# HIGH-YIELD NEUTRAL <br> SULFITE PULDS 

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# HIGH-YIELiD NEUTRAL SULFITE PULPS $=$ 

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## Summary

Neutral sulfite pulps were obtained from aspen, white oak, and jack pine. The yield range varied from the semichemical 70-74 percent to the fully pulped 50 percent. As the yield proceeded to low values, brighter pulps were obtained that required less chlorine for bleaching.

A few digestions with mildly acid cooking liquors indicated the possibility of drastic savings in chemicals and cooking cycles, but at the same time, considerable losses in strength were observed when the pulps were compared with neutral sulfite pulps of equal yield.

Bleached neutral sulfite pulps showed outstanding improvement in opacity as the yield gradually dropped to lower values. In the case of aspen, this was obtained at some sacrifice of the strength of the pulps.
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${ }^{2}$ Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

## Introduction

Neutral sulfite semichemical pulps possess certain characteristics that make them well suited for products such as corrugating board, where great stiffness is desired, and for well-hydrated papers, such as greaseproof and glassine. For certain other grades, however, the accompanying low opacity and certain other physical characteristics commonly attributed to the high content of hemicelluloses are a disadvantage. This report summarizes an investigation of the properties of pulps which were cooked to lower yields to determine the change in the physical properties of the pulps resulting from more drastic cooking.

The preparation of fully cooked neutral sulfite pulps has been previously described. The first publication was by Cross in 1880. Because of the several reviews of neutral sulfite pulping (1-7), the literature will not be discussed here. Data on the specific properties of the pulps have been infrequently reported, but some information is available on white spruce, western hemlock, slash pine (10), shortleaf pine (11), Douglas-fir (3), black spruce, and jack pine (12). Such pulps have been reported to be as bright as acid sulfite pulps and as strong or stronger than sulfate pulps. Chemical consumption was high and the cooking time extended, but the pulps were exceptionally strong and bleached readily. Commercially, the Keebra process ( 8,2 ) and the Sodite process (4) were in operation for several years.

The chief deterrent to full pulping has been the excessive consumption of chemicals, which were difficult to recover for reuse. However, several processes for the recovery of spent sulfite liquors are now available and show promise of successful development (13). In addition to this encouraging aspect, the recent work of Ross, Hart, Strapp, and Yean (14), Kerr and Harding (15), and Husband (16), shows that the chemical requirement and cooking time in the semichemical range can be sharply reduced by shifting the pH of the cooking liquor to the slightly acid side of neutral. To aid in the evaluation of the possibilities of these processes, more information is needed regarding the properties of the pulps in the yield range between the traditional semichemical $70-80$ percent and the fully pulped 50 percent.

## Experimental

Three species -- aspen, white oak, and jack pine -- were cooked to yields ranging from 50 to 75 percent in increments of 5 percent. Sufficient pulp for testing and bleaching trials was provided by duplicate digestions in an 0.8 -cubic-foot stainless steel, tumbling, digester. The cooking liquors were prepared from technical grades of sodium sulfite and sodium bicarbonate, except in a few instances in which a similar grade of sodium bisulfite replaced the sodium bicarbonate. Detailed cooking conditions are included in tables 1 and 2.

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The cooked material that passed through an 8-cut, flat, Vibrating screen was tested and bleached. Except in digestions o $\overrightarrow{\ddot{r}}$ the lowest yield, it was necessary to put the softened chips through an 8-inch, single-rotatingdisk attrition mill before screening. Tables 3, 4, and 5 report the chemical composition and strength properties of the pulps before and after bleaching. Testing was in accordance with the standard TAPPI methods (17).

The pulps were bleached to about 85 percent brightness by means of a conventional 3-stage chlorine, caustic extraction, calcium hypochlorite method. The chlorine requirement was estimated from a modified Tingle number determination (19). A high proportion of the total chlorine requirement was used in the first stage, so that the amount applied as calcium hypochlorite would be less than 2 percent, as recommended by Kingsbury and Sinmonds (18). The relationship between degree of cooking and chlorine consumption is included in table 5.

