# THE CHEMICAL PROPERTIES OF WHITE SPRUCE PULP PREPARED BY THE USE OF PHENOL

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## THE CHEMICAL PROPERTIES OF WHITE SPRUCE PULP PREPARED BY THE USE OF PHENOL

By

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### Abstract

The effect of varied times and temperatures on the yield and chemical properties of pulps prepared by the use of phenol on wood was determined. Optimum conditions appeared to obtain at about 90° C. with a 2-hour digestion time, and a ratio of phenol to wood of 8 to 1. The total and alpha-cellulose contents of the pulps were higher than for sulfite pulps, and the Roe chlorine number relatively low. Pentosans, extractives, and lignin appeared in about the same quantities as in easily bleached sulfite pulps, the lignin content decreasing with increasing time and temperature. The pulp was somewhat dark-colored, and yields were low. The strength properties were very low, as were the absorbency and porosity, while the opacity was high. portion soluble in alcohol-benzene was about the same as for sulfite oulp, while that soluble in ether was very low. The chemical properties of phenol pulp appear to make it suitable for the manufacture of cellulose derivatives. About 80 percent of the phenol was recoverable. In general, total yield decreased with increasing times and temperatures. Maximum screened yield was about 42 percent.

#### Introduction

When wood is heated with phenol, the lignin is dissolved, leaving an almost lignin-free cellulose. This reaction is greatly stimulated, apparently catalytically, both as to completeness and rapidity by very small amounts of mineral acids.

A portion of this report was submitted to the University of Wisconsin as a thesis for the degree of Bachelor of Arts by E. L. Fiedler.

Various attempts have been made to pulp wood by the phenol process because of the short time and low pressure and temperature required to reduce the wood to a pulp. Also, because of the increased activity by state health agencies against the pollution of streams by pulp mills, the attention of the industry is being directed towards the use of chemicals other than calcium bisulfite as pulping agents. Phenol has been reported to be an effective pulping chemical and, since unused phenol is readily recoverable from the spent pulping liquor and the residual phenol-lignin might be of use as a basis for the manufacture of plastics, it is felt that the use of the spent liquors might be so profitable that stream pollution would be eliminated. Commercial phenol pulping has not been attempted largely because of the prohibitive cost of phenol.

The study reported herein was undertaken to determine the chemical properties and yields of pulps produced by the use of phenol, and to determine the temperature and time for the production of the best pulp.

### Literature Survey

The first systematic study of phenol-lignin was made by Hillmer (8). L. Hochfelder (9) in a dissertation reviewed by Melander (13) described the digestion of dried spruce chips at 180° C. for 48 hours with phenol. The resulting phenol-lignin was composed of two fractions, one insoluble in alcohol (lignin alpha) and the other soluble in alcohol (lignin beta). The alpha fraction contained no carboxyl nor carbonyl groups, but the presence of three hydroxyls was established. Kalb and Schoeller (11) reported that phenol-lignin may be prepared by heating pine sawdust with phenol and hydrochloric acid for one hour at 90° C.

According to Legler (12) wood meal could be made lignin-free in 15 minutes with phenol and very small amounts of hydrochloric acid (0.03 percent of weight of phenol). In the absence of hydrochloric acid the wood was unaffected in seven hours. He likewise found the optimum temperature to be between 70° and 80° C. The phenol apparently condensed with the lignin to form phenol-soluble resins.

Wedekind, Engel, Storch and Tauber ( $\underline{15}$ ) showed that the reaction between phenol and lignin proceeds only while the phenol hydroxyl remains unchanged and they regarded the linking as occurring para to the phenolic hydroxyl and considered the possibility of a carbonyl condensation. Lignin was regarded by these workers as a methoxy compound in which 100 carbon atoms are combined with 110 hydrogen and 35 oxygen atoms. They proposed  $(C_8H_7O_2)$  (OCH<sub>3</sub>)  $(OH)(C_6H_4OH)$  as the simplest phenol-lignin. Phenol lignin was described as a light violet amorphous powder which begins to sinter at 190 to 195° C. and decompose at 200 to 225° C., and is somewhat hygroscopic, yields no phloroglucinol-hydrochloric acid reaction, and does not reduce Fehling's solution.

