The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The Application of Photomicrographic Techniques to Problems of the Pulp and Paper Industry

by Paul Clay Baldwin

June, 1940
THE APPLICATION OF PHOTOMICROGRAPHIC
TECHNIQUES TO PROBLEMS OF THE PULP AND PAPER INDUSTRY

A thesis submitted by

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INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

EDITORIAL OFFICE
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PART II

DEVELOPMENT OF THE MICRODIGESTER

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GENERAL INTRODUCTION

Wherever a microscope finds use, and the observations should be recorded, photomicrography offers the quickest, easiest and most accurate means available. The particular field of the microscope is in the investigation of details, structure, and movements which are so small that a resolution greater than that provided by the human eye is needed. Microscopic techniques have been widely adopted in industrial research; in the field of pulp and paper technology it is of value in the determination of particle size, fiber length and width measurements, for fiber identification, and other applications.

With the increased scope of the microscope, microscopists have applied many supplementary techniques to the solution of special problems. Among these are the use of fluorescence, microscopy by ultraviolet and infrared light, polarization, and stereoscopic photomicrography.

A new method of recording microscopic phenomena that are continually changing has been developed with the aid of the motion picture camera. Cinephotomicrography has already found wide application and with much success in medicine, biology, chemistry, physics, astronomy and in some problems pertaining to the pulp and paper industry.

In the present work two of the supplementary microscopic techniques have been applied to specific problems: (a) the location of extractives in wood has been investigated by fluorescence microscopy,
and (b) the effect of pulping agents on the microstructure of wood has been studied with the aid of cinephotomicrography. There remain many other important applications of these supplementary techniques in the field of pulp and paper technology.
PART I

THE USE OF FLUORESCENT ANALYSIS
FOR LOCATING THE EXTRACTIVES IN SPRUCE WOOD
INTRODUCTION

The extractives of woods have been the subject of extensive study and investigation because of the important role they play in the pulp and paper industry, the tanning industry, the naval stores industry, and many others. A large share of the experimental work in this field has been confined to the determination of the chemical nature of the extractives and the development of methods for the quantitative separation of these materials. Studies have also been made to determine the part of the tree containing the greatest amount of extractives, as well as the effect of the age of the tree on the extractives.

In general, it has been considered that the extractives are located in the wood rays and the resin ducts, although there has been very little experimental evidence of this. The stains used by the botanists for their work do not differentiate between the fatty and resinous portions of the extractives but merely indicate their location, alone or in combination. Since it has been shown that the fatty portion of the extractives is the most troublesome in the preparation of sulfites and groundwood pulp and in the utilization of this pulp in papermaking, it would be advantageous to know where this portion is actually located in the tree, whether in the rays, the tracheids, or in the resin ducts.

The purpose of this work, then, was to develop a technic which would differentiate the components of the total extractives while they are in their natural location in the wood elements and to determine
in what wood elements they are concentrated.

Certain investigators have used fluorescent analysis for examining paper for resin and fat specks and found they they could be easily differentiated. Other investigators have used fluorescence for examining the microstructure of wood and have reported that the wood rays and resin ducts could be easily distinguished. Therefore, fluorescent analysis seemed a likely method for accomplishing the purpose of this work.

Spruce was chosen as the subject of study since it is a typical resinous conifer.

HISTORICAL REVIEW

Extractives of Sprucewood

The extractives of sprucewood consist largely of resins, fats, waxes, hydrocarbons, gums, some tannins, and coloring matter.

Schwalbe (quoted by Siebers, 1) found that seasoned spruce contained 0.50 per cent fat and 0.48 per cent resin and that the fat was composed, for the most part, of the glyceride of oleic acid with small amounts of the esters of linolic and linolemic acids. Havley and Wise (2), using the methods of Schwalbe and Sieber, reported spruce (Picea excelsa) to contain 0.78 per cent ether-soluble material, 1.52 per cent alcohol-soluble material, and 2.34 per cent alcohol-benzene
soluble material. The same authors have reported white spruce (Picea glauca) to have an ether solubility of 1.36 per cent. Schwalbe (1) gave the pitch content for freshly cut spruce as 1.60 per cent and 1.00 per cent after seasoning. Richter (2) and Schwalbe and Grimm (5) found that the ether extract decreases and the alcohol extract increases as the wood is aged, although the increase in alcoholic extract did not balance the loss in the ether extract.

The alcohol- and ether-soluble extractives are said to occur (6) in the resin ducts and central wood ray cells and in the ray cells of those coniferous woods which do not have resin ducts. Borchers (7), Mage (8), and other workers have found the highest resin content in unbleached sulfite pulp located in the wood ray cells and have suggested the removal of these cells to alleviate pitch problems in the manufacture of paper.

The waxes (6) in woods are esters of sterols with fatty acids and are found largely on the surface of leaves and bark, although they do occur occasionally in specialized wood cells. The tannins are located almost entirely in the bark of the spruce tree and run as high as 7 to 8 per cent.

**Fluorescent Analysis**

Groot (2) defined fluorescence as the property of a substance to immediately radiate energy, which it has absorbed, in the form of
light, usually with an altered spectral composition.

If the spectral distribution of the fluorescent energy is peculiar to a particular substance, then this property may be used as a method of identifying it. The fact that many gases, liquids, and solids do have peculiar properties of fluorescence has led to the development of a broad field of fluorescent analysis.

In 1893 Hartley (10) published his observations of the fluorescence of unsized paper when illuminated by any part of the ultraviolet spectrum down to 2000 A. units. Since that time, much work has been done on the fluorescence of paper, wood pulp, waste liquor, and papermaking materials and many attempts have been made to convert these fluorescent methods of analysis to actual mill routine and control work.

Grant (11), Hadley and Grant (12), and Deribiene (13, 14) have given comprehensive reviews of the use of fluorescence in the paper industry and have included reference lists.

