining the softened wood chips to separate the fibers.

6. A semi-chemical process for forming pulp consisting essentially of the steps of cooking submerged hardwood chips for about 2½ to 7 hours with a sodium sulphite solution having a combined sulphur dioxide content of half the total sulphur dioxide content and having an initial pH within the range 4 to 5, the pH being not less than 3 during said cooking, the cooking being conducted at a temperature rising to about 155° C. until the middle lamellae of said wood chips are sufficiently softened and partially dissolved to enable the fibers readily to be mechanically separated but said fibers being coherent during the blowing of the cook, followed by mechanically refining the softened wood chips to separate the fibers.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,906,659

September 29, 1959

Rodger M. Dorland et al.

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

Column 5 and 6, Table 1, the heading thereof should appear as shown below instead of as in the patent:

Type of liquor	Lime-base sulfite		Soda-base sulfite		Bisulfite	
Cook No.	1	2	3	4	5	6
etc.						

column 5, Table 2, first column thereof, under the heading "Cook No.....", line 5 thereof, for "Time 110°, maximum hours" read -- Time, 110° to maximum, hours --; column 6, line 72, for "less" read -- more --; column 8, line 19, for "sulphite" read -- bisulphite --.

Signed and sealed this 10th day of May 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents