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A Study of the Coloring Matter in Fine Kraft Pulps

by Walter Frank Holzer

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A STUDY OF THE COLORING MATTER IN PINE KRAFT PULPS

A thesis submitted by

Walter Frank Holzer

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M.S., 1932, Lawrence College

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CHAPTER I.

INTRODUCTION

When wood is cooked by the kraft process, that is, with a liquor containing sodium hydroxide and sodium sulfide, the resulting pulp has a characteristic red brown color. It might be said that this pulp is noted for two things: first, its strength, and second, its resistance to bleaching. Even to-day what is considered a well bleached kraft still retains a marked yellow cast, for it is only by special bleaching and other chemical treatment of specially cooked kraft pulp that a bleached stock of good strength, satisfactory chemical constants, and high color can be secured. The cost of such treatment prohibits the general use of the product.

Those engaged in the manufacture of kraft pulp have considered that the color was due to sulfur dyes since the conditions in the digester are favorable to the formation of such compounds. It was not until 1933 that anyone attempted to actually determine the chemical nature of the coloring matter. Kuestel (4) definitely opened the problem when he presented his results which linked the color matter with the phlobaphenes and their derivatives, the phlobaphenins. His conclusions satisfy the color reactions of the pulp, but his treatment of the possibility of the presence of sulfur compounds and their influence on bleaching is by no
means complete. Further than this, his work was definitely limited to the identification of the coloring matter.

It is generally known in the industry that the atmosphere in a kraft digester is reducing in nature and that the pulp, when first dumped, is light yellow in color. This light color is stable when the stock is dry, but a short exposure in the wet state to air or to dissolved oxygen is sufficient to oxidize it to the well-known red brown color. Two methods are in use to produce a light colored kraft without bleaching. One is to overcook the pulp, but this gives a soft stock and reduces the yield. The second is to wash the pulp with dilute white liquor which is an expensive and questionable process. The use of hydro-sulfites in a reduction bleach is finding some favor, but here again we encounter the instability of the reduced form of these compounds for re-oxidation takes place to a greater or less degree during the paper making process, especially after the addition of the alkaline size. This instability outweighs in part the advantages of the reduction bleach. namely, low cost, ease of operation, and absence of the deterioration of the pulp. If some means of stabilizing the reduced form of the coloring matter could be devised, bright colors could be built on kraft without resort to the more costly and more harmful chlorine bleach. It might be added that since the reduced form, as already noted, is stable when dry, a partial inhibition of the oxidation is all that is necessary. A means of retarding the reaction long enough to allow the pulp to be converted to paper would be just as effective as a more permanent stabilization.
It will be the object of this work, therefore, to study the chemistry of the coloring matter of kraft pulp insofar as concerns the presence and influence of sulfur compounds and to attempt to carry the general chemistry a step further by studying the oxidation-reduction relations of the substance and the possibility of inhibiting the oxidation reaction.
CHAPTER II.

HISTORICAL.

It will be of interest to review in a very general way the evolution of the desired qualities in kraft pulp and to point out the more important points which shaped the course.

The kraft or sulfate process is the newest of all the common commercial methods of pulping. It is really a modification of the older soda process and was introduced by Dahl in 1896. To-day it is one of the three most important processes, chiefly because kraft is the strongest of all the wood pulps and second because woods unsuitable for other processes can be pulped by this one. The pulp has a characteristic red brown color which is very difficult to bleach. This has limited its use to papers in which strength was required and color was of minor importance. Until recently, this limitation has caused no difficulty. In fact as late as 1915 a considerable tonnage of dyed paper made from sulfate pulp was sold as kraft because the supply of regular kraft was insufficient to meet the demand. It is only natural that this seemingly insatiable demand should cause an uncurbed expansion in the kraft industry until now the mill capacity is in excess of demand.

During this same period of general expansion, the chemist, throughout the development of aniline dyes, has made the public color con-
scious. Unfortunately, the number and brightness of the colors that can be built on kraft are seriously limited by the dark color of the base stock. The producers of kraft have, therefore, been compelled to turn their efforts towards lightening the color of their pulp to retain their old markets, to say nothing of finding new ones for all the pulp they can produce.

Naturally the first attempts at color removal followed the existing practices of bleaching with hypochlorites. Semi-bleaching, the removal of the reddish brown color to produce a yellow colored stock on which certain fairly bright shades can be developed, is readily carried out at a minor cost and the resulting pulp is not seriously affected in strength. However, to produce a high white, even on the reddish cost, is expensive and the pulp is deteriorated in quality. The kraft has lost its premium of strength and can be substituted by bleached Mitscherlich sulfite at a lower cost. To produce a high white on kraft which approaches bleached sulfite in color without destroying the strength requires an expensive and complicated process so that the resulting pulp is high priced and limited from that standpoint in its sale. Naturally these obstacles have retarded the commercial development of the bleaching of kraft and the mills have waited for the research laboratories to devise simpler and less expensive processes.

The first mention of bleached kraft in the literature is made in 1912, when it was reported that kraft could be bleached to a high white with little loss in strength by allowing 5 per cent of hypochlorite
to stand on it for 24 hours and then treating with an additional 18
per cent of bleach. Baker and Jennison (9) studied the variables
in the bleaching of kraft in order that they might standardize the
procedure. They claimed to have obtained good color, but made no
report of strengths. Sutermeister (21) found that the addition of
small amounts of bleach to kraft decreased its strength, but that
larger amounts increased the strength over that of the original. A
maximum was reached at 32 per cent bleach powder. Michael-Jaffard
(15) was probably the first to report the application of chlorination
to kraft bleaching. With chlorination followed by alkaline extractions,
he obtained whites superior to those in hypochlorite bleaching.

After these early investigations, the development of kraft
bleaching has followed the general trend. By the development of suit-
able equipment Wolf (73) made high density bleaching commercially
feasible. The earlier bleach was modified and improved by Fletcher (12)
and by Collins (2). There is no need to give a detailed discussion of
the advantages of high density bleaching --- they are well known. Suffice
to say that these advantages are particularly helpful in the treatment of
kraft. Multistage bleaching was the next development and has been fol-
lowed more recently by the combination of a stage of direct chlorination
with a second of a high density hypochlorite bleach.

Wells (22) made a study of the cooking and bleaching of coni-
fereous woods by the kraft process. He found that more could be gained in
the yield and quality of bleached pulp by modifying the bleaching process
than by modifying the cooking. His best results were obtained in two stage bleaching. In this paper we find the first expression of the belief that the coloring matter in kraft is due rather to a small amount of coloring matter in the nature of a dye than to lignin. Kress and Davis (16) carried out a study of bleaching kraft by using direct chlorination in the first stage, following with an alkaline wash, and finishing with a high density hypochlorite stage. Good whites were obtained without loss of strength when the second stage was kept alkaline with caustic soda. The color was inferior when lime was used in place of caustic. 

Cirves (10) recommends a two-stage bleach when the best color and highest strength are required. Hae and Soong (20) obtained the best color at no sacrifice in strength when using direct chlorination followed by a high density hypochlorite bleach.

A second method of lightening the color of kraft pulp is the so-called reduction bleach first employed by Kress (6). This process describes an initial semi-bleach using sulfites or hydroxysulfites, followed by a high density hypochlorite stage to produce high whites. Later Kress (15) was granted a Canadian patent and Hirshkind (13) an American patent on the use of hydroxysulfites alone as a means of semi-bleaching kraft. Kress forms the hydroxysulfite in contact with the pulp by adding zinc dust, sodium bisulfite, and sulfuric acid in that order. Hirshkind adds the commercially prepared zinc hydroxysulfite to the pulp.

Knappel (4) has done the first work on the chemical nature of the coloring matter in kraft pulp. This thesis was made available to us prior to publication through the courtesy of Dr. G. E. Curran of the
U. S. Forest Products Laboratory, Madison, Wisconsin. Coloring matter was extracted from pulp and from black liquor, and was purified through the lead salt. When dyed on bleached cotton, it showed all the characteristics of kraft coloring, and, chemically, it showed all the color reactions of the phenobatans. From this Kostel concluded that the coloring matter was primarily due to tannins and that sulfur compounds and lignin had only a secondary effect.

A study on the alkaline hydrolysis of lignin is included here, not so much because it has a direct bearing on this work, but rather because it suggests some interesting possibilities which will be discussed later. König and Punge (114) digested some lignosulfonic acid in barium hydroxide solution for several hours. The yellowish brown precipitate which was formed was filtered off. The solution was saturated with carbon dioxide to precipitate the barium and liberate the acid. Since it contained twice as much barium as needed to react with the sulfonic acid group, it was apparent that the substance contained a carboxyl group. The solution had an astringent taste similar to tannic acid and behaved like a tannin of the catechol group with the exception of a red brown coloration with ferric chloride (instead of greenish black) and of no precipitate with bromine water. The residue on evaporation was a yellowish brown powder which contained sulfur.
CHAPTER III.