Following Hartley's work, Lewis (15, 16) devised a method of determining quantitatively the spectro-fluoroscopy of cellulose, sugars, and other substances. Through his method, a photograph was obtained which showed that only certain wavelengths produce fluorescence; the intensity of the fluorescence was measured by the density of the negative. Such a method allowed a more exact study of the fluorescent properties of these materials.
Klein (17) investigated the fluorescent properties of various wood pulps and found that their fluorescent spectra depended on the method by which they had been isolated. Hadley and Grant (12) found that, on bleaching, the vivid blue-white glow of the unbleached pulp changed to a dull dirty yellow, as the pulp was purified. The change is so marked and so clearly related to the bleachability of the pulp, that the authors found it easy to grade pulps in four categories ranging from strong, through easy bleaching to bleached and superbleached.

Because of the differences existing between the fluorescence of the bleached and unbleached pulps and between the pulps produced by different processes, it was only natural that the use of fluorescence should become an instrument for fiber identification. Moss and Sadler (18) and Schuls and Goetzel (19) used the primary fluorescence to distinguish between the bleached and unbleached fibers and then applied Rhodamine-6 G O.D. to differentiate the various kinds of bleached pulps with quite satisfactory results.

Gorgos (20), in his studies on the fluorescence of artificial tanning agents, found that lignosulfonic acid gave a characteristic violet fluorescence which changed to green in alkaline solution.

Fluorescence has also been used in the identification of dirt specks in the finished sheet of paper. Hadley and Grant (12) found that oil spots have a bright blue fluorescence and halo even in the finished paper, while resin and soot spots fluoresce yellow and black,
respectively. They also found that the fluorescence of that portion of the natural pulp resins which is soluble in alcohol is a much fuller yellow than the ether soluble portion which is usually held responsible for pitch trouble.

Since the cellulose fiber, the lignin, and the extractives, such as fats and resins, fluoresce in an isolated state when subjected to ultraviolet radiation; it would be expected that fluorescence could be very conveniently used in the study of the microstructure of wood.

O. Vichler (21) made a thorough investigation on the development of lignified membranes of monocotyledons, dicotyledons and gymnosperms by the use of fluorescent analysis. From his studies, he concluded that fluorescence, as well as Maule's reaction, is based on the presence of lignin. The fluorescence of lignified membranes is a consequence of the increasing concentration of lignin; however, in the case of very strong lignification, self-extinction may occur.

Fedrashc (22), in his study of the fluorescence of woods, found that the large vessels and wood rays can be distinguished easily by their fluorescence. It was his opinion that these fluorescent substances are formed within the vessel walls and reach the rest of the wood by the wood rays. The extractable portion of black locust (Robinia pseudoacacia L.) was found to consist of two materials. One was very soluble in ethyl alcohol and methyl alcohol and fairly soluble in chloroform and glacial acetic acid, and caused the solution to
fluoresce a brilliant blue-green when subjected to ultraviolet light. The second was especially soluble in acetone and ether and caused the extract to fluoresce in the yellow upon radiation with ultraviolet light.

Identification of Fats and Resin by Staining

In 1911 Klems (23) recommended the use of Sudan III in a mixture of three parts of alcohol with one part of water as a specific stain for resin in pulp. In this method, the sample to be tested is reduced to a pulp with water; the excess water is drained off, and the moist fibers treated with the Sudan III solution. The concentration of the Sudan III is such that there is no danger of the particles of resin being dissolved by the alcohol, and the fibers are sufficiently moist to prevent them from absorbing the dye stuff. After a few minutes’ immersion, the excess of the dye solution is removed as completely as possible with blotting paper, and the fibers are mounted in water for microscopic examination. The stained particles of resin are then observed as red amorphous bodies, chiefly in the wood rays. Their globular amorphous shape readily distinguishes them from any Sudan III crystal that might have been deposited by the dilution of the alcoholic solution.

Argy and L’Ehme (24) suggested that better results could be obtained by the maceration in alcohol of orein, the coloring constituent of alkanet (Alkanna tinctoria). The method recommended by the authors
The pulp to be examined is thoroughly defibered in water. A sample is taken, from which the water is pressed as completely as possible, and it is immersed in the coloring solution for one-half hour. The fibers are then removed, and the solution pressed out as much as possible. They are then placed on a slide in a drop of water for examination. The particles of resin are colored pink and are plainly visible. The tint may be less than that obtained with Sudan III, but the color is clear and none of the dye crystals deposit on the wood section or fibers to create confusion.

Potte (25) tested the procedure advanced by Kloeze (23) and found it unsatisfactory and offered a new procedure in its place. His procedure is as follows:

A small portion of pulp is teased out in the dry state and transferred to a Gooch crucible. The crucible is placed in a suitable vessel containing a 0.2 per cent solution of Sudan III in 70 per cent alcohol, in order that the solution may penetrate the perforations in the bottom of the crucible and cover the fibers. Staining is allowed to proceed for one hour. The fibers are then rinsed rapidly with 50 per cent alcohol and the crucible immersed immediately in 50 per cent glycerol. The preparation may remain in the glycerol until required for examination, but the time must be at least 15 minutes. The resinous portions of the pulp will be stained red, whereas the
nonresinous portions will be colorless.

The Sudan III staining method has also been recommended by another author (25) who claims that it may be used for roughly estimating the presence of large or small quantities of resin in pulp.

Noll and Bahn (27) have suggested the use of Sudan Black B and N2 and Indophenol for determining the amount of resin in wood pulps. The Sudan B and N2 stains the resin black, whereas the Indophenol stains it blue.

Sudan Orange RR, Indophenol, and Sudan Black B have been suggested (26) for locating the resin or so-called "resin material" in wood. The Sudan Orange RR stains the resin red, Indophenol stains it a pure blue, and Sudan B stains it black. Indophenol is very sensitive to acid conditions and enzymatic reduction and precautions must be taken against such conditions.

MATERIALS AND METHODS

Wood

The wood used in this study was black spruce which had been cut and stored for approximately one year. Disks were cut from the middle of an 8-ft. stick which had a diameter of about 6 in.; care was taken to select wood which had no areas of compression wood or decayed wood. Small blocks were cut from the sapwood of the disks.
and were aspirated in cold water until they sank; they were stored under water until they were sectioned.

