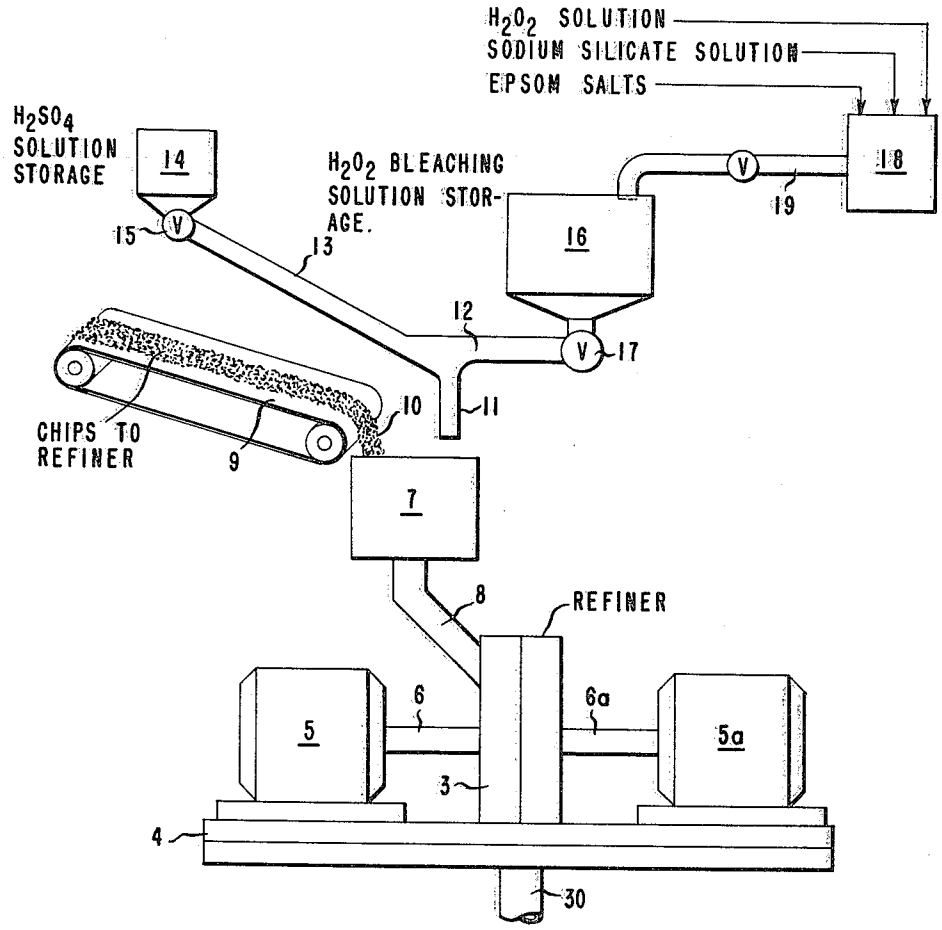
Dec. 18, 1962 F. LE ROY FENNELL 3,069,309