## Discussion

## Pulping

Low-yield pulps were obtained at the cost of sharply increased requirements in wood, chemicals, and digester capacity (table l). With aspen, for example, 1,356 pounds of sodium carbonate and 355 pounds of sulfur were required per ton of air-dry pulp at 51 percent yield, compared with 288 and 58 pounds, respectively, at 74 percent yield. The required times at maximum temperature were $7-1 / 2$ hours and 12 minutes.

The wood requirement per ton of pulp varies inversely with the yield. While this relationship is mathematical and therefore inflexible, wood costs can be minimized by taking advantage of the adaptability of the neutral sulfite process to use the less popular, denser hardwoods, which combine lower cost with a greater yield per cord of wood.

The chemical requirement at lower yields is obviously excessive for economical operation without recovery. However, the consumption could be greatly reduced with appropriate recovery methods.

The recent work of Husband and others, previously referred to, suggested that significant savings in cooking time and chemical would result if the wood was cooked in a mildly acid medium. The results of four such digestions with aspen chips (table 2) pulped with sodium bisulfite alone or a mixture of sodium sulfite and sodium bisulfite showed considerable advantage in these respects. Under conditions affording a spent liquor pH of 3.3 , the time required at maximum temperature for a yield of 55 percent was reduced from nearly 6 hours at $180^{\circ}$ to $1-1 / 2$ hours at $170^{\circ} \mathrm{C}$. The chemical consumption was lowered from a total of 1,300 pounds to 430 pounds per ton of pulp. A gain of 6 points in opacity was offset by a loss of 12 points in pulp bright-
ness and a severe loss in strength (table 4). A digestion under milder conditions ( $150^{\circ} \mathrm{C} ., \mathrm{pH} 4.7$ ) showed less saving in chemical and no saving in time, considerable loss in strength, but a good gain in opacity compared with bicarbonate-buffered pulp. In evaluating the gain in opacity, allowance must be made for the marked reduction in the brightness of the pulps, since dark-colored pulps are naturally more opaque.

## Chemical Properties of the Unbleached Pulps

There was a slight increase in the pentosan content of the pulps with more drastic cooking (table 3), showing that slightly less pentosan was removed than other wood constituents. Acid liquors removed considerably more pentosans than did neutral liquors.

With declining yields, lignin content decreased and holocellulose and alpha cellulose increased as usual. The rates of change were regular except at the lowest yields of aspen pulp, where the proportion of lignin extracted decreased as the amount in the pulp approached 1 percent. At this point, there were also signs of increasing attack on the cellulose.

Differences in the composition of the respective woods were evident in the analyses of the corresponding pulps. Differences between woods in the chemical constituents of the pulps at equal yields help to account for the divergent trends between woods shown in curves relating pulp strength to yield.

Physical Properties of the Unbleached Pulps
The correlation between yield and the strength properties of standard test sheets showed different trends for the three species of wood (table 4, figs. 1, 2, and 3). In the case of aspen, a significant maximum was shown at the $60-65$ percent yield range (fig. 1). Following the maximum, there was a minimum at 55 percent for bursting strength and breaking length. This minimum, followed by an upturn, was confirmed by 3 supplementary digestions at 57, 52, and 50 percent yield. Since the lignin content approached a very low figure at this point, it is evident that further reduction in yield was obtained only by the selective removal of carbohydrates.

With decreasing yield, the white oak pulps (fig. 2) showed a slight but consistent upward trend in bursting strength, while the breaking length fell off slightly after a maximum at 65 percent yield. The tearing resistance rose substantially, with a peak near 55 percent, then declined. The jack pine pulps (fig. 3) showed no maximums or minimums in strength with decreasing yields. There was a nearly constant increase in all categories through the entire range.