**Sectioning of Wood**

Transverse, radial, and tangential sections, about 20 μm thick, were cut on the Bausch and Lomb sliding microtome. These microtome sections were stored in water until they were needed.

**Extracting Agents and Extractions of Microtome Sections**

Ether, dioxane, and alcohol-benzene (1:2) were used for the extraction. The ether was redistilled twice over metallic sodium; the alcohol and the benzene were redistilled before mixing to the correct proportions. The dioxane was refluxed with sodium twice and then distilled before use in extractions.

The extractions of the microtome sections were carried out in a Soxhlet extractor, using a 1 L l crucible. The crucible was covered to prevent the liquid from dropping directly on the sections and damaging them.

The ether and dioxane extractions were carried out for 20 hours. The sections were then removed and washed with water prior to photographing. The alcohol-benzene (1:2) extraction was carried out for 12 hours, and the section was washed first in alcohol and then water.
Fluorescent Microscopic Apparatus

The fluorescent microscopic setup used in this study consisted of a standard Bausch and Lomb microscope equipped with a 16-mm. quartz objective and a 10x Huygenian eyepiece, and a high pressure mercury arc of the Mazda H3 type. The spectral energy distribution of this lamp is given in Table I (23).
### TABLE I

**Spectral Energy Distribution of the Mazda H3 Lamp**

<table>
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<tr>
<th>Principal Lines</th>
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<td></td>
<td>0.765</td>
</tr>
<tr>
<td>19300</td>
<td></td>
<td>0.65</td>
</tr>
<tr>
<td>13955-13570</td>
<td></td>
<td>0.94</td>
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<tr>
<td>12100-11900</td>
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<tr>
<td>11289</td>
<td>7420-6830</td>
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<tr>
<td>10140</td>
<td>6830-6550</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>6550-6390</td>
<td>0.34</td>
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<td></td>
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<td>5971-5770</td>
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<td>3.70</td>
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<tr>
<td>5861</td>
<td>5615-5390</td>
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<td>2421-2399</td>
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<tr>
<td>2323</td>
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<tr>
<td>2302</td>
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<tr>
<td>2279</td>
<td></td>
<td>0.034</td>
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FIGURE 1
TRANSMISSION OF VITRIOL-PASSING FILTER

Transmission in Per Cent

Wavelength in Millimicrons
The visible radiation was filtered out with an ultraviolet passing
filter having the transmission curve given in Figure 1. This transmission
curve was determined on the Bausch and Lomb quartz spectrograph
equipped with the Van den Akker multistep sector photometer.

The ultraviolet beam was focused on the sample by means of
a quartz condenser lens. Standard glass slides and cover glasses were
used, the sections were mounted in water while they were examined and
photographed. In each case reflected light was used. The thickness
of the cover glass alone allowed a sufficient amount of the near
ultraviolet light to penetrate to the sample for fluorescence studies.

A picture of the setup used is given in Figure 2.

Photographic Methods and Materials

A standard photomicrographic camera, having a fixed bellows
length of 250 mm., was used for all of the photographs. With the 16-mm.
optive and 10x eyepiece, the magnification was 100 diameters. To
prevent abnormally long exposure time for the pictures of the fluorescing
tions, Eastman Super Panatomic X plates, having a Weston speed
of 100 in daylight and 50 in tungsten light, were chosen. These plates
have a "cut-off" at approximately 600 m.μ.

D-19 developer was used in the development of the negatives.
They were developed for five minutes at 65° F.

The qualitative spectra of the fluorescing material in the
FIGURE 2
FLUORESCENT MICROSCOPIC ASSEMBLY
wood sections were determined by photographing the section with filters having transmissions in various parts of the spectrum placed between the eyepiece of the microscope and the camera. Thus, by taking pictures of the same section with this series of filters and examining them, a qualitative determination of the fluorescent spectra of the extractives was obtained.

The exposures were determined for each filter by means of test plates and these exposures were used for all of the remaining work.

The transmissions of these filters (Figure 3) were determined on the General Electric recording spectrophotometer. The filter referred to as the ultraviolet passing filter is the same as that used in the mercury arc beam and has the transmission curve given in Figure 1.

**Stains and Stain Technique**

The stain used for the determination of the extractives in the wood sections was Indophenol, a dye stuff recommended for this purpose by the I. G. Farbenindustrie A. G. This material stains the pitch and extractives a dark blue and is said to be specifically for them.

The staining solution was prepared in the following manner:

One-tenth g. of the dye stuff (Indophenol) was stirred with
50 cc. of a solvent consisting of 20 cc. of 96 per cent alcohol, 20 cc. of glycerin (31 D6), and 10 cc. of water; the suspension was heated to the boiling point, cooled, and filtered through a filter paper. The stain was then stored in a brown stoppered bottle.

The staining procedure was to allow the section to stand in the Indophenol for one hour and then to wash it thoroughly with distilled water.

**Preparation and Extraction of Sawdust**

Sections of the same spruce stick from which the microtome sections had been cut were transformed to sawdust, which was screened and that portion which did not pass a 60-mesh screen was discarded. A portion of the sawdust was then extracted in a Soxhlet extractor with ether which had been refluxed over sodium for 20 hours. The ether extract was then concentrated in vacuo and filtered. Another portion was extracted with redistilled alcohol-benzene (1:2) and the remainder was extracted with dioxane. The alcohol-benzene and dioxane extracts were also concentrated under vacuum to a thick syrup.

**RESULTS AND DISCUSSION**

**A Study of the Location of the Sprucewood Extractives by Means of Fluorescence**

A radial section of sprucewood was photographed under fluorescent light (Figure 4) and also in transmitted light to show its detail (Figure 5). It can be seen that the part of this section in the field
of the microscope contains all of the typical elements of sprucewood—
i.e., a resin duct with its surrounding epithelial cells, wood rays,
and the tracheids. The unextracted section shows a decided fluorescence
in the resin duct, in the ray cells, and in the pits of the tracheids.
The simple pits in the ray cells also fluoresce in some places.