PULP BLEACHING

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FIG. 1



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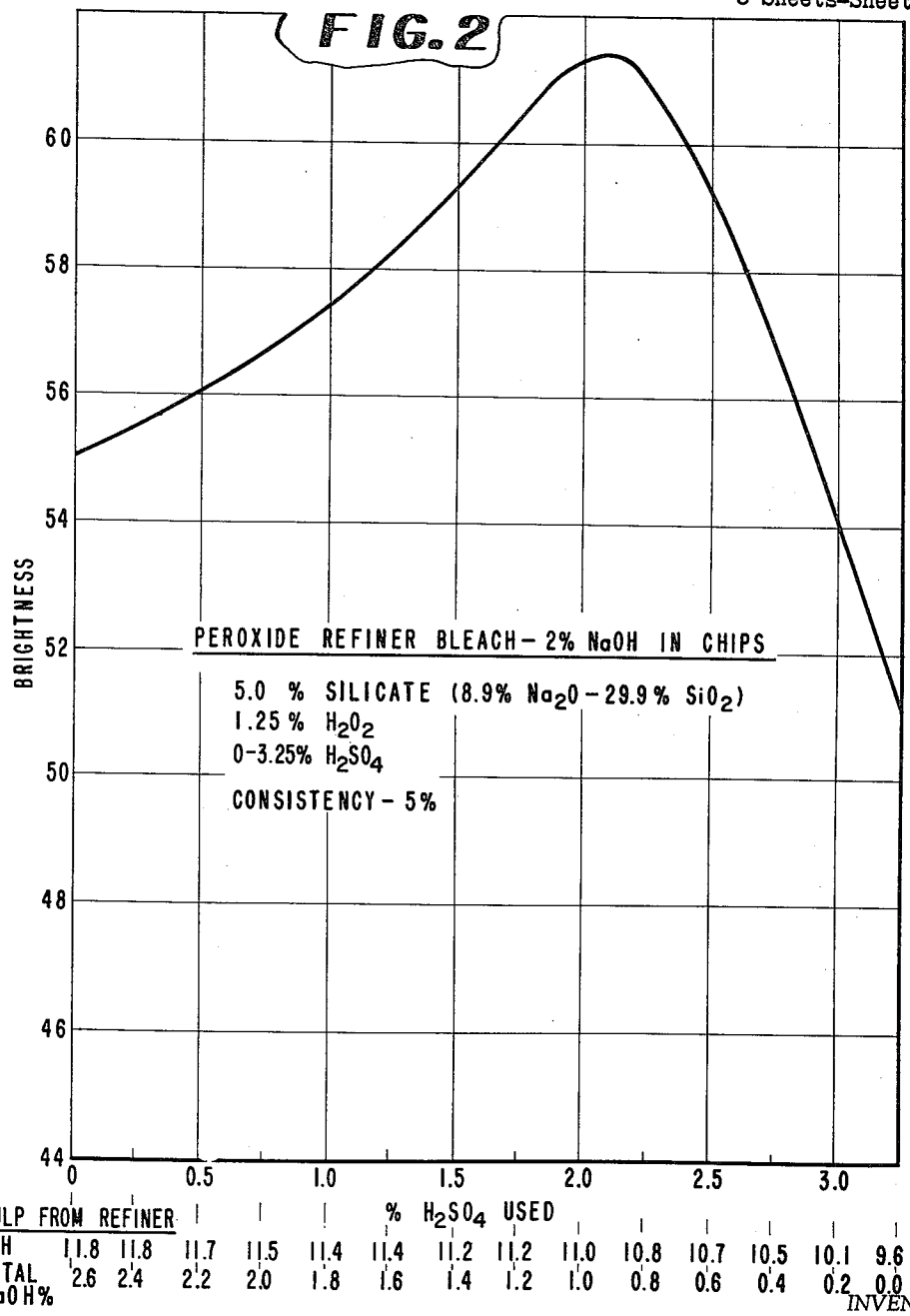
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PULP BLEACHING