THEORETICAL DISCUSSION.

A. TESTS FOR HOMOGENEITY OF THE COLORING MATTER.

One of the most baffling features in working with natural products is to devise a means of testing the homogeneity of the material under study. The common chemical method alternately determining physical constants and purifying by some means is usually inapplicable on account of the polymeric nature of the materials. Mixtures of different polymers of the same substance or of different substances of similar nature sometimes defy all attempts of separation and purification.

The measurement of the absorption spectrum of a colored compound is one of the accepted methods of identification in organic chemistry. That is, if an unknown has the same absorption spectrum as a known, very little additional evidence is needed to confirm its identity. The same might be said of two unknowns. If they show the same absorption spectrum, it is most likely that they are identical, although it is not possible to establish the exact identity of either. If, then, the substance under consideration may be a mixture, one way of testing it would be to isolate it from two different sources and by two different methods. Under these conditions it is unlikely that the various components would be present in exactly the same proportions and these variations
would change the absorption spectra.

In this study one of the first problems was to test the homogeneity of the extracted coloring matter. To do this two preparations were made. One was isolated from black liquor by means of the local salt. The other was extracted from pulp with solidified and alcohol. Absorption spectra and, more particularly, curves showing the width of the band of light transmitted as a function of concentration showed that there is little if any difference in the two preparations. Further confirmation is added by the study of color change with pH.

The coloring matter exhibits what is probably a tautomeric color change with change of pH. In alkaline solution it is a dark mahogany red which changes to a light yellowish brown in acid. The per cent change with change of pH was determined with buffers and a colorimeter and was found to be almost identical for the two preparations. The agreement would indicate that the two extracts are the same substance and under the conditions of their preparation are not a mixture. It must, however, be recognized that the coloring matter is in all probability polymeric in nature. It would, of course, be impossible from the above tests to assume that the extract is pure from the polymeric standpoint; that is, that all chains are of equal length. The statement as to purity refers only to the repeating unit and even here the final result may be only an average; that is, during formation or extraction some of the repeating units may have lost some of their modifying groups. These irregularities are inherent in polymeric compounds especially natural ones and it is only with these qualifications in mind that the above statement regarding
purity is made.

3. TANNINS AND THEIR RELATION TO THE COLOR OF KRAFT PULP.

According to Kustiel the coloring of kraft pulp is due to tannins and more particularly to phlobatannins. He discredits the idea that sulfur dyes are an important factor since, in the soda cook where no sulfur is used, the pulp has a similar brownish color.

Tannins are substances which are found in almost all plants, especially of the higher orders. Nothing is known of their origin; theories as to their function differ; and even their definition and classification are subject to argument. In general tannins are compounds which

1. Give bluish or greenish coloration to ferric chloride.
2. Have an astringent taste.
3. Are precipitated by gelatine, albumen, and certain alkaloids.
4. Have the property of converting hides to leather.
5. Contain certain aromatic nuclei.

One can easily understand that the chemistry of a group, whose definition is so vague, is still far from complete. However, considerable work, both analytical and synthetical, has been done on the more common members of the group. On the basis of this work Perkin (5) suggests the following classification of tannins:
1. Depsides - Tannins containing an aromatic nucleus consisting of two or more molecules of a phenol carboxylic acid joined through a hydroxy of one molecule to the carbonyl of the next. The commonest members of this group are gallotannins characterized by digallic acid.

![Depsides Diagram]

2. Diphenyllactones - Tannins containing allagia acid or a related compound as the aromatic nucleus.

3. Phlobotanins - Tannins which on boiling with dilute mineral acid precipitate insoluble red substances known as phlobaphenes.

The class to which an unknown belongs is determined by qualitative tests. Since previous work has pointed out that the coloring matter in kraft belongs to the third group, we will confine the discussion to that group.

Phlobotanins show the following reactions:

1. FeCl₃ - Greemish black coloration.
2. Bromine water - Orange precipitate.
3. Concentrated H₂SO₄ - Purple ring at the junction of the liquids.
4. Boiling dilute H₂SO₄ - Red precipitate or phlobaphenes.

The extracts gave positive tests in all the above cases except that the precipitate with the boiling acid was almost black instead of
red. This is direct confirmation of Kuebel's work. In addition, some of the extract was treated with bleach liquor. A large excess bleached the color to a yellow, but enormous amounts were required to decolorize completely the solution. This is further indication that these extracts are the cause of the difficulty in bleaching kraft.

G. RELATION OF SULFUR TO THE COLORING IN KRAFT PULP:

A special extraction of pulp was made with acidified amyl alcohol to obtain material for an organic sulfur analyses. The extract was not purified by means of the lead salt, since K2S is used in removing the lead and any sulfur analyses on the final product would then be meaningless. The extract was ash free but did contain appreciable amounts of sulfur. Since any inorganic sulfur would have formed an ash, all the sulfur present was organic. The presence of organic sulfur in the extract constitutes the chief difference between the coloring matter in kraft and phosphateins. Since the term "sulfur dye" can be applied to almost any organic compound that has been cooked with sodium sulfide or sulfur and has added sulfur as a result of the process, there appears to be sufficient justification in applying this name commercially to the coloring matter in kraft pulp. Further, sulfur or vat dyes are soluble only in alkali sulfides and in this solution are in a reduced leuco state. The extract exhibits anomalous behavior in being soluble in alkalis and capable of being reduced and reoxidized, thereby making the
relatiion to sulfur dyes more evident.

The work on sulfur in kraft was continued by making a series of four cooks in which the sulfidity was varied from 0 - 100 per cent. In the first place the color of the cooks varied with the sulfidity, soda pulp being the lightest, normal kraft much darker, and the high sulfide cooks increasingly dark. At the same time the organic sulfur increased regularly with the sulfidity of the cooking liquor. A series of alternate bleaches and alkaline extractions ending with a high white without regard to strength showed that the sulfur content of pulp was roughly proportional to the color yet undestroyed.

D. THEORY OF OXIDATION-REDUCTION POTENTIALS AND THEIR APPLICATION TO THE COLORING MATTER

When tannin solutions are exposed to the air, especially in the alkaline condition, they absorb oxygen and become dark. The dark oxidized solution can be reduced by such agents as hydrosulfites, titanic salts, etc.

Clark (6) has developed a method for studying oxidation-reduction reactions whereby the tendency of a substance to oxidize or reduce is referred to a relative scale of potentials. On this scale the more powerful oxidizing agents will have a greater oxidation potential and vice versa. The potential is determined by measuring the RHF
between a noble metal electrode and a standard reference electrode, both dipping in a solution of a substance capable of being oxidized or reduced while adding known amounts of an oxidizing or a reducing agent. It will be helpful to present in condensed form the theoretical relations as derived by Clark.

The accepted definition of oxidation states that it is the process by which an atom loses one or more electrons and reduction is the process by which the atom gains electrons. In many cases this can be stated as an equilibrium reaction such as:

$$\text{Fe}^{++} + e^- \rightarrow \text{Fe}^{++},$$

Or more generally

$$\text{Ox.} + ne \rightarrow \text{Red.},$$

where,

$$\text{Ox.} = \text{oxidant}$$

and

$$\text{Red.} = \text{reductant}.$$  

Then from the mass action law

$$\frac{[\text{Ox.}][e^n]}{[\text{Red.}]} = K.$$

Rearranging,

$$[e^n] = \frac{K[\text{Red.}]}{[\text{Ox.}]} = K$$

(1)

It will not be necessary to derive the well-known equation for the potential of an electrode which may be written

$$E = \text{O} + \frac{R}{T} \ln [e^n],$$

(2)
where \( C' \) is a constant depending upon the electrode, \( [e^-] \) is the concentration of electrons in solution, and all other symbols have their usual values. If the value of \( [e^-] \) from (1) is substituted in (2), the equation becomes

\[ \eta = C' - \frac{RT}{pF} \ln \frac{[\text{Red.}]}{[\text{Ox.}]} \]

which may be written

\[ \eta = C' - \frac{RT}{pF} \ln \frac{[\text{Red.}]}{[\text{Ox.}]} \]

Now, if \( F \) is known, the ratio \( \frac{[\text{Red.}]}{[\text{Ox.}]} \) is determinable and \( \eta \) and \( T \) are measured, the expression \( C' - \frac{RT}{pF} \ln \frac{[\text{Red.}]}{[\text{Ox.}]} \) may be defined for a given system.