This section was then extracted with ether and examined in
ultraviolet light for fluorescence. The most striking fact shown
by the photomicrograph (Figure 6) is the high intensity of the fluores-
cence radiated by the bordered pits in the tracheids. The fluorescence
has disappeared from the resin duct but remains to some extent in
the rays. The appearance of the high intensity fluorescence from the
pits is not easily explained. It is possible that the pits were
scattering ultraviolet light and that this caused them to appear
highly fluorescent. A yellow filter with a transmittance of about zero
at 400 m\(\mu\) was placed between the eyepiece of the microscope and the
camera and a picture was taken. The pits were still fluorescing to
the same degree as shown in Figure 6. This eliminates the possibility
that the high intensity fluorescence of the bordered pits was due to
scattered ultraviolet light, for no ultraviolet light could be trans-
mitted through the yellow filter and reach the photographic plate.
Therefore, the ether must extract some material which coats the pits
and which is highly absorbent in the ultraviolet.

After the ether-extracted section had been examined and
photographed, it was extracted with dioxane. The photomicrograph of
FIGURE 4
UNEXTRACTED RADIAL SECTION

FIGURE 5
RADIAL SECTION--TRANSMITTED LIGHT
FIGURE 6
ETHER-EXTRACTED RADIAL SECTION

FIGURE 7
ETHER-DIOXANE-EXTRACTED RADIAL SECTION
FIGURE 8
ETHER-DIOXANE-ALCOHOL-BENZENE-EXTRACTED RADIAL SECTION
FIGURE 9
UNEXTRACTED CROSS SECTION

FIGURE 10
CROSS SECTION--TRANSMITTED LIGHT
FIGURE 11
ETHER-EXTRACTED CROSS SECTION

FIGURE 12
ETHER-DIOXANE EXTRACTED CROSS SECTION
FIGURE 13
ETHER-DIOXANE-ALCOHOL-BENZENE EXTRACTED CROSS SECTION
the ether-dioxane extracted section (Figure 7) shows that nearly all
the highly fluorescent material in the rays and pits has been removed.
The bordered pits appear as pin points in contrast to the large fluores-
cent areas that appeared after the ether extraction.

This section was then extracted with alcohol-benzene (1:2)
and photographed (Figure 5). There is apparently little change in
the section after the alcohol-benzene extraction, for Figures 7 and
8 are very nearly the same. There is, however, a decrease in intensity
of fluorescence of the whole background.

To make this study more complete, the same procedure (examining
an unextracted section and extracting the section with ether, then
with dioxane and finally with alcohol-benzene) was carried out on a
cross and a tangential section.

Figures 9 to 13 are photomicrographs of the cross section
after the different steps in this procedure. Figure 9 represents
the unextracted cross section and shows fluorescent material present
in the resin ducts and the wood rays. Some of the fluorescence in
the resin duct can actually be attributed to the extractives located
in the epithelial cells surrounding these ducts. Figure 10 was taken
with transmitted light to give a clearer picture of the detail of
the section. Figure 11 is a photograph of this section after the
ether extraction. The resin ducts no longer fluoresce; the epithelial
cells in one or two places still show the presence of some fluores-
FIGURE 14
UNEXTRACTED TANGENTIAL SECTION

FIGURE 15
TANGENTIAL SECTION—TRANSMITTED LIGHT
FIGURE 16
ETHER-EXTRACTED TANGENTIAL SECTION

FIGURE 17
ETHER-DIOXANE-EXTRACTED TANGENTIAL SECTION
FIGURE 16
ETHER-DIOXANE-ALCOHOL-BENZENE EXTRACTED
TANGENTIAL SECTION
cent material; the rays, however, still retain most of their fluorescence. The cross section after the ether and dioxane extractions (Figure 12) shows the epithelial cells to be completely devoid of fluorescent material, and the intensity of the ray fluorescence to be reduced. Figure 13, the cross section which had been extracted with ether, dioxane, and alcohol-benzene (1:2), shows a more decided fluorescence of the tracheid walls and better detail of the section. It is possible that the alcohol-benzene removed the material covering the fiber walls. The rays, however, are still fluorescing at a higher intensity than are the tracheid walls.

Figures 14 to 18 are photomicrographs of the tangential sections after the various extractions to which the radial and cross sections had been subjected. Figure 14 is the unextracted tangential section with fluorescent light; Figure 15 is the same section in transmitted light; Figure 16 is a photomicrograph of the section after an ether extraction; Figure 17, after the ether and dioxane extraction; and Figure 18, after the ether, dioxane, and alcohol-benzene extraction.

The tangential sections do not show details as well as the radial and cross sections, but they agree very well with conclusions drawn from the photomicrographs of these sections.

From the series of photomicrographs in Figures 4 to 18, the following conclusions may be drawn:

The material in sprucewood that is soluble in ether, dioxane, or
alcohol-benzene (hereafter, these will be termed extractives) fluoresces when illuminated with near ultraviolet light to a greater extent than do the cellulose and lignin in the fiber walls.

The extractives are located principally in the rays, the resin ducts with their surrounding epithelial cells, and apparently in the pits of the ray cells and tracheids.

The materials in the resin ducts are, for the most part, extractable with ether.

The fluorescent material in the ray cells is soluble in ether only to a slight extent.

The ether apparently removes some substance covering the tracheid pits and thus, after an ether extraction, they fluoresce brilliantly. This increased fluorescence of the bordered pits after an ether extraction might also be due to a change in the physical state of the material coating these pits which is caused by a partial solubility in the ether.

Methane removes most of the fluorescent material from the rays and from the bordered pits of the tracheids.

The Location of Sprucewood Extractives as Shown by Indophenol

Indophenol is a stain which is said to be specifically for pitch or resin; this is stained dark blue without affecting the fiber walls to any extent. The use of a specific stain allowed a check to
be made on the fluorescent technic.