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Jonas  $(\underline{10})$  believed the phenol and lignin reaction to be a condensation of the phenolic hydroxyl with the lignin molecule (perhaps accompanied by partial cleavage of the complex).

Hagglund, Johnson and Trygg (7) indicate that phenol-lignins are ring condensation products. The phenol hydroxyl first reacts with the lignin aldehyde to form a acetal-like compound. This then reacts further through wandering of the aldehyde residue and is converted into a ring condensation product.

Buhler (3,4,5) showed that phenols at temperatures above 150° C. dissolve resins, lignified materials and other incrustants. Increasing the temperature and pressure promoted the solution.

Hartmuth (6) recommended the addition of small quantities of hydrochloric acid to the reaction.

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Buckland, Brauns, and Hibbert (2) showed that the phenol reacts with lignin in such a way that new phenolic hydroxyl groups appear in the derivative, two different products being formed in the ratio of 3 to 1, one etherinsoluble and the other ether-dicxane soluble. The ether-insoluble fraction contains three new phenolic hydroxyls and it is probable that during condensation one methoxyl group is split off. Apparently as many as 15 or 21 molecules of phenol condense with the lignin in the ether-dioxane soluble portion. While the mechanism of the reaction between phenol and lignin has not been definitely established, there is little doubt that the phenol reacts with the lignin in such a way that new phenolic hydroxyl groups appear in the lignin derivative.

Brauns and Hibbert ( $\underline{1}$ ) proposed  $C_{42}H_{32}O_6(OCH_3)_5$  (OH) $_5$  as the unit of "native lignin. The ether soluble phenol-lignin with one phenol-ether linkage and three phenol groups present in nuclear condensation was postulated as  $C_{42}H_{32}O_6(OCH_3)_4(OH)_5(OC_6H_5)$  .  $3C_6H_5OH$ . The ether-dioxane soluble phenollignin is possibly either  ${\rm C_{42}H_{32}O_6(OCH_3)_4(OH)_5(OC_6H_5)}$  . 15  ${\rm C_6H_5OH}$ , or  $^{\text{C}}_{42}^{\text{H}}_{32}^{\text{O}}_{6}^{\text{(OCH}_{3})}_{4}^{\text{(OH)}}_{5}^{\text{(OC}}_{6}^{\text{H}}_{5}^{\text{)}}$  . 21  $^{\text{C}}_{6}^{\text{H}}_{5}^{\text{OH}}$ .

### Experimental

The wood used was white spruce (Picea glauca) and was obtained from Forest Products Laboratory shipment 1423. The chemical analysis of the wood is given in table 1 (14).

The wood was reduced to 5/8-inch chips in the laboratory chipper and screened to remove knots, oversized chips, and fines. In the case of the cooks made on sawdust, the chips were further reduced in a Wiley mill and then screened on a 40-mesh wire screen, the portion passing through being rejected. In all cases oven-dried material was used.

### Table 1.--Chemical analysis of white spruce wood, shipment 1423

Cellulose	60.6 percent
Alpha cellulose	42.1 percent
Lignin	
Chlorine consumption	
Total pentosans	

### Solubility in

Hot 1-percent NaOH solution	10.7 percent
Hot water	2.1 percent
Alcohol-benzene	2.3 percent
Ether	1.1 percent
Hydrolysis number	29.4 percent

The digestions were made in corrosion-resistant alloy bombs having a capacity of 350 cubic centimeters. The bombs were immersed in a glycerine bath which was stirred by a motor-driven screw pump agitator and equipped with two heating elements of about 400-watt capacity. The temperature of the bath was maintained within  $\pm 1^{\circ}$  C. by the use of a bimetallic thermoregulator.

Twenty-five grams of oven-dried chips (or sawdust) were placed in the bombs and covered with 200 grams of molten phenol (at about 60° C.) to which had been added 1 cubic centimeter of concentrated hydrochloric acid. Complete immersion of the chips in the phenol was insured by covering them with a perforated disk of stainless alloy, so constructed as to prevent the chips from floating. The temperature of the bath was raised 4° C. above the cooking temperature for each bomb immersed, to allow for the heat capacity of the metal. Three minutes were allowed after immersion for the bomb and its contents to reach thermal equilibrium.