It is impractical to determine the absolute potential \( \eta \), but if two half cells are set up, the potential between them can be measured. Further, if one of these half cells is considered standard, definite voltages can be assigned to the cell and thus refer the tendency of a substance to oxidize or reduce to a scale of electrode potentials. In practice the potential of a platinum black electrode, saturated with hydrogen gas at atmospheric pressure and immersed in a solution at \( 25^\circ \text{C} \), in which the hydrogen ions are \( 1 \text{N} \), is referred to as zero. Now \( \eta_n \) can be substituted for \( \eta \), if \( \eta_n \) is defined as the difference between the observed potential and that of the standard electrode. Since \( C' = \frac{RT}{pF} \ln K \) is a constant for any system and is expressed in volts, \( \eta_n \) can be substituted for it. The equation then becomes:

\[ \eta_n = \eta_n - \frac{RT}{pF} \ln \frac{[\text{Red.}]}{[\text{Ox.}]} \]
when

\[ \text{[Red.]} = \text{[Ox.]} \]

then

\[ E_n = E_0 \]

Thus \( E_0 \) is the potential of the system when the oxidant and reductant are present in equal amounts and is accordingly defined as the oxidation potential of the system.

A cell of the type recommended by Clark and modified by Consat (11) was set up and by use of known compounds was tested and found to be working. However, stable potentials could not be obtained with a solution of the coloring matter. Similar behavior was observed when known phenol carboxylic acids were tested. This shows that the method is not valid for all types of compounds, among which are acids, a fact which is not reported in the literature. It further suggests that the coloring matter is acidic in nature.
CHAPTER IV.

EXPERIMENTAL PROCEDURES AND RESULTS.

A. COLORING MATTER.

1. Extraction.

The coloring matter was extracted from black liquor and from pulp according to the methods developed by Kustel (4).

Extraction of Coloring Matter from Black Liquor

Skim off any insoluble soaps and filter out any solids. Acidify the filtrate with HCl, avoiding a large excess. H$_2$S is evolved and a curdy chocolate brown precipitate is formed. When the evolution of H$_2$S becomes particularly copious, the solution is near the neutral point. The precipitate is filtered or centrifuged and the clear filtrate allowed to stand for several days. A fine precipitate of sulfur forms on standing and is separated by filtration. When no more sulfur separates, add an excess of lead acetate and filter the voluminous tan precipitate which forms. Wash the lead salt in hot water, dry, suspend in alcohol, and gas with H$_2$S. When all the lead has been converted to PbS, filter, and concentrate the reddish brown solution in warm. The final stages of the concentration should be carried out in a vacuum desiccator over concentrated sulfuric acid. The residue is a dark, red brown, viscous liquid which should be extracted repeatedly with boiling petroleum ether until only a powder is
Four liters of concentrated black liquor obtained from a nearby kraft mill running on jack pine were treated according to the procedure given above. It was found necessary to centrifuge the lead salts since they were so fine that no filter would hold them. When the concentrated extract was treated with petroleum ether, nothing was extracted, even on refluxing for several hours.

When petroleum ether failed to extract the resins, the following solvents were tried:

**Chloroform** - The coloring matter was partially soluble, but the residue was gummy.

**Ethyl ether, Turpentine, and Benzene** - Same as chloroform.

**Acetone, Ethyl acetate** - Coloring matter soluble.

Since no satisfactory results were obtained with pure solvents, mixtures were tried. In choosing solvents for the mixtures, one was taken in which the substance was completely soluble and one or more in which it was only partially soluble or insoluble. The following mixtures were tried:

**Ethyl alcohol and Petroleum ether** - Complete solution in the alcohol with reprecipitation as a gummy substance on the addition of petroleum ether.

**Ethyl alcohol and Turpentine** - Same as above.

**Ethyl acetate and Ethyl ether** - Same as above.

**Ethyl acetate, Acetone, and Turpentine** - Same as above.
Ethyl alcohol and Acetic Acid - No precipitate.

Removal of the resins was finally accomplished by precipitation with acids. The coloring matter could be dissolved in very dilute ammonia and on making slightly acid, a yellow flocculent precipitate separated and was filtered. The filtrate was a very pale yellow, but darkened to the original color on neutralization with ammonia. This solution showed all the color reactions described by Kuegel.

Small amounts of coloring matter could be extracted from pulp by use either of dilute sodium hydroxide or of acidified amyl alcohol. Kuegel recommends fusel oil, but none was immediately available and amyl alcohol was successfully substituted. The pulp was made from jack pine wood and was obtained from the above mentioned kraft mill along with the black liquor.

Extraction with Amyl Alcohol

Boil 200 grams of pulp with water for two to three hours to extract any soluble material. Drain the pulp as dry as possible on a suction and wash well. Reflux the extracted pulp for six hours with 100 cc. of 6N HCl, 300 cc. of amyl alcohol, and enough water to make the consistency about 6 per cent. The alcohol becomes colored and may be replaced with fresh reagents several times, repeating the refluxing each time. The combined alcohol extracts are washed thoroughly with distilled water to remove the acid and any soluble cellulose degradation products. The washed extract is vacuum distilled to a thick syrup, concentrated in
a vacuum over concentrated sulfuric acid for several days, and finally extracted with petroleum ether. The red brown product may be purified by means of the lead salt, but in this case it was not. On account of the small amounts of color that could be extracted from pulp, the use of this preparation was restricted to color curves and sulfur analyses. Of course, any use of HgS in connection with the removal of lead would have made the sulfur analyses meaningless.

**Extraction with Sodium Hydroxide**

Treat 200 grams of pulp with 2 per cent of sodium hydroxide for a week. Filter the liquor and neutralize. The filtrate was a reddish brown, which turned yellow on the addition of acid, a brownish flocculent precipitate settling out at the same time. The precipitate is filtered, washed, and dried in a vacuum desiccator over concentrated sulfuric acid.

2. **Color Absorption Curves.**

Spectrophotometric absorption curves were run on a Bausch and Lomb Universal Spectrophotometric outfit.

Since the color of the extracts was so sensitive to pH changes, it was necessary to control the hydrogen ion concentration quite carefully. This was done by making the solution slightly ammoniacal and boiling until the last traces were expelled. Any excess acidity was, of course, neutralized by the ammonia and the excess alkalinity could be boiled
off. The solutions were checked with litmus to see that no fixed alkalis were present.

On account of the method of purification (precipitating the resins with acid), it was impractical to adjust the concentration to a definite weight per unit volume. Accordingly, the concentration of one was adjusted so that a reading on the spectrophotometer could be made fairly well into the blue. The second was adjusted so that the reading at 600 millimicrons was very nearly the same as that of the first. Readings of the per cent transmission were taken at intervals of 20 millimicrons from 460 - 720 millimicrons. Every reading recorded below was the average of at least three but more often four or five matches with the spectrophotometer. The results are recorded in Table I and are shown in Figure I.

### Table I

**Transmission of Light by Kraft Extracts According to Wavelength**

<table>
<thead>
<tr>
<th>Wavelength (Millimicrons)</th>
<th>% Transmission Poly Extract</th>
<th>% Transmission Liquefied Extract</th>
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<tbody>
<tr>
<td>480</td>
<td>0.77</td>
<td>0.2</td>
</tr>
<tr>
<td>500</td>
<td>2.10</td>
<td>0.9</td>
</tr>
<tr>
<td>520</td>
<td>5.70</td>
<td>6.5</td>
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<tr>
<td>540</td>
<td>13.30</td>
<td>16.5</td>
</tr>
<tr>
<td>560</td>
<td>24.00</td>
<td>27.2</td>
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<td>50.2</td>
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<tr>
<td>640</td>
<td>65.20</td>
<td>57.2</td>
</tr>
<tr>
<td>660</td>
<td>71.40</td>
<td>59.6</td>
</tr>
<tr>
<td>680</td>
<td>74.40</td>
<td>65.0</td>
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<tr>
<td>700</td>
<td>78.40</td>
<td>68.6</td>
</tr>
<tr>
<td>720</td>
<td>81.60</td>
<td>66.7</td>
</tr>
</tbody>
</table>
FIGURE 1.

SPECROPHOTOMETRIC ABSORPTION CURVES OF WAFF ELUENTS.

Wave Length in Millimicrons.
The two curves show a striking similarity. When we consider that it was not feasible to adjust the concentration more accurately and further that there is a large inherent error in any determination that depends solely on the visual matching of colors, the difference in the two curves does not appear very large.

The effect of concentration was eliminated in another way. The wavelength of the point of total absorption of light by the extracts was determined and its change with concentration was followed. The constant deviation spectrometer was removed from the spectrophotometer outfit. A tube containing the solution was mounted in front of the slit and illumination was obtained from a 6-volt lamp lighted by a storage battery. The original concentration in the tube was adjusted so that a band of light was just visible where transmission was greatest. Readings were taken at the limits of visibility on both edges of the band. The solution was diluted by a known amount and readings were taken showing how the width of the band had increased. The process was repeated until further dilution showed very little increase in the width of the band. The readings in the longer wave lengths were limited to 800 millimicrons by the scale of the spectroscope. This was not serious, however, since 800 millimicrons is practically the upper limit of the visible spectrum.