Figure 19 is a photomicrograph of a radial section which had been stained with Indophenol. The resin ducts and rays are definitely stained, indicating the presence of pitch or resin. The pits in the ray cells and the bordered pits are darker than the tracheid walls. The results with this stain, therefore, agree very well with those obtained with the fluorescent technic as to the location of extractives in the spruce wood elements. This section was extracted with ether and, after restaining, was photographed (Figure 20). The ether has taken most of the extractives from the resin duct but does not remove any appreciable amount from the epithelial cells. The rays are stained to about the same depth as they were before the ether extraction. The borders of the tracheid pits are still stained in some places.

Figure 21 is a photomicrograph of the same radial section after it had been extracted with dioxane and restained with Indophenol. The epithelial cells are still stained, the rays are apparently stained to about the same degree as they were after the ether extraction. The alcohol-benzene extraction (Figure 22) does not remove much more of the stained material.

The same procedure was carried out on a spruce cross section (Figures 23 to 26). Figure 23 is a photomicrograph of the stained unextracted cross section; Figure 24 is the same section after ether
FIGURE 21
STAINED ETHER-DIOXANE-EXTRACTED RADIAL SECTION

FIGURE 22
STAINED ETHER-DIOXANE-ALCOHOL-BENZENE-
EXTRACTED RADIAL SECTION
FIGURES 25
STAINED ETHER-DIOXANE-EXTRACTED CROSS SECTION

FIGURE 26
STAINED ETHER-DIOXANE-ALCOHOL-BENZENE-
EXTRACTED CROSS SECTION
extraction; Figure 25 is the same section after ether-dioxane extraction; and Figure 26 after the ether, dioxane, and alcohol-benzene extraction, with restaining in each case.

Again the stained material is shown to be located in the resin duct and its surrounding epithelial cells, and the wood ray cells, and the pits.

Figures 27 to 30 show the effects of ether, ether-dioxane, and ether, dioxane, and alcohol-benzene extractions on a tangential section as shown by Indophenol staining. Figure 27 is a photograph of the stained unextracted tangential section; Figure 28 is the same section after an ether extraction and restaining; Figure 29 after the ether and dioxane extractions; and Figure 30 is the restained ether, dioxane and alcohol-benzene extracted section.

In general, the staining technic confirmed the fluorescent studies. However, the fluorescent technic is more positive for the identification and location of the extractives.

**Determination of the Fluorescent Spectra of the Extractives**

Since there is a difference in the solubilities of the fluorescing material located in the wood elements, it must be a mixture of different materials, including fats and resins. Different materials or compounds have different fluorescent spectra and, therefore, work was carried out to determine qualitatively the spectra of the fluores-
FIGURE 27
STAINED UNEXTRACTED TANGENTIAL SECTION

FIGURE 28
STAINED ETHER-EXTRACTED TANGENTIAL SECTION
FIGURE 29
STAINED ETHER-DIOXANE-EXTRACTED
TANGENTIAL SECTION

FIGURE 30
STAINED ETHER-DIOXANE-ALCOHOL-BENZENE-
EXTRACTED TANGENTIAL SECTION
sent material in the wood sections. The method used was that of placing filters passing different wavelength bands between the eye-
piece of the microscope and the camera and photographing the section, 
Thus, by taking pictures of the same section with this series of filters, a qualitative determination of the fluorescent spectra could 
be obtained.

The filters chosen for this work, with their spectral 
transmission curves are given in Figure 3.

From the previous studies, it is evident that the radial 
section is the most satisfactory for a study of the extractives and 
their location, and consequently all the remaining work was done on 
radial sections alone. A radial section having all of the typical 
elements of sprucewood was chosen for the photomicrographs in Figures 
31 to 37.

Figure 31 is a photograph of the section with no filter 
between the eyepiece and camera; Figure 32 is a photograph taken with 
the ultraviolet passing filter; Figure 33 with Filter D 35; Figure 34 
with Filter E 45; Figure 35 with Filter 17; Figure 36 with Filter 16; 
and Figure 37 with Filter 22. The data taken from these photographs 
are assembled in Table II, and the filters are listed in order of 
increasing effective wavelength of their spectral transmission.
FIGURE 31
UNEXTRACTED RADIAL SECTION
NO FILTER

FIGURE 32
UNEXTRACTED RADIAL SECTION
ULTRAVIOLET PASSING FILTER
FIGURE 33
UNEXTRACTED RADIAL SECTION
FILTER D 35

FIGURE 34
UNEXTRACTED RADIAL SECTION
FILTER E 45
FIGURE 35
UNEXTRACTED RADIAL SECTION
FILTER 17

FIGURE 36
UNEXTRACTED RADIAL SECTION
FILTER 16
TABLE II

COLLECTION OF DATA FROM FIGURES 31 TO 37

<table>
<thead>
<tr>
<th>Filter</th>
<th>Resin Duct</th>
<th>Epithelial Cells</th>
<th>Wood Rays</th>
<th>Tracheids</th>
<th>Pits</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Light walls dark at junction of ray cells</td>
<td>Light walls dark at junction of tracheids</td>
<td>Sample</td>
</tr>
<tr>
<td>U.V. Passing</td>
<td>Fluorescing</td>
<td>Dark</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Fluorescing</td>
<td>Dark</td>
<td>Light walls dark at junction of cells</td>
<td>Light walls dark at junction of tracheids</td>
<td>Light</td>
</tr>
<tr>
<td>D 35</td>
<td>Fluorescing</td>
<td>Dark</td>
<td>Light walls dark at junction of cells</td>
<td>Light walls dark at junction of tracheids</td>
<td>Fluorescing</td>
</tr>
<tr>
<td>H 45</td>
<td>Fluorescing</td>
<td>Dark</td>
<td>Light walls dark at junction of cells</td>
<td>Light walls dark at junction of tracheids</td>
<td>Fluorescing</td>
</tr>
<tr>
<td>16</td>
<td>Fluorescing</td>
<td>Fluorescing</td>
<td>Light junctions light in center of some walls</td>
<td>Light at junction dark walls</td>
<td>Dark</td>
</tr>
<tr>
<td>22</td>
<td>Fluorescing</td>
<td>Fluorescing</td>
<td>Light junctions light in center of some walls</td>
<td>Light junctions dark walls</td>
<td>Dark</td>
</tr>
</tbody>
</table>
A comparison of Figures 31 to 37 and the data in Table II show that:

(1). The resin duct fluoresces from the near ultraviolet through the yellow, whereas the epithelial cells surrounding it fluoresce only in the yellow.