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FIG. 2



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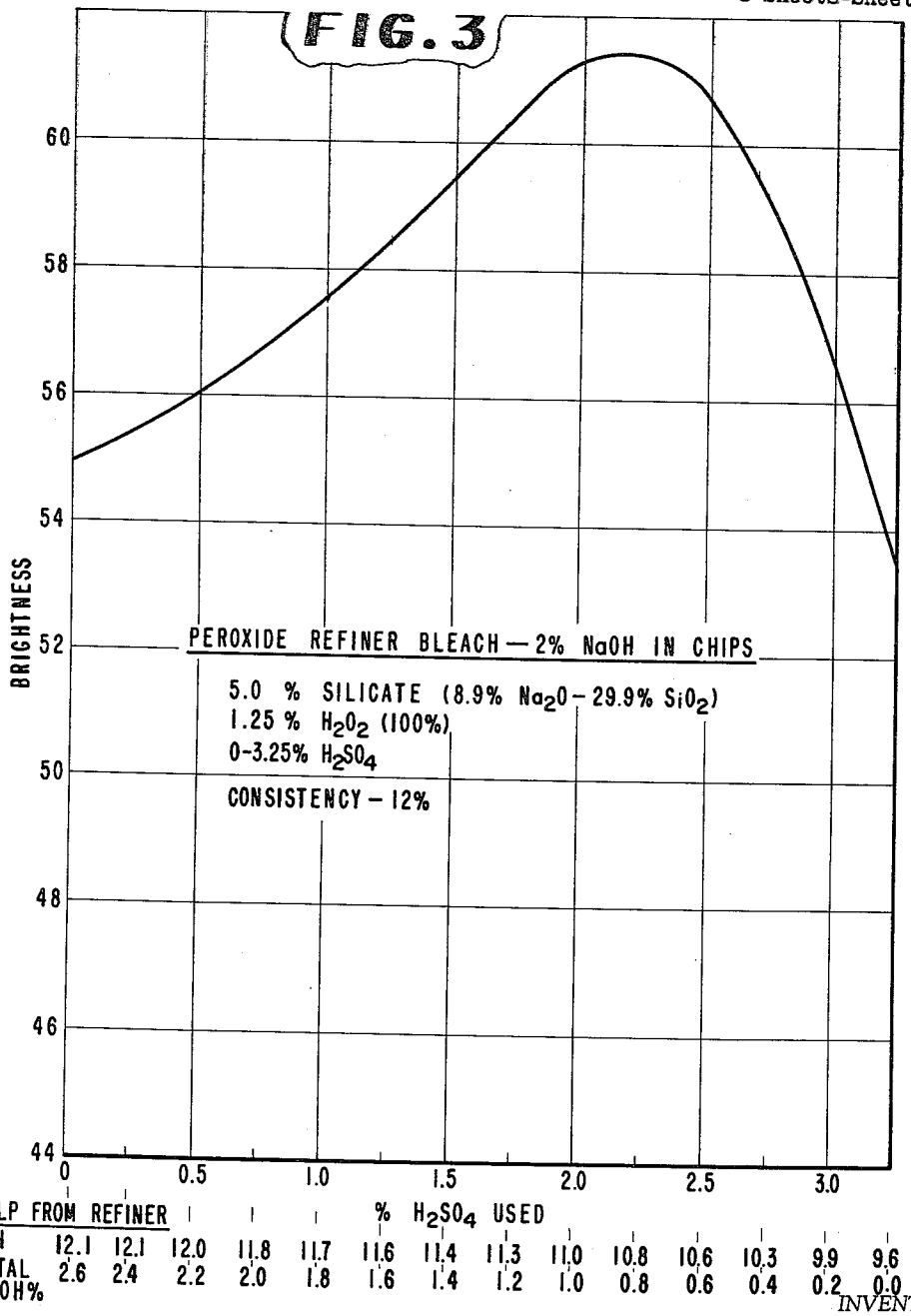
ATTORNEY

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PULP BLEACHING

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FIG. 3



PULP FROM REFINER														
pH	12.1	12.1	12.0	11.8	11.7	11.6	11.4	11.3	11.0	10.8	10.6	10.3	9.9	9.6
TOTAL NaOH%	2.6	2.4	2.2	2.0	1.8	1.6	1.4	1.2	1.0	0.8	0.6	0.4	0.2	0.0

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United States Patent Office

3,069,309

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3,069,309

PULP BLEACHING

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Filed Feb. 1, 1961, Ser. No. 86,553
1 Claim. (Cl. 162—26)

This invention relates to pulp bleaching and more particularly it relates to the bleaching of cold soda pulp chips during the refining of the chips.