The figures reported are an average of at least three or four settings. Those for the black liquor extract are given in Table II and for the pulp extract in Table III. The volume of the cell was 23 cc.
### TABLE II.

**CHANGE OF POINTS OF TOTAL ABSORPTION OF LIGHT WITH DILUTION.**

<table>
<thead>
<tr>
<th>Number of Dilutions</th>
<th>Total Volume</th>
<th>Limits of Visibility in Millimicrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>23</td>
<td>627</td>
</tr>
<tr>
<td>1.1</td>
<td>30</td>
<td>612</td>
</tr>
<tr>
<td>2.0</td>
<td>46</td>
<td>564</td>
</tr>
<tr>
<td>5.0</td>
<td>69</td>
<td>568</td>
</tr>
<tr>
<td>4.0</td>
<td>92</td>
<td>552</td>
</tr>
<tr>
<td>5.0</td>
<td>135</td>
<td>545</td>
</tr>
<tr>
<td>7.0</td>
<td>161</td>
<td>525</td>
</tr>
<tr>
<td>9.0</td>
<td>207</td>
<td>510</td>
</tr>
<tr>
<td>12.0</td>
<td>276</td>
<td>500</td>
</tr>
<tr>
<td>20.0</td>
<td>460</td>
<td>470</td>
</tr>
</tbody>
</table>

### TABLE III.

**CHANGE OF POINTS OF TOTAL ABSORPTION OF LIGHT WITH DILUTION.**

<table>
<thead>
<tr>
<th>Number of Dilutions</th>
<th>Total Volume</th>
<th>Limits of Visibility in Millimicrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23</td>
<td>617</td>
</tr>
<tr>
<td>2</td>
<td>46</td>
<td>564</td>
</tr>
<tr>
<td>3</td>
<td>69</td>
<td>568</td>
</tr>
<tr>
<td>5</td>
<td>92</td>
<td>568</td>
</tr>
<tr>
<td>7</td>
<td>135</td>
<td>552</td>
</tr>
<tr>
<td>9</td>
<td>161</td>
<td>545</td>
</tr>
<tr>
<td>12</td>
<td>207</td>
<td>525</td>
</tr>
<tr>
<td>20</td>
<td>276</td>
<td>510</td>
</tr>
</tbody>
</table>
The two solutions were not at the same concentration at the start and had to be corrected before direct comparison could be made. After the last dilution the two solutions were compared on a Du Bosquet-type colorimeter and the pulp extract was found to be 10 per cent stronger than the black liquor extract. Correcting for this, the 276 cc of pulp extract were equivalent to 304 cc. of the liquor extract at its final dilution. If the original concentration of the black liquor be taken as standard,

\[
\frac{304}{276} = \frac{x}{23},
\]

then

\[x = 15.2.\]

The original volume of each was 23 cc., but the coloring matter in the pulp extract was equivalent to only 15.2 cc. of the liquor extract. Now by dividing the actual volume of the pulp extract by 15.2, the apparent dilution in terms of the black liquor extract are obtained.

**TABLE IV.**

<table>
<thead>
<tr>
<th>Volume in cc.</th>
<th>Equivalent Dilutions Volume / 15.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>1.51</td>
</tr>
<tr>
<td>45</td>
<td>3.02</td>
</tr>
<tr>
<td>69</td>
<td>4.53</td>
</tr>
<tr>
<td>92</td>
<td>6.06</td>
</tr>
<tr>
<td>115</td>
<td>7.59</td>
</tr>
<tr>
<td>161</td>
<td>10.57</td>
</tr>
<tr>
<td>207</td>
<td>13.59</td>
</tr>
<tr>
<td>276</td>
<td>18.12</td>
</tr>
</tbody>
</table>
After applying the corrections in Table IV to the data
in Table III, the results along with those in Table II are shown in
Figure II. It is easily seen that when the effects of difference
in concentration are eliminated, the similarity of the curves of the
two preparations is even more striking. When allowance is made for
the probable 3 - 5 per cent error in readings due to the inherent
inaccuracy of such optical measurements, the differences between the
two curves become negligible and it seems safe to assume that the color-
ing matter is an individual compound rather than a mixture.

Further evidence was obtained by studying the relation between
color change and pH. Slightly on the acid side of the neutral point,
the color of the extracts changes from a dark red brown to a much lighter
brownish yellow. The change when examined in a colorimeter is not as
sharp as that of dyes chosen for indicators. In the latter case most of
the change takes place within two pH units. Appreciable changes were
found in the coloring matter under study from pH 3 to pH 11. The sharpest
changes, however, were between pH 6 and pH 7 and again between pH 4 and
pH 5. The measurements were made as follows:

One cc. of the extract placed in 10 cc. of each known
buffer of the range to be studied (in this case pH 3
to pH 11). Samples of two consecutive buffers, e.g.,
pH 10 and pH 11 are placed in a colorimeter and are
matched. The higher buffer is then removed and replaced
by the one next lower than the one remaining. In the
above pH 11 is replaced by pH 9 and another match is
made. The process is repeated until all samples have
been compared. Since the change is more one of lightening rather than a change of color and since the change per pH unit is comparatively small in most cases, fairly accurate readings of the relative amount of change can be taken by this method. The darkest sample, that is the most alkaline, can be taken as 100 per cent and the others can be expressed in relative percentages of the first. Table V lists these readings. Graphs are given in Figure III.

**TABLE V.**

PER CENT CHANGE IN KRAFT COLORING MATTER WITH pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Black Liquor Extract</th>
<th>Pulp Extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5</td>
<td>100 per cent</td>
<td>100 per cent</td>
</tr>
<tr>
<td>9.5</td>
<td>92 per cent</td>
<td>90 per cent</td>
</tr>
<tr>
<td>7.7</td>
<td>80 per cent</td>
<td>81 per cent</td>
</tr>
<tr>
<td>6.9</td>
<td>72 per cent</td>
<td>72.5 per cent</td>
</tr>
<tr>
<td>6.1</td>
<td>48 per cent</td>
<td>52 per cent</td>
</tr>
<tr>
<td>5.0</td>
<td>47.5 per cent</td>
<td>46 per cent</td>
</tr>
<tr>
<td>3.8</td>
<td>26 per cent</td>
<td>26.5 per cent</td>
</tr>
<tr>
<td>2.8</td>
<td>22 per cent</td>
<td>20 per cent</td>
</tr>
</tbody>
</table>

As has been pointed out, it is highly improbable that a mixture of compounds will be extracted in the same ratio from different sources using different procedures. Further, it is just as improbable that two compounds, even of similar nature, would exhibit such close agreement in two different properties. This close agreement of the two preparations in the two properties, absorption of light and change of color with pH, can be taken, therefore, as conclusive evidence that the coloring in kraft
FIGURE III.

CHANGE OF COLOR WITH pH.

X-rayt Extract
OMGneq Extract

Per Cent of Original

0 10 20 30 40 50 60 70 80 90 100

pH

2 3 4 5 6 7 8 9 10 11
pulp is due primarily to a single compound and that this compound can be extracted either from the spent liquor or from the pulp itself. Here again, the term "single compound" is used with the qualification made earlier. It does not refer to the polymeric purity but only to the structure of the major repeating unit. From this point on, all work was done with black liquor extract since it could be prepared in larger amounts.


The chemistry and classification of tannins are vague at best, but there are some reactions which appear to be specific, when taken as a group, for each class. The black liquor extract gave positive reactions with these tests used in identifying the phlobatannins: namely,

1) FeCl₃ - Greenish black coloration.
2) Saturated bromine water - Orange precipitate.
3) Concentrated H₂SO₄ - Purple ring at the junction of the two liquids.
4) Boiling dilute mineral acid - Dark precipitate.

In this case the precipitate is much darker than the one expected, being almost black instead of red. The most probable explanation of this is that the extract is a tannin derivative rather than the original compound. This will be discussed later.