After the elapse of the predetermined time, the bomb was removed, opened, and its contents emptied on a 70-mesh wire screen and washed with a warm, 0.5-percent caustic solution. The pulp was then broken up with a motor-driven stirrer, again washed with dilute caustic, and finally with tap water. The residue was dried overnight at 105° C. and weighed. The total yield was calculated as

weight of residue x 100 = percent total yield.
weight of chips

The dried pulp was broken up again in water and screened through 0.012-inch slots in a bronze plate on a diaphragm screen. The screenings were dried at 105° C. and weighed, the yield of screenings being reported as a percentage of the wood. The screened yield was reported as the difference between the total yield and the screenings. The cooking conditions and yields are reported in table 2.

Althonical line   Lignin   Total   Solubility in   Althonical line   Lignin   Total   Solubility in   Althonical line   Lignin   Total   Solubility in   Light   Lig	
2.0 4.4 0.5 2.2 2.2 4.3 1.1 1.1 1.2 2.2 4.3 1.3 1.3 1.3 2.5 2.3 2.3 2.3 2.3 2.3 2.3 2.3 2.3 2.3 2.3	
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2.82 2.89 3.06 3.06 3.06 3.06 1.40 1.40 1.30 1.30 1.30 1.30	** ** *
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23. 24. 25. 25. 25. 25. 25. 25. 25. 25. 25. 25	4.5. 4. 00 -
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In the case of the digestions using sawdust, it was impossible to wash the residue thoroughly with water or caustic. Hence the contents of the bombs were transferred to an extraction thimble and extracted with methyl alcohol in a Soxhlet apparatus until the extracting alcohol was colorless. The sawdust pulps were not screened, the total yield alone being determined and reported. Table 3 presents the cooking conditions and yields of the sawdust digestions.

Table 3.—Cooking conditions, yields, and properties of phenol pulps prepared from white spruce sawdust

														_				Solubi		-
	tion																			
	numbe	r:	ture	:	÷	:	:		: 4	Alpha	:	Total	:		:	sans	: A	lcohol-	- ; <u>F</u>	lther
	-10001000	:		:		VI. A GENORALI	:		:		:		å		:		: b	enzene	:	
8	<u>P</u>	2	°C,	;	Hours	:Per-	:		:	Per-	:	Per-	:	Per-		Per-	: <u>P</u>	ercent	: ፲੶	ercent
•		:		3		cent	:		:	cent	:	cent	:	cent	:	cent	:		:	
	43	X	100	ř	0.25	:69.2	:	26.7	:	50.0	:	70.5	:	19.3	:	8.3	:	0.7		0
	<b>4</b> 5		100	¢	• 50	:66.8	:	29.1	:	45.5	:	64:6	:	25.6	ı	9.6	:	. 9	:	0
	46		100	:	.75	:47.2	;	21.6	í	57.8	:	76.4	:	16.0	ķ	7.1	:	1.3	4	0
	44	4	100	ì	1.00	:41.6	:	5.47	:	74.6	•	96.9	:	1.7	:	3.4	:	. 3	3	0
	47	:	100	ŧ	2.00	:40.0	:	6.20	;	69.0	*	92.4	:	1.5	÷	3.5	:	.5	1	.3

In order to obtain some idea of the quantity of recoverable phenol remaining, two digestions were made with sawdust, following which the contents of the bombs were extracted with ether, the unused phenol being distilled from the ether extract. These results are presented in table 4.

Table 4.—Cooking conditions, vields, and amount of phenol recovered from phenol cooks using white spruce sawdust

	:pera-	4	: 8	ven-dry sawdust used	:	• • (0 • (0)	Used	 -:E	lecovere		Loss
. <u>P</u>	: °C.	:	Hours:	Grams						:	Grams
			0.5 : 1.5 :	25 25		-			162.3 156.0		

The following chemical constants of the pulps were determined; total and alpha cellulose, lignin, total pentosans, solubilities in alcohol-benzene

and ether, and the Roe chlorine number. The color of the pulp was also determined.