Mechanical wood pulp has for years been produced from the softwoods and semi-hardwoods, such as aspen, by grinding. The softwoods have become largely depleted but substantial supplies of hardwoods are available for wood pulp production. Hardwoods cannot, however, be used to produce mechanical pulp by the conventional process of grinding on stones. Many attempts have recently been made to first produce hardwood chips and then refine these chips in a so-called refiner which will disintegrate the ½-inch square chips into a pulp mass composed of small fibers suitable for paper manufacture. In most cases the hardwoods must be chemically treated to soften the chips so they may be adequately refined in one to three refining stages. Probably the most satisfactory chemical treatment comprises a treatment with a strong alkaline agent such as NaOH. Such treatment of hardwood chips, however, produces a darker pulp than that obtained from mechanically ground softwoods.

The softened hardwood chips (softened by soaking in NaOH solution) containing residual NaOH are customarily fed at a controlled rate to a refiner, or a series of refiners, for disintegration into pulp. The pulp from the refiner varies in brightness from 40 to 50 G.E. units as measured by a General Electric brightness meter. The brightness will to some extent depend upon the wood species used, the concentration of NaOH used in the softening treatment and the chip storage time prior to refining. Due to the brightness limitations of this process, the resulting pulp requires bleaching for subsequent use in most grades of paper and paperboard manufacture.

Such pulp can, of course, be bleached in conventional bleaching stages involving large bleaching towers, pulp washers, pulp mixing equipment, pulp pumps, piping, etc. Such pulp bleaching processes involve a large capital investment in equipment and require many hours of bleaching to attain the desired bleached brightness.

Attempts have been made to bleach with H_2O_2 the hardwood chips in the refining operation, i.e., during the process of disintegrating the chips into a pulp mass. Such attempts have heretofore been oftentimes unsatisfactory because the total alkalinity of the chips entering the refiner cannot be readily controlled. The alkalinity of the chip varies as a result of the following variables:

(1) The hardwood chips require different concentrations of NaOH to develop suitable pulp strength.

(2) The caustic demand will vary with the species of wood used and with changes in wood chip mixtures.

(3) The temperature, time and chemical concentration varies as a result of variations in hardwood chips and thereby affects the residual caustic control of the wood chips entering the refiner.

Variation in total alkalinity of the chips not only produces nonuniform bleaching results during the refining operation but when unduly alkaline, there will be a great waste of H_2O_2 by decomposition without bleaching of the pulp.

It is an object of this invention to bleach in a satisfactory uniform manner hardwood chips with H_2O_2 during the refining of the chips.

It is another object of this invention to bleach hardwood chips with H_2O_2 during the refining thereof with a uniform bleaching effect and without substantial waste of H_2O_2.

It is another object of this invention to provide a new and improved bleaching process for the bleaching of cold soda pulp within a time period of 10 to 30 minutes.

Other objects of this invention will appear hereinafter.

The objects of this invention may be accomplished, in general, by finely disintegrating cold soda hardwood pulp chips in the presence of a sufficient quantity of a sodium silicate-containing hydrogen peroxide bleaching solution and an adjusted quantity of sulfuric acid to produce a pulp mass having a consistency of 3 to 20% and a total alkalinity as it passes from the disintegrating step of 0.5% to 1.6% NaOH.

Hardwood pulp chips are composed of poplar, oak, elm, gum, beech and other hardwoods. The chips are produced by gouging out wood flakes usually about ½ inch square and having a thickness varying from 1/32 to ⅛ inch. Before these chips or flakes can be further comminuted or disintegrated to form pulp they must be chemically treated to soften and somewhat loosen the bonding material of the wood, holding the fibers together. The chips are most satisfactorily treated with caustic soda and the pulp made therefrom is referred to as "cold soda pulp." Regardless of how carefully these chips are treated they will contain varying proportions of NaOH. If the amount of NaOH added during the treatment is insufficient, then the chips will not be readily disintegrated and the power input for refining operation will be unduly high, and pulp quality will suffer. It is, therefore, customary to add an excess of caustic soda to the chips before they are disintegrated in a pulp refiner. The excess amount of NaOH added is objectionably wasteful of hydrogen peroxide of a hydrogen peroxide bleach solution without obtaining the desired degree of bleaching brightness.