(2). The walls of the tracheids and the wood rays fluoresce in the near ultraviolet and blue but are for the most part dark in the yellow. The junctions of these cells—i.e., tracheid-to-tracheid or ray-to-ray—are in the blue end of the spectrum but fluoresce brilliantly in the yellow.

(3). The simple pits fluoresce in the near ultraviolet and blue but are dark in the yellow. The centers of the bordered pits fluoresce in the near ultraviolet and blue, but the borders are dark. The bordered pits are not visible when observed through yellow filter.

A Study of Location of Ether-, Dioxane-, and Alcohol-Benzene-Soluble Constituents by Means of Fluorescence

A section extracted successively with ether, dioxane, and alcohol-benzene (1:2) did not give the effect of the dioxane and alcohol-benzene alone, and thus the following experiments were so designed that they would show the effect of ether, of dioxane, and of alcohol-benzene on the extractives.
Since the extractives are apparently made up of at least two materials, one of which fluoresces in the blue and the other in the yellow, it was decided to use the ultraviolet passing filter, Filter H 45, and Filter 16 for any further studies.

Figures 38, 39, and 40 are photographs of an unextracted section with the ultraviolet passing filter, Filter H 45, and Filter 16, respectively. Figures 41, 42, and 43 are photographs of this same section after an ether extraction with the three filters used in the order listed. A study of these photomicrographs shows that the ether has apparently extracted most of the blue fluorescent material from the resin duct leaving its detail very distinct. The pits have become more distinct both in the rays and in the tracheids; in fact the detail of the ether-extracted section is much better than that of the unextracted sections. This would tend to substantiate the theory that the ether has extracted some substance that is highly absorbent in the ultraviolet regions. The ether, however, has not removed from the rays the material that is fluorescent in the yellow, nor has it removed this material in the epithelial cells surrounding the resin duct.

Figures 44, 45, and 46 are photographs of an unextracted radial section with the ultraviolet passing filter, Filter H 45, and Filter 16, respectively. Figures 47, 48, and 49 are of the same section after it has been extracted in dioxane with the filters used in the order listed above. This series of photomicrographs shows that
FIGURE 38
UNEXTRACTED RADIAL SECTION
ULTRAVIOLET PASSING FILTER

FIGURE 41
ETHER-EXTRACTED RADIAL SECTION
ULTRAVIOLET PASSING FILTER
FIGURE 39
UNEXTRACTED RADIAL SECTION
FILTER H 45

FIGURE 42
ETHER-EXTRACTED RADIAL SECTION
FILTER H 45
the dioxane extracts the blue fluorescent material from the pits in
the wood rays and some of that in the resin duct. The apparent blue
fluorescence of the resin duct after the dioxane extraction (Figure 48)
is undoubtedly partially due to the walls of the epithelial cells
behind the duct and partially due to remaining extractives. The
intensity of the resin duct fluorescence is not much greater than that
of the tracheids. The resin duct has lost all its yellow fluorescence
after extraction with dioxane and most of the yellow fluorescent material
has been extracted from the epithelial cells. After the dioxane
extraction, the pits become more distinct in the tracheids. The rays
still fluoresce in the yellow after the dioxane extraction.

Figures 50, 51, and 52 are photomicrographs of an unextracted
section with the ultraviolet filter, Filter H 45, and Filter 16 used
in the order mentioned. Figures 53, 54, and 55 are photomicrographs
of the same section extracted with alcohol-benzene (1:2) with the
filters in the same order. The alcohol-benzene acts in much the
same manner as the dioxane. The yellow fluorescent material is com-
pletely extracted from the resin duct but not from the rays. The
blue fluorescence of the simple pits in the wood rays has disappeared,
as has most of the blue fluorescence from the resin duct.

From these photomicrographs, the following conclusions may
be drawn:

(1). The ether extracts the blue fluorescing material from
FIGURE 44
UNEXTRACTED RADIAL SECTION
ULTRAVIOLET PASSING FILTER

FIGURE 47
DIOXANE-EXTRACTED RADIAL SECTION
ULTRAVIOLET PASSING FILTER
FIGURE 45
UNEXTRACTED RADIAL SECTION
FILTER H 45

FIGURE 46
DIOXANE EXTRACTED RADIAL SECTION
FILTER H 45
FIGURE 46
UNEXTRACTED RADIAL SECTION
FILTER 16

FIGURE 49
DIOXANE-EXTRACTED RADIAL SECTION
FILTER 16
FIGURE 50
UNEXTRACTED RADIAL SECTION
ULTRAVIOLET PASSING FILTER

FIGURE 53
ALCOHOL-BENZENE-EXTRACTED RADIAL SECTION
ULTRAVIOLET PASSING FILTER
FIGURE 51
UNEXTRACTED RADIAL SECTION
FILTER H 45

FIGURE 54
ALCOHOL-BENZENE-EXTRACTED RADIAL SECTION
FILTER H 45
the resin duct and a small amount of the yellow fluorescing material. It apparently does not extract the yellow fluorescent material from the rays or epithelial cells.

(2). Dioxane extracts part of the blue fluorescent material and part of the yellow fluorescent material.

(3). Alcohol-benzene (1:2) extracts most all of the blue fluorescent material from spruce wood but does not extract the yellow fluorescent material from the rays.

(4). The ray extractives are apparently the most resistant to extraction.

From the previous work it would appear that the material extracted by the ether would fluoresce predominantly in the blue, since it extracts the blue fluorescing material from the resin ducts and only a small amount of the yellow fluorescing material. On the other hand, the material extracted by dioxane and by alcohol-benzene should tend to fluoresce more in the yellow than would the ether extract.