From these color reactions it is logical to classify the coloring matter as a phlobatannin as Knittel, who has gone into this phase more thoroughly, has done.
Some further qualitative reactions are of interest. A small amount of cotton was soaked in the black liquor extract for a few minutes and dried. In color it approached very closely that of kraft, being only slightly yellower, and behaved with acids, reducing agents, and bleach liquor in the same manner as kraft pulp. The experiments with bleach liquor were carried further by adding 10 drops of hypochlorite (30 g.p.l.) to one cc. of the extract. On the basis of solid materials this must have been a large excess of bleach, yet the extract was only half decolorized. An enormous excess of bleach, about 3 cc. of the concentrated liquor, was required to remove completely the color from one cc. of the extract. It was noticed in the case of partial bleaching that there was a tan precipitate when the hypochlorite was exhausted and that the solution was neutral. The sample was shook and divided into two equal portions. One was made alkaline with filtered lime water; the other, with dilute soda hydroxide. The lime water partially dissolved the precipitate, but the caustic completely dissolved it. This is direct confirmation of the work of Kress and Davis. The more recent trend is toward an alkaline bleach, especially in the last stage. Kress and Davis (16) found that in the bleaching of kraft a better color was obtained when the high density hypochlorite stage was kept alkaline and that much better results were obtained with sodium hydroxide than with calcium hydroxide. Previous work on the pH of bleaching with the glass electrode (3) shows that as a hypochlorite bleach nears exhaustion, it passes the neutral point and becomes very slightly acid. The usual end point is at a pH of 6.7 - 6.9. Apparently the bleach forms a com-
pound with the coloring matter that is soluble in strong alkali, but becomes insoluble in neutral solutions. If the bleach is kept alkaline, the color matter is rendered soluble and can be washed out. If the bleach is allowed to become neutral or is kept alkaline with a weak alkali such as lime, the coloring matter is precipitated on the fiber and can be removed only by bleaching. This requires enormous amounts of bleach which is harmful to the fiber. All recent developments in bleaching emphasize the importance of rendering the lignin and coloring matters soluble and washing them out rather than actually bleaching them. Advantages are twofold: first, chemical requirements are lower, and second, the product is superior in quality.


Wherever this study has paralleled the work of Knittel, it has confirmed the earlier work on the more important points. The actual coloring matter has been extracted and its reactions studied as was done before. In addition it has been shown through physical properties that the coloring matter is a single compound and some relations to bleaching ability have been discussed. The question of the presence and influence of organic sulfur in the coloring matter of kraft pulp still remains to be discussed.

It has been mentioned earlier that kraft operators have usually attributed the color of kraft pulp to sulfur dyes. These compounds are formed by heating vegetable material or organic compounds with sodium
sulfide either without or with sodium hydrosulfite and either dry or wet, depending upon the conditions needed by the particular dye required. Dyes of this type are soluble only in alkaline sulfide solutions and are applied to vegetable fibers in hot baths containing sodium hydrosulfite and sodium sulfite. The color in the vat is in the reduced form and develops full strength only after being oxidized by the air.

When the conditions under which kraft pulp is made are checked against those given above, it is seen that they are favorable to the formation of sulfur dyes and the fixation of these on the pulp. Wood is cooked at a temperature as high as 165°F. in a liquor containing 10 per cent sodium hydrosulfite and 5 per cent sodium sulfite. While the conditions are not drastic enough to form dyes in commercial quantities, they are ideal for the fixation of any dye that is formed. Further, the development of the color on oxidation is analogous to that step encountered in the application of sulfur dyes. It is only natural under these circumstances that the formation of sulfur dyes has been accepted as the cause of the color without proof or argument.

Samples of a number of sulfur dyes were obtained from the E. I. du Pont de Nemours & Company, Inc. Several of the samples were dialyzed in a cellophane membrane to remove the excess of inorganic salts and elemental sulfur was removed by extraction with carbon disulfide. After dialysis they were stable in acid, some even on boiling. When applied to pulp from an alkaline bath they exhibited the same behavior towards reducing agents, and the same resistance to bleaching as does kraft pulp.
Sulfur can be determined in organic compounds by the well-known method of fusing with sodium peroxide and precipitating the sulfates thus formed with barium chloride in the usual manner. The coloring matter in kraft pulp was tested for sulfur by the following procedure:

About 500 grams of commercial kraft pulp are boiled with distilled water for three hours to remove any soluble material and the pulp is washed with hot distilled water until the filtrate is almost colorless. The washed pulp is extracted with amy1 alcohol and hypochloric acid and the coloring matter is recovered as described under the extraction of coloring matter from pulp. The residue is not purified by means of the lead salt since the use of Eos in the removal of lead would render only subsequent sulfur determinations valueless. The residue is divided into two parts. One part is ashed and the other is fused with sodium peroxide to determine the total sulfur. By subtracting the inorganic sulfur in the ash from the total sulfur found after oxidation, the organic sulfur is determined.

Kraft pulp is produced under alkaline conditions and any inorganic sulfur present after a reasonable exposure to the air would be present as sodium sulfate, or possibly calcium sulfate. Both of these
compounds are stable during ashing so that any that may be present would be found in the ash. Analysis of coloring matter extracted from kraft pulp by amyl alcohol, and not purified with lead, gave the following results:

<table>
<thead>
<tr>
<th>Per Cent Ash</th>
<th>0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Per Cent Sulfur from</td>
<td>0.78</td>
</tr>
<tr>
<td>Na₂O₂ fusion</td>
<td></td>
</tr>
</tbody>
</table>

The ash was so small that it was not analyzed. Even if it contained sulfur or were the product of the decomposition of a sulfate, the amount would be insignificant compared to the amount of sulfur found after oxidation. There is definite proof that the coloring matter in kraft contains appreciable amounts of organic sulfur and can accordingly be called a sulfur dye.

Lignin was isolated by Mr. Ward D. Harrison of the Institute of Paper Chemistry from black liquor obtained for this study and was found to contain 9.1 per cent sulfur. The lignin was isolated by precipitating with acid, filtering, and washing thoroughly over an extended period of time. A sample was kindly furnished for further study. It was insoluble in water, slightly soluble in alcohol, and readily soluble in fairly strong ammonia, reprecipitating on neutralization. An ammonical solution of the lignin was compared with an ammoniacal solution of the coloring matter on the General Electric Recording Color Analyzer. A copy of the curve is given in Figure IV and shows that the solutions are quite different, the lignin solution being much more yellow.
This recalls the above reference to the work of König and Fuchs (14) on alkaline hydrolysates of lignin. To repeat, they hydrolyzed lignin sulfonic acid with barium hydroxide and obtained a sulfur containing product, which gave many of the reactions ascribed to phlobotannins. The case history was greatly different from that of the coloring extract from kraft and for that reason a direct comparison is questionable. Furthermore, the kind of wood from which their lignin was obtained was not mentioned. However, since their product did not give two of the important classification reactions of the phlobotannins, that is, a red coloration with ferric chloride instead of the usual greenish black and no precipitate with bromine water, it is doubtful whether lignin can be seriously considered as a source of the coloring matter under discussion. The possibility has not been eliminated and the subject of the possible relation between tannins and lignin suggests interesting possibilities for future work.

In the light of this study, confirmed in some points by previous work, it can be said that the coloring matter in pine kraft pulps is an individual compound of the nature of a sulfur dye which reacts similarly to the phlobotannins.

B. RELATION OF ORGANIC SULFUR TO THE COLOR AND BLEACHING OF KRAFT PULP.

The theory that the color in kraft pulp is due to sulfur dyes has often been discredited by the fact that soda pulp, in whose production
no sulfur is used, has a similar brown color. If it is true that the coloring in kraft is due to a sulfur derivative of a tannin or some other complex organic compound, the color of soda in all probability is caused by the tannin or complex organic compound itself. In order to gain additional data on the relation of organic sulfur to the color in kraft and point out any differences between soda and kraft, the following series of cooks was made:

1) Soda cook - 20 lb. NaOH / 100 lb. wood.
2) Kraft cook - 17-1/3 lb. NaOH + 6-7/3 lb. MgCl₂ / 100 lb. wood.
3) High sulfide kraft cook - 10 lb. NaOH + 15 lb. MgCl₂ / 100 lb. wood.
4) Sodium sulfide cook - 40 lb. MgCl₂ / 100 lb. wood.

Since sodium sulfide is not as active a pulping agent as sodium hydroxide, it was necessary to increase the ratio of chemical to wood when the sulfidity was raised above that of normal kraft in order that the pulping action might be maintained. It is well known that small traces of iron in the cooking liquor have a very deleterious effect on the color of pulp. For this reason the cooking liquor was filtered to remove the iron which had precipitated as the sulfide. For the same reason all cooks were made in stainless steel digesters.

Cooks were made in stationary chrome nickel steel autoclaves which have a capacity of 500 grams of bone dry wood. The autoclaves are supported on three legs high enough so that a gas burner can be placed underneath for indirect heating. The cover is held by eight 5/8" bolts
and the seal is made by a lead gasket. The cover is fitted with a 250 lb. pressure gauge, a thermometer well, and a blow-off valve. See Figure I.

FIGURE V.

AUTOCLAVE FOR EXPERIMENTAL COOKING

The significant data on the four cooks is given in Table VII.
### TABLE VII.