It has been found, in accordance with this invention, that the objectionable effect of excess caustic may be avoided and the pulp bleached without waste of H_2O_2 by adding a controlled amount of H_2SO_4 to the H_2O_2 bleaching solution with which the pulp chips are treated during the refining operation. Moreover, the refined pulp can be thereby bleached with a holding period of between 10 and 30 minutes.

The hydrogen peroxide bleaching solution for use in accordance with this invention is one that contains a sodium silicate buffering agent with or without a stabilizing agent, for example, Epsom salts. The buffering agent used in the bleaching solution of this invention is sodium silicate, however, other known buffering agents such as sodium pyrophosphate, sodium tripolyphosphate, sodium tetraphosphate, sodium hexapolyphosphate, or borax may be used in addition to sodium silicate. Epsom salts may be added, if desired, to inhibit the decomposition of H_2O_2 by the catalytic effects of metals such as copper, manganese or iron that may be present. The use of Epsom salts is desirable if the bleach solution is stored for a period of hours before using. On the other hand, if the bleach solution is used as it is mixed, the use of Epsom salts is unnecessary.

The bleaching solution of this invention may have a greatly varied composition. In the first place, the bleaching solution may be added in such amount that the pulp mass passing from the refiner has a consistency between 3% and 20%. Secondly, the pulp should be treated with such quantity of bleaching solution that between 0.15% and 2% of H_2O_2, based on the bone dry weight of the pulp, is added. Similarly, the amount of sodium silicate added should be between 3% and 7.5%, the Epsom salts, if used, between 0.05% and 0.5% and the amount of sulfuric acid added, between 0.3% and 5%, all based on the bone dry weight of the pulp.

Moreover, the bleach solution may be produced in a more concentrated form and water added simultaneously with the addition of the bleaching solution, or alternatively, the bleaching solution may be diluted with the water before passing the same into the refiner. The bleaching solution may contain the sulfuric acid before mixing with the pulp in the refiner or the hydrogen peroxide. Alternatively, hydrogen peroxide, Epsom salts, sodium silicate and a portion of the water may be passed into the refiner and the sulfuric acid and a further portion of water simultaneously passed into the refiner in a separate stream whereby the several constituents of the bleaching solution are mixed in the presence of the pulp mass in the refiner.

If other buffering agents than sodium silicate are used in addition to sodium silicate, they should be present in an amount so that the total is chemically equivalent to the above-said amount of silicate. Small quantities of other compatible bleaching ingredients may, of course, be present, as desired.

The sulfuric acid constituent should be added to the bleach solution in such amount that the total caustic content of the pulp mass immediately as it emerges from the refiner is between 0.5 and 1.6 weight percent regardless of the consistency of the pulp mass which, as stated, may vary between 3% and 20%. This corresponds approximately to a pulp mass pH of between about 10.4 to 11.5. The total caustic content measure is more accurate than pH value since variations in pH value may be present without corresponding variation in total caustic content.

The pulp mass flowing from the refiner, therefore, should contain between 0.15% and 2% of H_2O_2, between 3% and 7.5% sodium silicate (based on a Na_2O content of 8.9%), if used between 0.05% and .5% Epsom salts, and a total caustic content of 0.5% to 1.6%, all based on the bone dry weight of the pulp.

The details of the invention will be more clearly apparent by reference to the following description when taken in connection with the accompanying illustrations, in which:

FIGURE 1 is a side elevational, diagrammatic view of an embodiment of apparatus suitable for use in accordance with this invention;

FIGURE 2 is a graphic curve showing the peak brightness to be obtained with bleach having a given residual caustic content in the refiner pulp mass and a pulp consistency of 5%;

FIGURE 3 is a similar graphic curve showing the peak brightness of a similar bleach having a pulp consistency of 12%.