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Optical Properties of the Unbleached Pulps
Extensive cooking was effective in improving the brightness of the hardwood pulps (table 4). Aspen cooked with neutral liquors showed a brightness increase from 53.3 at 73.7 percent yield to 67.2 at 50.8 percent yield. The material from the oak, considerably darker in color, increased from 30.7 at the highest yield to 37.3 at the lowest. The improvement in the case of the latter is of minor interest, since brightness is rarely a critical property in the darker colored pulps. At about 60 percent brightness and above, however, suitable pulps can be blended into some grades of printing papers without bleaching. It has already been mentioned that the substitution of sodium bisulfite for sodium bicarbonate gives darker pulps, the degree of darkening depending on the cooking conditions.

The unbleached aspen pulps were significantly higher in opacity at the lower yields, the improvement between the highest and lowest yields being 5.5 points at 500 -milliliter freeness and 8.4 points at 250 -milliliter freeness. Since the pulps at the lower yields were also considerably brighter, the improvernent in opacity was real. The values for the unbleached oak pulps are of little practical significance, since the high opacity was partly the byproduct of the color, and, as mentioned above, the optical properties of papers and boards in this range of brightness are not important.

## Bleaching

As the pulps were cooked to progressively lower yields, the chlorine required for bleaching decreased rapidly as lignin was removed from the wood in the digester (table 5). However, in the case of aspen, the pounds of chlorine consumed per pound of lignin present in the pulp (as determined by the TAPPI standard procedure) increased from 1.2 to 2.0. This does not necessarily mean a proportionately greater consumption by the residual lignin at low yields, since chlorine can well be lost physically or consumed by other constituents present. The oak series showed a minimum requirement per pound of ligain at intermediate yields.

The shrinkage in the amount of pulp due to bleaching, shown in table 5, was considerably reduced when the pulps had been well cooked. Where the spread in yield among the unbleached pulps was about 23 percent, the spread among the bleached pulps was only 12 percent. This means that, although the wood requirement was 50 percent greater per ton of pulp at an unbleached yield of 50 than at 75 percent, the increment was considerably less on the basis of the bleached pulps.

## Properties of the Pulps after Bleaching

Generally speaking, the bleaching of fully cooked neutral sulfite pulps gives a denser sheet that shows improved strength properties, especially folding endurance. This increase is not so high as in the case of the bleaching of neutral sulfite semichemical pulps and varies according to the wood used.

Neutral sulfite oak pulps show a better improvement in strength after bleaching than the aspen pulps. In the particular case of jack pine, the low-yield bleached pulp is not stronger than the unbleached pulp except for folding endurance.

With progressive cooking the folding endurance, bursting strength, and breaking length of the aspen bleached pulps showed considerable decline, with the tearing resistance also decreasing after a short rise (fig. 4). On the other hand, the white oak bleached pulps indicated maxima at 5l-52 percent bleached yield, corresponding to 64 percent unbleached yield (fig. 5). Data on the properties of bleached jack pine pulps are limited, but in general the bleached pulp prepared from wood cooked to 52 percent yield was slightly stronger than that from wood cooked to 64 percent yield (table 6).

The outstanding improvement in the quality of the bleached pulps as a result of cooking to low yields was the increase in opacity. In the case of aspen, this value increased from 69 (unbleached yield of 74 percent) to 81 (unbleached yield of 51 percent). With the oak pulps the increase was 7 points, with a maximum of 83.5 . The increase observed with jack pine pulps was 11 points.

## Conclusions

The high chemical consumption, long cooking cycles, and increased wood requirements typical of low-yield neutral sulfite pulping were confirmed. The pulps obtained were brighter as the yield was progressively reduced, and could be readily bleached to high brightiness levels.