**COOKING DATA.**

<table>
<thead>
<tr>
<th>Cook number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moist weight of wood, grams</td>
<td>642.0</td>
<td>642.0</td>
<td>642</td>
<td>642</td>
</tr>
<tr>
<td>Dry weight of wood, grams</td>
<td>600.0</td>
<td>600.0</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Volume of cooking liquor, cc.</td>
<td>13200.0</td>
<td>13200.0</td>
<td>13200</td>
<td>13200</td>
</tr>
<tr>
<td>Concentration of liquor, g.p.1.</td>
<td>37.5</td>
<td>37.5</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Total cooking chemical, grams</td>
<td>120.0</td>
<td>120.0</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>NaOH, grams</td>
<td>120.0</td>
<td>80.0</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Na₂SO₃, grams</td>
<td>40.0</td>
<td>40.0</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Weight of chemical / 100 lb. dry wood</td>
<td>20.0</td>
<td>20.0</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>NaOH</td>
<td>20.0</td>
<td>12-1/3</td>
<td>12-1/3</td>
<td>12-1/3</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>20.0</td>
<td>12-1/3</td>
<td>12-1/3</td>
<td>12-1/3</td>
</tr>
<tr>
<td>Maximum pressure, lb. / sq. in.</td>
<td>115.0</td>
<td>115.0</td>
<td>115</td>
<td>115</td>
</tr>
<tr>
<td>Time to maximum pressure (minutes)</td>
<td>55.0</td>
<td>55.0</td>
<td>55.0</td>
<td>55.0</td>
</tr>
<tr>
<td>Time at maximum pressure (minutes)</td>
<td>190.0</td>
<td>185.0</td>
<td>190</td>
<td>190</td>
</tr>
<tr>
<td>Total time, hours</td>
<td>8.0</td>
<td>8.0</td>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>

All cooks were washed thoroughly on a screen immediately after dumping and were screened through a plate with 3/32" perforations. All four samples of pulp were well cooked, but No. 4 contained slightly more screenings than the rest. Since color and organic sulfur content were the only data required, no yields, screenings, physical tests, or chemical constants were run.

The pulps showed differences in color as might be expected. The soda cook was lightest, followed by the others. The difference between the soda and the normal kraft was the greatest between any two consecutive cooks. The color of the soda was a yellowish brown, whereas that of the kraft was darker and on the red side. The hue of the kraft cook was about the same but the color becomes darker as the sulfide in
the cooking liquor was increased. Samples are attached in Figure VI.

**FIGURE VI.**

**SAMPLES OF PULP SHOWING VARIATION OF COLOR WITH SULFIDITY OF COOKING LIQUOR**

<table>
<thead>
<tr>
<th>Cook No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

Reflection curves of the four pulps were run on the General Electric Recording Color Analyzer. There is a decided difference in the slope of the soda pulp and the kraft pulp. This is shown in the two graphs reproduced in Figure VII. The curves of the three krafts are so nearly identical that only one was reproduced. This supports the observation that the color is the same in hue, differing only in darkness.

The pulps were next analysed for organic sulfur. The method of determination, that of subtracting the sulfates found in the ash from those found after a HgO2 fusion, has already been discussed under the analysis of the color extract. Pulps which were analysed for organic sulfur were electrodialysed to reduce the inorganic ash content as much
as possible. This was done in a redwood box 12" x 12" x 12". In the
center a cell 12" x 12" x 12" was constructed by stretching cheesecloth
over a frame fastened to the sides of the box. On either side of the
cell a carbon electrode 3" x 8" was suspended and in back of each
electrode an overflow outlet was arranged. The pulp to be dialysed was
dispersed in water and placed in the center cell. Distilled water was
run into the cell and overflowed in back of the electrodes. An EMF
of 150 volts D.C. could be impressed on the electrodes. This forced a
current of 0.2 - 0.5 amperes through the cell. The procedure used with
the pulp is as follows:

Before analysis about 70 grams of pulp (dry weight) is
placed in the dialyser described above and dialysed
for 6 - 8 hours. The ash content is reduced by this
procedure to about 0.3 per cent. The pulp is then
dried and two 30 gram samples are weighed out. One
is ashed and the ash is analysed for sulfates in the
usual way after removing silica by dehydration; the
second sample is burned with Na₂O₂ in a Pennock and
Martin crucible. About 1/2 gram of pulp is mixed
with 5 times its weight of Na₂O₂. The cover is placed
on the crucible and the mixture ignited with a red hot
wire. As soon as the crucible is cooled, a second
charge is set off. Usually three charges can be igni-
ated before washing out the melt with distilled water.
All the extracts are collected and acidified. Any
unburned carbon is filtered and the sulfates precipitated with barium chloride. The volume is so large and the amount of sulfates so small that it is necessary to allow the solution to stand several hours for complete precipitation of the sulfates before filtering.

The results of these analyses are presented in Table VIII and Figure VIII.

<table>
<thead>
<tr>
<th>Cook Number</th>
<th>Per Cent Sulfdity</th>
<th>Per Cent BaSO₄ in Ash</th>
<th>mg. BaSO₄ in Ash</th>
<th>mg. BaSO₄ from Organic Sulfur</th>
<th>Per Cent Organic Sulfur</th>
<th>Found Organic Sulfur / Ton of Pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.35</td>
<td>18.5</td>
<td>17.3</td>
<td>0.001</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>38-1/2</td>
<td>0.20</td>
<td>24.6</td>
<td>59.0</td>
<td>0.015</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>0.43</td>
<td>101.5</td>
<td>173.4</td>
<td>0.033</td>
<td>0.66</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>0.27</td>
<td>27.5</td>
<td>215.0</td>
<td>0.085</td>
<td>1.70</td>
</tr>
</tbody>
</table>

It will be seen that the organic sulfur content varies with the sulfdity of the cooking liquor as does the color of the pulp. More correctly, perhaps, the organic sulfur content varies with the sulfdity of the cooking liquor and the color varies with the sulfur content. The de-cided change in color between the soda and kraft cooks and the small changes between the kraft cooks indicate that there is an important difference between soda and kraft coloring. It has been shown that the coloring mater
Figure VIII.

Variation of Slipper in Mud with Salinity of Cooking Liquor.
in kraft is a sulfur derivative, probably of a tannin. In that case the coloring of soda pulp from the same wood would be due to the tannin itself.

The darkening of kraft and the increase of organic sulfur content with sulfidity is most logically explained on the basis of concentration of sulfur in the cooking liquor. Sulfur dyes are compounds of unknown structure and of somewhat variable composition. The more drastic the conditions of preparation and the greater the concentration of sulfur in the reactants, the greater the sulfur content, within limits, of the final product. The same is probably true of the sulfur dye in kraft pulp. The higher the concentration of sulfur in the cooking liquor and the more drastic the cook, other variables being constant, the greater will be the amount of sulfur substituted in the coloring matter and the darker will be the color. Since in this series of cooks the substance from which the coloring matter is formed was a constant, the variation in color was undoubtedly caused by an increase in the percentage of sulfur content, as was found in the analyses.

A second means of studying the relation of organic sulfur is to watch its behavior during bleaching. For this phase the following outline was followed: About 100 grams of commercial kraft pulp was broken up in a beaker and washed thoroughly with hot distilled water until the filtrate was practically clear. One-quarter of the pulp was reserved for sulfur analysis; the remainder of the pulp was semi-bleached with C.P. bleach liquor. Twelve per cent chlorine on the weight of the pulp was added and allowed to exhaust itself. The pulp, which was bleached to a
manila color, was then washed with hot distilled water and one-third reserved for sulfur analyses. The remainder was extracted for 3 hours with 2 per cent NaOH and washed. One-half the pulp was retained for analyses; the other half subjected to further bleaching. An additional 10 per cent chlorine as hypochlorite brought its color to a good white for kraft. The sample was washed and saved for analysis.

The bleach liquor was prepared by dissolving a calculated amount of 6 N NaOH in distilled water and adding chlorine gas from a tared cylinder until the liquor contained 3.0 grams chlorine per liter. A careful test for sulfates showed them to be absent.

A different method of analyzing for sulfur was used in this series. The inorganic sulfur was determined in the ash as before, but the pulp was oxidized in a mixture of concentrated nitric acid and potassium chlorate. This method permitted the use of a larger sample, offered fewer chances of loss, and required less attention than the method using $\text{H}_2\text{O}_2$. It was carried out as follows:

The entire sample of pulp (50 grams) is placed in a Kjeldahl flask, covered with concentrated nitric acid and heated gently until brown nitric acid fumes are evolved freely. Until the pulp is hydrolyzed the reaction generates enough heat to maintain the rate of reaction. When the violent reaction subsides, heat is applied to complete the oxidation and boil off the excess acid. Small amounts of potassium chlorate are
added occasionally to aid in the oxidation and furnish an alkali cation to combine with the sulfates formed by the oxidation. The flask is boiled just to dryness to drive off all nitric acid; the residue is then taken up in hydrochloric acid and analyzed for sulfates in the usual way. There is little danger of losing sulfur as HgS on the addition of the acid because concentrated nitric acid will oxidize the sulfide before it can escape.