In order to obtain sufficient pulp for a physical analysis, cook P65 was made. In a 12-liter flask 3.43 pounds of chips at a moisture content of 7.4 percent were covered with 27.44 pounds of molten phenol. The flask and its contents were submerged in water in a steam-jacketed autoclave and maintained at 90-100° C. for 1.25 hours. Following cooking, as much liquid as possible was drained off the chips and the residue placed in about 25 gallons of dilute caustic soda and broken up with an electric stirrer. The liquor was washed from the pulp in a screen box and the pulp again treated with about 25 gallons of dilute caustic and stirred. Following washing, the pulp was screened and the yield determined. The pulp was pebble-milled and tested for physical properties, the physical data of which are given in table 5. The cooking conditions, yield, and chemical analysis of this pulp are presented in table 2.

Table 5.—Cooking conditions, yield, and physical characteristics of pulp prepared by the use of phenol

					У.	3	${\cal L}_{\rm L}$	1 1		
Digestion number		الأنام	P.	-65			43	14		
Temperature, °C.			91	200	٠,	200	e	4.		
Time, hours						23	7			
					ġ.	15	9			
Bleach used, percent	-			0		15				
Color, Ives parts:			_	_						
Red						88				
Green	٠,		5	4		86				
Blue			4	9		80				
Bleach required, percent			20	C						
										- 9
Pebble mill tests (Ream 25x40 - 500)	:		2		1		6		15	
after milling, minutes		0		20		40	'n,	60	š	80
Bursting strength, points per pound per	ä.	•	ä	20	÷		ŝ		Ŷ	
ream		0 47	1	0 40		0.57	į	0.49	i	0.48
Tearing strength, grams per pound per	•	0.47		0.49		0.57		0. ±3		0.40
	1	0.0	Ģ	0.5	ŝ		Ì	0.0	i	F 4
ream				-				. 86		
Folding endurance, double folds	*	36	3	36	1	77	Ž	= 37	÷	55
Tensile strength, pounds per square inch.	3	2965	:	2895	9	3540	:	3685	1	4525
Freeness, SR. cc.	;	845						390		290
Solid fraction	à	0.41	:	0.46		0.54	:	0.50	1	0.57
Absorbency, seconds per cc	÷	390	ć	461		1184	:	1350	3	2580
Forosity, seconds per 100 cc	Ţ.,	42		29	â	140	ě,	205	3	827
Opacity, contrast ratio		0 00		0 07	1.	0.06		0.05		
	*	0.30	i.	ن. ن ق• ∩	7	0.30	٠,	0.30	٠	0.00
					- 4					

### Discussion of Results

Figure 1 shows the change in total yield with increasing cooking time at different temperatures. The yield decreased as the time increased, the decrease in yield being very great in the early stage of the digestion. At 80° C. the yields tended to approach a minimum of about 45 percent, at 90° C., a minimum of about 42 percent, at 100° C., a minimum of about 38 percent, at 130° C., a minimum of about 33 percent or less, while at 150° C. complete solution of the wood would apparently occur in about 2 hours. The yields using sawdust run slightly higher than when chips are used.

Figure 2 presents the effect of digestion time on the yield of screenings. The screenings decreased with increase in digestion time and temperature. The screened yield, as given by the difference between total yield and screenings, was optimum at a digestion temperature of 90° C., being about 42 percent after a 2-hour pulping period (table 2). It is doubtful if screened yields above 43 percent could be obtained using phenol in this manner. Temperatures above 110° C, result in rapid and drastic decreases in yield.

The effect of temperatures on total yield is brought/in figure 3 at two different times. The desirability of avoiding higher temperatures is confirmed by these curves. In figure 4 it is shown that at 110° C. the screenings are reduced to an acceptable percentage in 1 hour.

Figure 5 shows the effect of increasing time, at various temperatures, on the chemical constants of the pulp. The lignin is readily removed by the action of phenol. However, it appears to be impossible to reduce the lignin content to below 1.0 percent by the use of phenol in this manner. There appears to be a tendency for the phenol to lower the total cellulose after the lignin has been reduced to less than 1.5 percent. In general the total cellulose is nigh in comparison with commercial sulfite pulps. Phenol apparently degrades the alpha cellulose readily. At 80° C. the percentage of alpha cellulose begins to drop off markedly in as short a time as 1.0 hour, and this point is reached earlier if the temperature is increased. In general, however, the percentage of alpha cellulose in pulps prepared with phenol is relatively high.