In order that this might be investigated, a portion of spruce sawdust was extracted with ether, another portion with dioxane, and a third portion with alcohol-benzene. These extracts were concentrated under vacuum and drops of the concentrate were placed on a slide and allowed to air-dry until the solvent was completely evaporated. These films were examined with ultraviolet light and their fluorescence compared. As was expected, the ether-extracted material fluoresced much more in
FIGURE 52
UNEXTRACTED RADIAL SECTION
FILTER 16

FIGURE 55
ALCOHOL-BENZENE-EXTRACTED RADIAL SECTION
FILTER 16
the blue than did the dioxane- and alcohol-benzene-soluble portions.

SUMMARY AND CONCLUSIONS

The location of the extractives in sprucewood has been determined by means of a technic involving fluorescence. Microtome sections of sprucewood were illuminated with ultraviolet light and the fluorescence of the extractives observed by microscopic examination. Visual observation was supplemented with a number of photomicrographs. The wood sections were extracted with ether, dioxane, and alcohol-benzene, and the effect of the extractions on their fluorescence was observed. The fluorescence technic was checked by the use of a stain, Indophenol, which is said to be specific to fats and resins. A qualitative method for the determination of the fluorescent spectra was developed and the spectra of the extractives was investigated.

From this work the following conclusions have been drawn:

The sprucewood extractives are located in the resin ducts with their surrounding epithelial cells, in the rays, and apparently in the simple and bordered pits. The staining technic confirmed the fluorescence work with regard to the location of the extractives.

The extractives consist of two materials or groups of materials. One of these fluoresces in the blue and the other in the yellow. The blue-fluorescing material is located almost entirely
in the resin ducts. The yellow-fluorescing material is located in
the resin ducts, in the wood rays, and in the epithelial cells.

Ether extracts the blue-fluorescing material from
the resin ducts and a small amount of the yellow-fluorescing material
from the resin ducts. Dioxane and alcohol-benzene, on the other hand,
extract the blue- and some of the yellow-fluorescing material from
the epithelial cells.

The ether extract from sprucewood meal fluoresces
more in the blue; the dioxane and alcohol-benzene extracts fluoresce
predominantly in the yellow.

The walls of the tracheids and the wood rays fluoresce
in the near ultraviolet and blue but are for the most part dark in
the yellow. The junctions of these cells—i.e., tracheid to tracheid
and ray to ray—are dark in the blue end of the spectrum but fluoresce
brilliantly in the yellow.

PROPOSAL FOR FUTURE WORK

Since ether dissolves nearly all the blue fluorescent material
and only a small amount of the yellow fluorescent material, whereas
alcohol-benzene dissolves the blue and more of the yellow fluorescent
material, it would appear that the blue-fluorescing material is the
fatty portion of the extractives and the yellow-fluorescent material
could be the resin acids and salts of the resin acids. Time has not
permitted a definite test of these indications.

A future program of work in this field should most certainly include a chemical separation of these extractives into their class components followed by a study of the fluorescent spectra of each component. With this knowledge, the location of such components of the extractives in the wood elements can be estimated by means of the technic described in this paper.

This technic has been developed on spruce which is a wood containing a limited amount of extractives material; it might be adapted with even more success to wood containing greater quantities of extractives such as the southern pines and the hardwoods.
LITERATURE CITED


PART II

DEVELOPMENT OF THE MICRODIGESTER
INTRODUCTION

During the past few years investigators have studied the effect of commercial pulping agents on the microstructure of wood in order to understand better the pulping processes used in industry. The method of investigation has been to subject wood, or wood sections, to commercial pulping liquors for varying lengths of time, to remove the sections, and to examine them under the microscope.

A continuous observation of the same section throughout a complete cooking process would be extremely valuable in a study of this nature for it should show at what periods during the cook the lignin is attacked by the pulping liquor; how the action of the various commercial pulping liquors on the physical structure of the wood compare; and the elements of the wood structure most susceptible to attack by the commercial pulping liquors.

A technic of this kind would require a reaction cell or microdigestor which would stand commercial pulping temperatures and pressures, which would be both acid and alkali resistant, which would be sufficiently small to fit on a microscope stage, and which would have windows thin enough to allow microscopic observations at reasonably high magnification. In addition it should be fitted with a sample mount which would allow the liquor to be in contact with the wood section and, at the same time, prevent the section from fluttering.
with the circulation of the cooking liquor.

The object of this work was to develop such an apparatus and to adapt it to the study of the effects of commercial pulping agents on the microstructure of wood.

HISTORICAL REVIEW

The object of any chemical pulping process is to remove all the constituents of the wood that would diminish the value of the cellulose for papermaking and, at the same time, to separate the individual fibers in such a manner that they may be felted uniformly into a sheet of paper. The reactions of the different pulping agents, both acid and alkaline, with the various constituents of the wood have been the object of much investigation; at the present time, much is known concerning this phase of pulping.

In order that the structure of the pulp fiber, resulting from the treatment of wood with the common pulping agents, might be better understood, the effect of these pulping agents on the wood structure must be thoroughly investigated. Some very excellent work has been done on this problem, but before this work is discussed a short review of the more prevalent theories of the microscopic structure of wood will be given.
Kerr and Bailey (2), Bixler (3), and Clarke (4) have given comprehensive reviews of fiber structure with excellent reference lists.

Figure 56 is a diagram of a mature wood fiber according to Kerr and Bailey (2).

A. Diagramatic transverse section of one entire tracheid and of parts of seven others.

B. Section of adjacent walls more highly magnified.
   a. Truly isotropic intercellular substance.
   b. Cambial or primary wall.
   c. Outer layer of secondary wall.
   d. Central layer of secondary wall.
   e. Inner layer of secondary wall.

Kerr and Bailey believed that in typical cells the wall has three distinct regions: the middle lamella, the primary wall, and the secondary wall. The middle lamella is formed from the cell plate division and is the truly isotropic intercellular substance shared by adjacent cells. It is composed of lignin and polyuronides. The primary wall is developed from the cambial wall; it is anisotropic in nature and is composed of cellulose, hemicelluloses, polyuronides, and lignin. The secondary walls consist of cellulose and lignin.