The sample numbers are as follows:

1) Unbleached kraft pulp.
2) Semi-bleached kraft pulp.
3) Semi-bleached kraft pulp — alkali extracted.
4) Fully bleached kraft pulp.

The data on these pulp are given in Table IX. The graph, Figure IX, could not be drawn as a curve because there was no regular relation between the samples — they were rather spot tests.

Again the almost unbelievable resistance of this color to hypochlorites is exhibited. The pulp had been treated with 32 percent chlorine, nearly one-fourth its own weight, yet a decided yellow cast still persisted and a corresponding amount of organic sulfur was found.
FIGURE IX.

DECREASE IN SULFUR IN PULP DURING BLEACHING.

1 - Unbleached Kraft
2 - Partially Bleached Kraft
3 - Partially Bleached Kraft Alkaline Extracted
4 - Fully Bleached Kraft
## Table IX.

### RELATION OF ORGANIC SULFUR TO COLOR IN BLEACHING OF KRAFT

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Per Cent Ash</th>
<th>mg. BaSO₄ from Ash</th>
<th>mg. BaSO₄ from pulp</th>
<th>mg. BaSO₄ from Organic Sulfur</th>
<th>Per Cent Organic Sulfur</th>
<th>Found Organic Sulfur / Ton of Pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.68</td>
<td>94.6</td>
<td>299.6</td>
<td>115.4</td>
<td>0.071</td>
<td>0.69</td>
</tr>
<tr>
<td>2</td>
<td>0.38</td>
<td>26.5</td>
<td>92.6</td>
<td>66.3</td>
<td>0.015</td>
<td>0.36</td>
</tr>
<tr>
<td>3</td>
<td>0.37</td>
<td>7.5</td>
<td>44.5</td>
<td>37.0</td>
<td>0.019</td>
<td>0.29</td>
</tr>
<tr>
<td>4</td>
<td>0.26</td>
<td>6.0</td>
<td>20.4</td>
<td>14.4</td>
<td>0.004</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Some soda mills add small amounts of sulfur to their digesters to make the pulp easier to bleach. It is true that it requires less chlorine to bleach a low sulfide kraft than a soda. This gives the impression that the coloring matter in kraft is more easily bleached than soda. To complete the story, however, it should be mentioned that a small amount of sulfide in soda liquor makes it far more efficient in removing lignin. For small amounts of sulfide, the decrease in chlorine demand of lignin is greater than the increase in demand due to the presence of sulfur in the color. While very high sulfide krafts will probably never be encountered commercially, a few data taken from previous work will illustrate the effect that the introduction of sulfur in the coloring matter has on bleaching.

When pulp is chlorinated, the lignin is rendered soluble and practically all of it can be removed by an alkaline wash. The pulp is not lightened in color. In fact, it is usually darker, but the hypo-chlorites required to bleach it are substantially reduced. Kress and Voigtman (18) have studied the chlorination of a Mitscherlich sulfite
pulp which had a chlorine demand of 6.6 per cent and a lignin content of 3 per cent. In chlorination 50 per cent of the demand was used and in every case at least 90 per cent of the lignin was removed. From this it seems reasonable to assume that 3.4 per cent chlorine will render 2.7 per cent lignin soluble or 1 per cent chlorine will react with 0.8 per cent lignin. Kress and McDougal (17) have reported the results of a study of the influence of sulfidity on the physical and chemical characteristics of kraft pulp. Data pertinent to the discussion have been taken from that paper and are reproduced in Table X.

### TABLE X.

**DATA SHOWING THE EFFECT OF SULFUR ON THE BLEACHING OF KRAFT.**

<table>
<thead>
<tr>
<th>Cook Number</th>
<th>Cooking Liquor</th>
<th>NaOH</th>
<th>NaS</th>
<th>Per Cent Lignin</th>
<th>Per Cent Cl Required for Lignin Calculated</th>
<th>Per Cent Cl Chlorine Used</th>
<th>Per Cent Cl Available for Bleaching Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>6-2/3</td>
<td>13-1/3</td>
<td>8</td>
<td>5.3</td>
<td>10.0</td>
<td>8.2</td>
</tr>
<tr>
<td>2</td>
<td>6-2/3</td>
<td>5</td>
<td>6.5</td>
<td>6.5</td>
<td>6.6</td>
<td>12.0</td>
<td>15.0</td>
</tr>
<tr>
<td>3</td>
<td>6-2/3</td>
<td>13-1/3</td>
<td>5.5</td>
<td>6.5</td>
<td>6.6</td>
<td>12.0</td>
<td>15.0</td>
</tr>
<tr>
<td>4</td>
<td>6-2/3</td>
<td>13-1/3</td>
<td>8.2</td>
<td>10.2</td>
<td>10.0</td>
<td>20.5</td>
<td>20.5</td>
</tr>
<tr>
<td>5</td>
<td>6-2/3</td>
<td>13-1/3</td>
<td>7.2</td>
<td>9.0</td>
<td>9.0</td>
<td>17.5</td>
<td>17.5</td>
</tr>
</tbody>
</table>

**Notes:** Cooks No. 1 and No. 9 inclusive were for 3 hours. Cook No. 5 was for 4 hours. Cook No. 7 was for 6 hours.

In this table the per cent chlorine used was that amount required to obtain as good a white as possible in a two stage bleach, using a low density chlorination first stage and a high density hypochlorite second stage. Even with this type of a bleach it was impossible to get
good whites in the high sulfide cooks.

Since a chlorination stage was used, it seems reasonable to use the figure (2 per cent chlorine will remove 0.5 per cent lignin) as obtained above. From this figure the values in column 5 are calculated. In column 6 the actual amounts of chlorine used are listed. Column 7 is the difference between these two. It is roughly the chlorine used over and above the amount needed to remove the lignin and by far the larger part of it is used to bleach the coloring matter. Here it is seen that a normal kraft requiring less total bleach than a soda still uses more chloring to remove the coloring matter. The lignin content is so much lower than that in the soda that the decrease in chlorine demand from this source is greater than the increase required by the coloring matter. Of course, the pulp produced by the high sulfide liquors are not commercial, but they serve to emphasize the increase in chlorine demand of the coloring matter containing sulfur. This is especially true of Cooks No. 6 and No. 7. By lengthening the time of cooking the lignin was reduced, but the bleach requirement was actually raised. The lengthened contact with the dye in the liquor apparently increased the sulfur content of the dye or at least made it more difficult to bleach.

The calculations concerning the amount of chlorine required to remove the lignin can be disregarded and similar conclusions can be drawn. Referring to the column on lignin content, it will be seen that the lignin content of the soda cook is about the same as that of Cooks
No. 4 and No. 5. From this we might assume that the degree of pulping is comparable. The column containing the amount of chlorine used shows that the high sulfide krafts required 127 per cent and 152 per cent as much chlorine as the soda cook. This represents an enormous increase, but it is probably caused by a chemical change in the coloring matter which represents a very small percentage of the total weight.

To sum up briefly, it has been shown that other variables being constant the color of kraft is proportional to its organic sulfur content and that this coloring matter is very resistant to bleaching, more so in fact than the coloring matter in soda pulp.

C. OXIDATION-REDUCTION OF COLORING MATTER.

An oxidation reduction cell of the type described by Clark (6) and modified by Conant (11) was constructed. The cell consisted of a reaction chamber, which was a glass vessel of about 100 cc. capacity with a large rubber stopper, and a second vessel to contain the reference electrode. The two vessels were connected by an agar bridge. In the stopper of the reaction chamber were inserted a platinum electrode, a burette for addition of the oxidizing or reducing solution, a mercury seal stirrer, an inlet and an outlet for nitrogen, and the agar bridge to the reference electrode. Separation of the two electrodes prevented any possible harm to the reference electrode from the reactants. The cell, burette, and stirrer were supported on ring stands. See Figures X and XI.
FIGURE X.

DIAGRAM SHOWING LAYOUT OF THE REACTION CHAMBER.

Inlet for Nitrogen

Mercury Seal Stirrer

Inlet for Ager Bridge

Outlet for Nitrogen

Inlet for Burette

Platinum Electrode

FIGURE XI.