Drastic savings in chemicals and cooking time resulted from use of mildy acid cooking liquors. There was considerable loss in the strength of the pulps compared with pulps of equal yield cooked with neutral liquors. Since the pulping variables with acidic liquors are quite critical, and only a cursory investigation was made, it is possible that the optimum conditions were not used.

The correlation between yield and the strength properties of the unbleached pulps was not the same for all three species of wood. Jack pine showed a consistent increase in strength as the yield was reduced, whereas the aspen and oak pulps showed numerous maximums, and in two instances a minimum, at
various intermediate yield levels.
Outstanding improvement in the opacity of the bleached pulps was observed, regardless of species, as the yield was lowered. In comparison with bleached semichemical pulps, the maximum increase in contrast ratio varied from 7 points for oak to 10 to 12 points for jack pine and aspen.

In general, well-cooked hardwood neutral sulfite bleached pulps are weaker than the corresponding bleached semichemical pulps. Folding endurance was the chief casualty, with a 50 to 75 percent loss. Losses in the other strength criteria varied from 10 to 20 percent.

Where bleached pulps were prepared, the increased wood and chemical costs due to prolonged cooking were offset significantly by the savings in chlorine and the reduced shrinkage on bleaching. A summary of the requirements at different yield levels is provided in table 7 .

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Table l.--Cooking conditions and chemical charged in neutral sulfite pulpingl


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Table 2.--Cooking conditions and chemical charged in aspen sodium bisulfite pulping


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Table 3.--Chemical composition of neutral sulfite unbleached pulps

Table 4.--Strength properties of the unbleached neutral sulfite pulps

Table 4.--Strength properties of the unbleached neutral sulfite pulss (Cont.)

Table 5.--Bleachine data


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Table 6.--Strengtin propexties of the bleached neutral sulphite pulps

Opacity . 70 | 3 |
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$\vdots$
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 Gri. $: \begin{gathered}\text { Percent: } \\ \text { percent: } \\ \text { Percent } \\ :\end{gathered}$ -
 77.3
 .71 : SS• : OTE : S己
 200: . 59 : JACK PINE
 $10,600: 560: 1,010$
$11,000:$
$720: 1,300$ $8,150:$
$10,600:$ $51.1: 82.8: 1.21: 1.45: 1.55: 1.32$
$46.4: 86.3: 1.42: 1.50: 1.15: 1.00$
ICanadian standard freeness.
${ }^{-}$Contrast ratio.

Table 7.--Effect of the degree of cooking on the wood and chemical requirement per ton of airdry bleached pulp



Figure 1. --Relation of physical properties of aspen neutral sulfite unbleached pulps to yield of pulps at 350 fubic centimeters freenesa (Canadian Standard).


Figure 2. --Relation of physical properties of white oak neutral sulfite unbleached pulps to yield of pulp at 350 cubic centimeterg freeness (Canadian Standard).


Figure 3.--Relation of physical properties of jack pine neutral sulfite unbleached pulps to yield of pulp at 350 cubic centimeters freenese (Canadian Standard).


Figure 4. --Relation of physical properties of aspen neutral sulfite bleached pulps to yield of puips at 350 cubic centimeterg freeness (Canadian Standard).


Figure 5. -- Relation of physical properties of white oak neutral gulfite bleached pulps to yield of pulpa at 350 cubic centimetern freeness (Canadian Standard).


[^0]:    ${ }^{\text {lCooking conditions: Chips steamed } 0.5 \text { hour at atmospheric pressure before adding cooking }}$ liquor; Aspen-cooking liquor added, 45 gallons per 100 pounds moisture-free wood, 2.5 hours to maximin temperature; Oak--cooking liquor, 32 gallons per 100 pounds of wood, 2.5 hours to maximum temperature; Jack pine-wcooking liquor, 50 gallons per 100 pounds of wood; l-hour inpregnation at $120^{\circ} \mathrm{C}$. followed by removal of free liquor and completion of cooking with a mixture of direct and indirect steaming. Digester heated indirectly unless otherwise stated.