The Roe chlorine number values obtained are plotted in figure 5. The Roe number decreases with increasing time and temperature. If the sulfite Roe number (to a hypochlorite bleach requirement factor of approximately 5) is applicable to phenol pulps, then these values would indicate that most of the pulp could be classed as easy-bleaching — that is, have a standard hypochlorite bleach requirement of less than 15 percent.

The phenol pulps are characterized by relatively high total and alpha cellulose and low lignin contents and low Roe numbers. Since these properties are usually considered desirable for the manufacture of cellulose derivatives, the possibility of using phenol pulps for this purpose is indicated. Confirmation by actual trial is necessary, however, to establish this point.

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The total pentesans, alcohol-benzene, and ether solubilities of the pulps were about the same as for sulfite pulps. The unbleached color was slightly darker.

Referring to the physical data on cook P65, presented in table 5, it is seen that pulp possesses extremely poor strength characteristics. It has a very low porosity and absorbency, and a high opacity.

The theoretical quantity of phenol used up by the wood can be calculated from the formulas of Brauns and Hibbert (1), and Buckland, Brauns, and Hibbert (2). If 15 molecules of phenol are present in the ether-dioxane-soluble portion of the phenol-lignin, which makes up 25 percent of the total phenol-lignin, the following formulas may be assumed to hold:

$$^{\text{C}}_{47}^{\text{H}}_{52}^{\text{O}}_{16} + ^{4\text{C}}_{6}^{\text{H}}_{5}^{\text{OH}} \longrightarrow ^{\text{C}}_{52}^{\text{H}}_{54}^{\text{O}}_{16} \cdot ^{3\text{C}}_{6}^{\text{H}}_{5}^{\text{OH}}$$
 (1)

"native lignin"

Ether-insoluble phenol-lignin

$$^{\text{C}}_{47}^{\text{H}}_{52}^{\text{O}}_{16}^{\text{I}_{6}} + ^{\text{I}_{6}}^{\text{C}}_{6}^{\text{H}}_{5}^{\text{OH}} \longrightarrow ^{\text{C}}_{52}^{\text{H}}_{54}^{\text{O}}_{16} \cdot ^{\text{I}_{5}}^{\text{C}}_{6}^{\text{H}}_{5}^{\text{OH}}$$
 (2)

"native lignin" ...

Ether-dioxane-soluble phenol-lignin

Molecular weight of "native lignin" = 872

Molecular weight of phenol = 94

Molecular weight of ether-insoluble phenol-lignin = 1216

Molecular weight of ether-dioxane-soluble phenol-lignin = 2344

Let a = grams phenol used in (1)

b = grams phenol used in (2)

a + b = t = total phenol used

c = grams phenol-lignin formed in (2)

3c = grams phenol-lignin formed in (1)

x = grams native lignin in (1)

Since 25 grams of sawdust were used, which had a lignin content of 27.8 percent (table 1), the total lignin in (1) and (2) is 6.95 grams.

Therefore

$$\frac{4 \cdot 94}{872} \cdot x = a$$

and

$$\frac{16 \cdot 94}{872} \cdot (6.95 - x) = b$$

$$10452.8 - 1504x = 872(a+b) = 872t$$
 (1)

also  $\frac{1216}{872}$  • x = 3c

1216x = 2616c (2)

also 
$$\frac{4 \cdot 94}{1216} \cdot 3c = a$$

From the three simultaneous equations in x, c, and t (1), (2), and (3): t = 3.56 grams phenol to react with the lignin of 25 grams of white spruce wood, if the ether-dioxane soluble portion of the phenol-lignin has 15 molecules of phenol condensed with it.

Similarly, if the ether-dioxane soluble portion of the phenol-lignin has 21 molecules of phenol condensed with it, 25 grams of the wood would require 4.91 grams of phenol.

Comparing these calculated values with those of table 4, which were experimentally obtained, it is noted that the latter are approximately ten times greater. This may be due to the fact that, in addition to the formation of phenol-lignin, the phenol is also used up by the cellulose and certain extraneous materials of the wood. From these data it appears doubtful if much more than 80 percent of the theoretically unused phenol can be considered as recoverable by ether extraction.