OXIDATION-REDUCTION CELL.
The system set up to measure the oxidation-reduction potentials is represented by:

\[
\text{Pt} \mid \text{Oxidation-reduction mixture in buffer} \mid \text{XG1 - agar} \mid \text{Buffer} \mid \text{Saturated calomel cell bridge}
\]

Conant (11) recommends the use of hydrogen electrode in place of the calomel cell. On account of the definition of \( E_R \) as the difference between the observed potential and that of the hydrogen electrode, if the hydrogen electrode is used as the reference electrode, the observed potential will be \( E_R \) without further correction. However, considerable trouble was encountered in the operation of the hydrogen electrode and it was discarded in favor of the glass electrode. The calomel half cell was adopted as the reference electrode and the glass electrode was used only in pH measurements, according to the following scheme:

\[
\text{Pt} \mid \text{H SO}_3 \mid \text{Glass} \mid [\text{K}^+] \mid \text{Saturated calomel cell}
\]

The necessary pH control was obtained by using the buffers recommended by Clark. The buffers were standardized after preparation by means of the glass electrode.

The cell was tested by using known compounds. Those chosen were \( \frac{1}{10} \text{Fe} \left( \text{NH}_4 \right)_2 \left( \text{SO}_4 \right)_2 \) and \( \frac{1}{10} \text{ Fe}_2 \text{Cr}_2 \text{O}_7 \), both solutions being \( \frac{1}{10} \) with respect to \( \text{H}_2\text{SO}_4 \). To 20 cc. of the ferrous solution in the cell, 30 cc. of \( \frac{1}{10} \text{ H}_2\text{SO}_4 \) were added to make the volume up to 50 cc. The same acid was placed in the beaker containing the reference electrode. The air in the reaction cell was displaced with tank nitrogen, which was
washed in alkaline pyrogallol to remove any oxygen and the stirrer started. The burette was filled with the dichromate solution, the nitrogen stopped, and the cell sealed in and allowed to come to equilibrium. As soon as a constant potential was attained, the titration was started. Potentials took only a short time to come to equilibrium and were quite stable. The data in Table XI and graphed in Figure XII show that the cell was working smoothly.

**TABLE XI.**

<table>
<thead>
<tr>
<th>cc. added</th>
<th>EMM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.296</td>
</tr>
<tr>
<td>2</td>
<td>.392</td>
</tr>
<tr>
<td>4</td>
<td>.414</td>
</tr>
<tr>
<td>6</td>
<td>.431</td>
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<td>8</td>
<td>.444</td>
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<td>10</td>
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<td>12</td>
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<tr>
<td>14</td>
<td>.482</td>
</tr>
<tr>
<td>16</td>
<td>.498</td>
</tr>
<tr>
<td>18</td>
<td>.505</td>
</tr>
<tr>
<td>20</td>
<td>.505</td>
</tr>
</tbody>
</table>

With the cell operating properly the following work was proposed:

1) Measure the oxidation-reduction potential of the coloring matter at regular intervals on the pH scale from 3 to 11.

2) At a definite pH, to be selected, measure the effect of known inhibitors of oxidation.

The following procedure for a run was modified from the work of Clark and Conant.
Figure III.

Titration of Fe(III)²⁺ (SO₄)²⁻ with K₂Cr₂O₇.
Place 45 cc. of the buffer to be used into the oxidation cell and add 5 cc. of a neutral solution of the coloring matter. Slip the vessel into place and start the stirrer and the nitrogen. Fill the beaker, used for the glass electrode and calomel cell, with the buffer and check the pH. Make up the reducing solution by dissolving the desired amount of the reducing agent in the buffer. Fill the burette and protect the solution from the air with a little benzene. When the nitrogen has run for 30 minutes, turn it off, seal in the cell, and allow the potential to come to equilibrium. When a stable potential is obtained, add the reducing agent in suitable increments, taking a reading after each addition as soon as equilibrium is attained.

The first reducing agent tried was sodium hydrosulfite (Na$_2$S$_2$O$_3$) since it is used successfully in reduction bleaching of kraft pulp. No stable potentials could be obtained. The addition of only a few drops of hydrosulfite would cause enormous changes in voltage and the potential would drift back until after about 20 minutes it would be higher than it was originally. For example, in one case the cell came to equilibrium at an EMF of 207 millivolts. The addition of one cc. of Na$_2$S$_2$O$_3$ (1 gram / liter) changed the potential to 47 millivolts. After 20 minutes the reading was 220 millivolts and still drifting.
The entire equipment was thoroughly overhauled and possible sources of error were checked individually until the only ones remaining were the reducing agent and the coloring matter itself. Other reducing agents including ferrous ammonium sulfate, hydroquinone, and titrous chloride were tried. The first two were not strong enough to reduce the coloring matter and the third behaved the same as hydro-sulfite — the potentials were unstable.

It should be mentioned that titrous chloride can be obtained only in strongly acid 50 per cent solution. It was recovered as the crystalline hexahydrate by saturating the solution with anhydrous HCl while cooling, filtering in an atmosphere of carbon dioxide, washing with ether, and drying in a vacuum dessicator over potassium hydroxide.

Known organic compounds were next substituted for the coloring matter. Salicylic acid gave the same unstable potentials noticed with the coloring matter. Hydroquinone was oxidized with dichromate and the quinone thus formed was reduced with titrous chloride. In this case the potentials were stable and the curve representing the reduction almost exactly duplicated representing the oxidation. See Table XII and Figure XIII for the data.

Apparently one cc. of \( \text{K}_2\text{Cr}_2\text{O}_7 \) is approximately equal to \( \frac{1}{4} \) cc. of \( \text{H}_2\text{O}_7 \). If the two curves are plotted on the same co-ordinates, making this correction, as has been done in Figure XIII, it will be seen that they are almost identical.
A further test using tannic acid gave the usual unstable potentials. The known compounds with which unstable potentials were obtained were acidic in nature. Apparently this type of compounds is not amenable to study by this method. In the literature all compounds which have been studied belong to the quinone family. No suggestions are available as to what compounds cannot be studied by this method. Conant (11) points out that the conjugate system -o-O-C=O- may be intimately bound up with the reaction. It may be that the application of this procedure is limited to this type. It is certain that acidic compounds are one type not subject to study by this means. It also suggests that the coloring matter is acidic in nature.

The failure of the method naturally prevented any further study of the possibility of inhibiting the oxidation of the coloring matter.
Under the conditions it would appear that further study in lightening the color of kraft would be most profitable if carried out along the lines of modern bleaching, that is, to study the constitution and chemistry of the coloring matter with the idea of rendering it soluble and remove it by washing.
The main part of this study has been concerned with the presence of organic sulfur in the coloring matter in kraft pulp and the relation of this sulfur to the properties of the coloring matter.

Samples of pulp cooked with liquors of varying sulfidity have shown that there is a marked change in color when sulfur is first introduced. Thereafter, an increasing sulfidity merely darkens the color. These coloring matters give all the classification reactions of the phlobatannins. In this particular point this study confirms the earlier work of Knittel (4). In soda pulp made from pine wood the coloring would undoubtedly be due to phlobatannins and in all probability the basic organic structure of the coloring in kraft pulps is essentially the same. However, in the latter case it has been shown that the color and stability has been greatly changed by the addition of sulfur.

It is unfortunate that phlobatannins and sulfur dyes behave similarly to tannins which are applicable to both. This refers to lightening in color in acids and reducing agents and reoxidation after being reduced. Further the phlobatannins in being converted to sulfur dyes have not been modified to the extent where they no longer give characteristic tannin reactions. The only means of differentiation have been
covered, namely:

1) Observation of color.
2) Study of sulfur content.
3) Difference in stability to hypochlorite.

In the light of this study, therefore, the coloring matter in jack pine kraft pulps is due primarily to a sulfur dye which has a phlobotanin as its organic constituent. The presence of sulfur darkens the color of kraft over that of a comparable soda pulp and makes the kraft harder to bleach in proportion to its organic sulfur content.

A summary of the main points covered follows:

1. Coloring matter has been extracted from kraft black liquor and pulp.

2. By means of color absorption curves and change of color with pH, these extracts have been shown to contain the same coloring matter which under the conditions of extraction is obtained as a single type of compound. Here again, the qualification that this statement does not refer to polymeric homogeneity must be applied.

3. The chemical characteristics of the coloring matter are similar to those of the phlobotanins.

4. Analyzes of the coloring matter reveal the presence of organic sulfur in it; hence the material is not an ordinary phlobotanin, but is probably a sulfur derivative of a phlobotanin.

5. Analyzes for organic sulfur in kraft pulp show that, other variables
being constant, the sulfur content is dependent on the sulfidity of the cooking liquor and in unbleached and bleached pulps the color varies directly with the sulfur content.

6. Data have been presented which show that the introduction of sulfur into the coloring matter makes it more difficult to bleach.

7. An attempt has been made to study the oxidation-reduction of the coloring matter in kraft pulp by means of Clark's electrometric titration method with the idea of inhibiting the reaction and making reduction bleaching more valuable. It was shown that the method is inapplicable to the compound and by analogy it was suggested that the coloring is acidic in nature.
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