Referring to FIGURE 1, reference numeral **3** designates a pulp refiner comprising two oppositely disposed and oppositely rotating comminuting pulp defibering discs having a multitude of opposing teeth. The oppositely disposed discs are rotated in the refiner housing by means of shafts **6** and **6***a* driven by motors **5** and **5***a*, mounted on base **4**.

In another excellent form of pulp refiner one defibering disc is stationary and an opposing disc is rotated in the refiner housing, thus requiring only a single motor.

The pulp chips **10** are metered and passed into the mouth of funnel **7** by means of an endless belt **9**, as shown. The bleaching solution and H_2SO_4, with sufficient water to provide a pulp consistency of between 3 and 20, is also metered, e.g., through valves **15** and **17**, and passed into funnel **7** simultaneously with the passage of the pulp chips. The refined material is passed from the refiner through outlet **30** from which it is passed to a holding receptacle (not shown) at the desired consistency.

The pulp mass is preferably kept in the holding receptacle for a period of 10 to 30 minutes, whereby it is further bleached by the residual H_2O_2 contained therein. After completion of the bleaching operation the pulp is usually neutralized with SO_2 to a pH of between 5 and 7, screened, cleaned and forwarded to subsequent paper-making operations. If desired, the pulp may be washed prior to neutralization.

The hydrogen peroxide, sodium silicate and Epsom salts of the bleach solution may be mixed with a desired amount of water in a mixing tank **18** and then flowed through pipe **19** to H_2O_2 bleaching solution storage tank **16**. From storage tank **16** the H_2O_2 bleaching solution is passed through pipe line **12**, and H_2SO_4 is passed from storage tank **14** through pipe line **13**, the two passing together through common pipe line **11** into funnel **7**. The H_2SO_4 solution should have such an adjusted strength that the pulp mass passing from the refiner will have a total alkalinity of between 0.5 and 1.6% NaOH based on the bone dry weight of the pulp. The concentration of H_2SO_4 passed into the refiner will, of course, depend upon the caustic content of the chips and the percentage of silicate in the bleach solution. The H_2SO_4 may, if desired, be mixed with the bleaching solution in tank **16** or, alternatively, it may pass directly into funnel **7**, and the bleaching solution and, if necessary, additional water passed independently into the funnel and the two mixed in the refiner. The H_2O_2 and silicate may be mixed in mixing tank **18** and passed directly into funnel **7**, in which case no stabilization agent such as Epsom salts will be required.

FIGURES 2 and 3 clearly show the peak brightness to be obtained when the total NaOH of the pulp as it emerges from the refiner varies between 0.5% and 1.6%. Both illustrations show a peak brightness of over 58 when the bleaching solution contains between these percentages of total NaOH content regardless of the fact that the pulp consistency of the pulp mass may vary from 5% to 12%. The peak brightness will be obtained between these percentages of total NaOH content regardless of the hydrogen peroxide or sodium silicate content within the limits above set forth although the total brightness may be somewhat enchanged by higher concentrations of H_2O_2. In order to obtain an economically useful result by a peroxide bleaching operation, the bleached brightness for hardwood pulp for most paper or paperboard operations should be at least 58 G.E. units.

The following examples are given to illustrate certain preferred embodiments of the process of this invention.

In fourteen tabulated examples set forth below, hardwood pulp chips composed of equal parts of birch, beech and maple having an average unbleached brightness of 42 G.E. units as measured on a General Electric brightness meter are passed into a refiner. These chips had an average of 2% NaOH total alkalinity.

At the same time a peroxide bleaching mixture consisting of the following ingredients is passed into the refiner.

Bleaching Solution Ingredient	lbs./100 gals.
H_2O_2 (100%)	10.4
Epsom salt ($MgSO4.7H_2O$)	0.42
Sodium silicate (8.9% Na_2O—29.9% SiO_2)	41.6

The bleaching solution was fed at a rate of 240 gals. per ton of moisture-free pulp. This solution feed will deliver to the refiner 0.05% Epsom salt, 5% sodium silicate and 1.25% H_2O_2 (100% basis) all based on the weight of moisture-free pulp.