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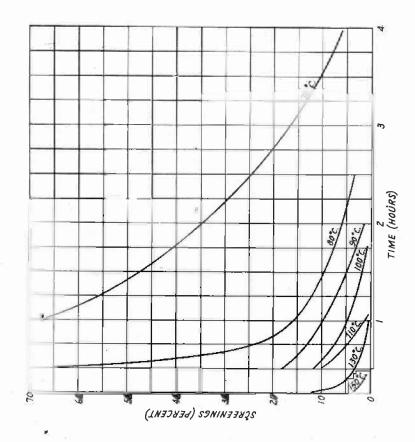


FIG. 2 EFFECT OF TIME ON YIELD OF PULP SCREENINGS

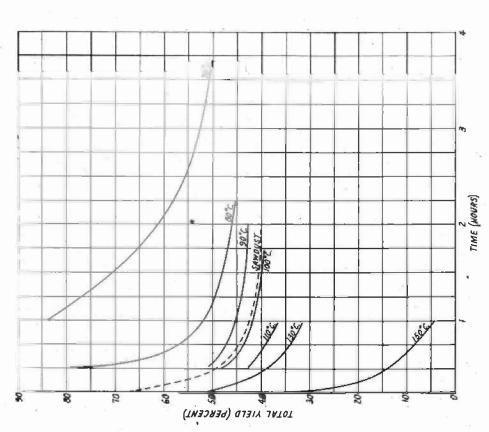


FIG. 1 2 M 43806 F

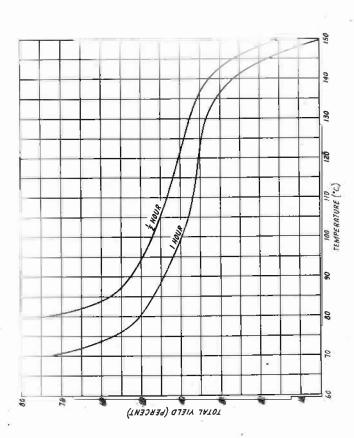
SCREENINGS (PERCENT)

SOREENINGS (PERCENT)

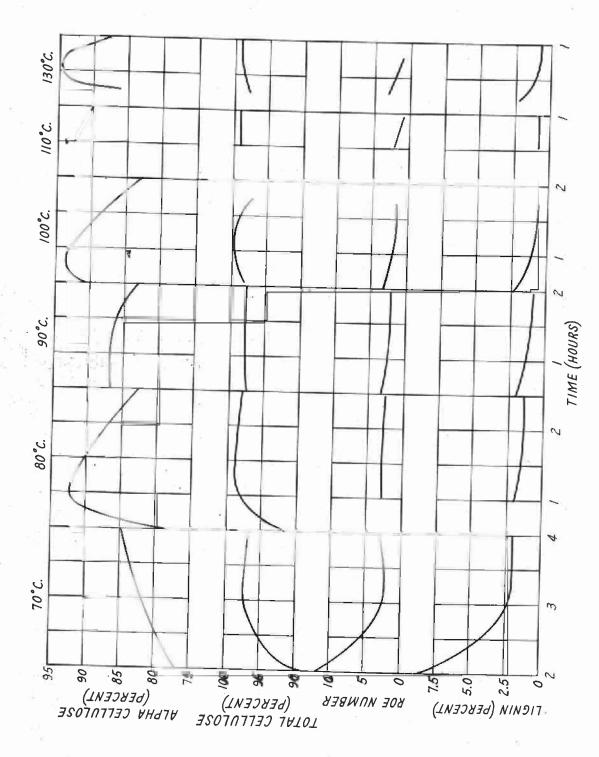
SCREENINGS (PERCENT)

FIG. 3 EFFECT OF TEMPERATURE ON THE TOTAL VIELD OF PULP

FIG. 4
EFFECT OF TEMPERATURE ON YIELD OF PULP SCREENINGS



Z N 4 3807 F



EFFECT OF TIME ON THE CHEMICAL CONSTANTS AT VARIOUS TEMPERATURES F16.5 Z M 43808 F