Sulfuric acid, 66° Bé., was added in such amount that the residual total alkalinity, measured as percent NaOH varied in the examples between 0% and 2.6%.

The fourteen examples were carried out at a pulp consistency of 5% and repeated with a pulp consistency of 12%.

The results are given in Tables I and II below. These results are graphically represented in FIGURES 2 and 3.

In all of the examples the refiner was operated to maintain in the pulp mass flowing from the refiner a temperature of approximately 180° C. which temperature is generated by the disintegrating action of the refiner. In

some cases, with low density pulp, it may be necessary to maintain the elevated temperature by the addition of steam. The pulp mass flowing from the refiner was in each case passed into a relatively small-capacity holding receptacle in which the pulp was held for 15 minutes to complete the bleaching operation.

The bleached pulp is then passed from the holding receptacle, diluted to a consistency of about 3%, and neutralized to a pH of 6.0 (Beckman pH meter) with SO_2.

The pulp is then diluted with distilled water to a consistency of about 0.3%, the pH adjusted to between 4 and 4.5 with dilute H_2SO_4, made into a handsheet and air-dried, all in accordance with TAPPI standard procedure. The brightness of the sheets was then measured on a G.E. brightness or reflectance meter.

alkali the H_2SO_4 will be varied in accordance with the varying amount of alkali to provide a total residual alkalinity in the pulp of between 0.5% and 1.6% NaOH.

This is a continuation-in-part of my copending application Serial No. 861,369, and now abandoned, filed December 22, 1959.

Throughout the specification and claims, any reference to parts, proportions and percentages refers to parts, proportions and percentages by weight unless otherwise specified.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claim.

Table I.—Refiner Bleaching With Peroxide—5% Consistency Pulp (Results Shown in FIGURE 2)

[Series 1—14 examples at varying alkalinity]

Ex. No.	Chemicals/M.F. Pulp From Refiner					Total Alkalinity "T.A.," [1] Percent	Bleach Time, Min.	Pulp Temp., ° F.	Pulp pH		Residual Peroxide [2] After 15 Min., Percent	Pulp Brightness	
	NaOH in Chips to Refiner, Percent	Epsom Salts, Percent	Sodium Silicate, Percent	H_2O_2, Percent	H_2SO_4, Percent				From Refiner	After 15 Min.		Air Dry	Oven-Dry 1 hr., 105° C.
	2.0					2.0		180	12.1			44.9	43.2
1	2.0	0.05	5.0	1.25		2.6	15	180	11.8		0.0	55.3	53.8
2	2.0	0.05	5.0	1.25	0.25	2.4	15	180	11.8	11.6	0.0	56.0	54.5
3	2.0	0.05	5.0	1.25	0.50	2.2	15	180	11.7	11.2	0.0	57.6	55.4
4	2.0	0.05	5.0	1.25	0.75	2.0	15	180	11.5	11.4	3.0	56.8	55.1
5	2.0	0.05	5.0	1.25	1.00	1.8	15	180	11.4	11.1	3.0	56.9	55.7
6	2.0	0.05	5.0	1.25	1.25	1.6	15	180	11.4	11.2	10.0	58.5	57.3
7	2.0	0.05	5.0	1.25	1.50	1.4	15	180	11.2	11.0	19.0	59.5	58.0
8	2.0	0.05	5.0	1.25	1.75	1.2	15	180	11.2	10.7	26.0	60.1	59.1
9	2.0	0.05	5.0	1.25	2.00	1.0	15	180	11.0	10.5	47.0	60.4	58.8
10	2.0	0.05	5.0	1.25	2.25	0.8	15	180	10.9	10.1	47.0	59.7	58.7
11	2.0	0.05	5.0	1.25	2.50	0.6	15	180	10.7	10.1	51.0	59.8	58.2
12	2.0	0.05	5.0	1.25	2.75	0.4	15	180	10.5	10.0	85.0	55.8	55.4
13	2.0	0.05	5.0	1.25	3.00	0.2	15	180	10.1	9.8	85.0	54.3	53.6
14	2.0	0.05	5.0	1.25	3.25	0.0	15	180	9.6	9.0	85.0	51.3	50.3

[1] T.A. includes NaOH from chips plus NaOH from silicate minus NaOH neutralized by H_2SO_4.
[2] Percent residual peroxide as percent of total H_2O_2 applied to refiner.

Table II.—Refiner Bleaching With Peroxide—12% Consistency Pulp (Results Shown in FIGURE 3)

[Series 2—14 examples at varying alkalinity]

Ex. No.	Chemicals/M.F. Pulp From Refiner					Total Alkalinity "T.A.," [1] Percent	Bleach Time, Min.	Pulp Temp., ° F.	Pulp pH		Residual Peroxide [2] After 15 Min., Percent	Pulp Brightness	
	NaOH in Chips to Refiner, Percent	Epsom Salts, Percent	Sodium Silicate, Percent	H_2O_2, Percent	H_2SO_4, Percent				From Refiner	After 15 Min.		Air Dry	Oven-Dry 1 hr., 105° C.
	2.0					2.0		180				44.1	43.6
1	2.0	0.05	5.0	1.25		2.6	15	180	12.1		0.0	55.1	53.8
2	2.0	0.05	5.0	1.25	0.25	2.4	15	180	12.1		0.0	55.3	54.9
3	2.0	0.05	5.0	1.25	0.50	2.2	15	180	12.0		0.0	56.0	55.3
4	2.0	0.05	5.0	1.25	0.75	2.0	15	180	11.8		0.0	56.6	56.2
5	2.0	0.05	5.0	1.25	1.00	1.8	15	180	11.7		0.1	58.0	57.3
6	2.0	0.05	5.0	1.25	1.25	1.6	15	180	11.6	11.1	10.0	59.8	58.5
7	2.0	0.05	5.0	1.25	1.50	1.4	15	180	11.4	11.0	16.0	60.1	59.0
8	2.0	0.05	5.0	1.25	1.75	1.2	15	180	11.3	10.8	22.0	59.1	58.8
9	2.0	0.05	5.0	1.25	2.00	1.0	15	180	11.0	10.8	21.0	61.0	60.3
10	2.0	0.05	5.0	1.25	2.25	0.8	15	180	10.8	10.4	24.0	61.8	61.1
11	2.0	0.05	5.0	1.25	2.50	0.6	15	180	10.6	10.3	32.0	59.6	59.2
12	2.0	0.05	5.0	1.25	2.75	0.4	15	180	10.3	9.8	63.0	59.9	59.9
13	2.0	0.05	5.0	1.25	3.00	0.2	15	180	9.9	9.3	89.0	56.7	56.3
14	2.0	0.05	5.0	1.25	3.25	0.0	15	180	9.6	8.6	100.0	53.2	51.9

From the tables and FIGURES 2 and 3 it will be seen that the H_2SO_4 of the bleach must be added in such quantity, based upon the NaOH content of the silicate and NaOH content of the chips to produce in the pulp mass passing from the refiner a total alkalinity of between 0.5% and 1.6% NaOH in order that the bleached brightness will be over about 58.

Where the hardwood chips have a varying content of

I claim:

The process of chemically and mechanically refining hardwood chips previously softened with NaOH which comprises finely disintegrating said softened hardwood chips containing in excess of 1.6% NaOH based on the dry weight of the chips and simultaneously passing in contact therewith 0.3% to 5% H_2SO_4 and a sufficient quantity of aqueous hydrogen peroxide containing be-

tween 0.15% and 2% H_2O_2, between 3% and 7.5% sodium silicate (based on 8.9% Na_2O and 29.9% SiO_2), all based on the dry weight of said chips to produce a pulp mass having a consistency between 3% and 20% and a total alkalinity, as it emerges from the disintegrating step, of between 0.5% and 1.6% NaOH, and maintaining said pulp mass in the aforesaid condition for between 10 and 30 minutes.

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