Bailey (2) has shown that both the primary and secondary walls of typical cells of the higher plants are composed of a porous
but firmly coherent matrix of anisotropic cellulose, whose finer structural details grade down to the limits of microscopic visibility. Lignin and other noncellulosic constituents may be deposited in the elongated, intercommunicating interstices of the cellulose, thus resulting in two continuous, interpenetrating systems. In heavily lignified forms either system may be dissolved without seriously modifying the continuity of the structural pattern of the other.

The complexity and variability of the visible structural patterns of the secondary wall is due to the variation in porosity in different parts of the cellulose matrix; to varying orientations of aggregates of chain molecules in successively formed parts of the wall; to variations in the distribution of noncellulosic substances; and in some cases to the presence of noncellulosic layers.

He has also proved that well-defined planes of structural weakness exist in the cellulose matrix. Because of this, the secondary wall, on dissection, will yield layers, fibrils, fusiform bodies, dermatosomes, and fragments of varying shapes and sizes. Each of these fragments is heterogeneous and much larger than the finer visible structural details of the cellulosic matrix.

To Lüdtke (6, 7, 8,) the middle lamella is heterogeneous and is made up of several thin lamella. The middle lamella contains all of the lignin interspersed in a carbohydrate material. Lüdtke believed that there is no cambium layer and that the secondary wall is
made up of primary, secondary, and tertiary lamella. The larger part of the cell is cellulose which is deposited in a framework of skin-like substances. The cellulose is composed of micelles and micelle rows. The micelle row is the longest structural unit of cellulose and is approximately 0.3 by 0.5 micron in size. The skin substance encloses completely the fibril sections, the micelle rows, and the micelles; it forms the primary lamella and is the dividing substance between the secondary and tertiary lamella. There are also according to Lüdtke, cross membranes that pass completely through the fiber at regular intervals. He attributed the ballooning during swelling to these cross members and denied the occurrence of lateral winding of cellulose fibers in the outer layers of the secondary walls.

The chemical identity of the skin substances is still in doubt; Lüdtke (6) believed it to be closely related to lignin but not identical with the middle lamella lignin.

Figure 57 is a diagram of a transverse section of a tracheid according to Lüdtke.

**Figure 57**

Transverse Section of a Tracheid according to Lüdtke

- a. Middle lamella
- b. Primary lamella
- c. Secondary lamella
- d. Tertiary lamella
- e. Lumen
Freudenberg (2) pictured the fiber as a matrix of jellylike material composed of lignin, hemicellulose, and pectin which holds the cellulose fibrils imbedded like matchsticks in a piece of cheese. He pictured the middle lamella as amorphous, isotropic, and without a cambium layer. The primary lamella or layer has two lamellae imbedded in crisscross fashion in the jellylike material. The secondary layer is similar but it has more lamellae and makes up the most of the fiber wall. The fibrils here are oriented at 0 to 20° to the fiber axis and are composed of micelles series of 60 to 80 micelles of 60 glucose residues each. This micelles series is the same as the fibril mentioned by Ritter (10). Freudenberg believed that cellulose and lignin are chemically combined. Figure 56 depicts Freudenberg's idea of a tracheid.

**Figure 56**

Transverse section of Tracheid According to Freudenberg

![Diagram of fiber structure](image)

- **a. Middle lamella**
- **b. Primary layer with two lamellae**
- **c. Secondary layer with three lamellae**
- **d. Tertiary lamella, absent in conifers**.
Ritter (10, 11, 12) believed that fibers are made up of concentric layers or sleeves which are cemented together by hemicellulosic materials having the same refractive index as the fibrils. The fibrils, compactly wound and cemented together also by hemicellulosic materials, are wound at an angle to the fiber axis and sleeves. The windings of the outer layer are arranged approximately at right angles to the fiber axis. The sleeves under this are at angles of from 5 to 30° to the fiber. Ritter spoke of the fibers as being made up of fusiform bodies and these of spherical units. Bailey (5) objected to this theory.

Ritter (13) and Ritter and Chidester (14), on the isolation of the lignin from a wood section by the 72 per cent sulfuric acid method, found two types of lignin, the middle lamella and the cell wall lignin. The middle-lamella lignin shows some structural characteristics; the cell-wall lignin is amorphous. Ritter found the middle lamella to consist chiefly of the lignin with some hemicellulose.

A. J. Bailey (15) agreed with Ritter that there is definite evidence of fibril structure. He also found in his work with cotton, sulfite, and soda pulps lateral windings in the outer layers of the secondary walls of the fibers.

Carpenter and Lewis (16) found a sheath of lignified material covering very raw cooked fibers. It was their belief that the sheath is formed by the splitting of the middle lamella. The presence of this sheath allows the fibers to swell only to a slight extent. Lewis (17)
by means of a cinephotomicrographic technic in the study of the fiber swelling characteristics, found the fiber under the lignin sheath to be composed of an outer primary lamella of laterally wound fibrils. These laterally wound fibrils account, at least in part, for the constrictions and ballooning observed in swelling. Lewis believed that a cellulosic, semipermeable elastic membrane is located beneath the primary lamella.

After this brief background of the various theories of wood structure, the history of the problem of the effect of the various pulping and bleaching agents on wood structure will be discussed.

Abrams (15) treated microtome sections of different woods with NaOH sodium hydroxide, sodium bisulfite, and other chemicals. The sodium hydroxide caused the cell walls to swell and striate. The resin ducts were acted on first in the early stages of the digestion; the middle lamella and the medullary rays were attacked at a much slower rate. The middle lamella split away from the cell walls, but a portion of the corners of the cells persisted. Abrams concluded that both the sulfite and caustic had very little effect on the cell wall but did attack the middle lamella.

Gergen and Hoffman (19) designed a glass autoclave for the digestion of wood sections by the sulfite process. The digester and its method of operation were described by the authors but no results have been published.
A. J. Bailey (20) in an attempt to explain the effects of chemical digestion—i.e., the stiffness of digested chips when dried in their intact condition after cooking, avoiding any macerating or disintegrating action—made a comparative study of the wood anatomy prior and subsequent to digestion. Digestion with soda liquor affected the middle lamella chiefly, tending to cause its disappearance until the secondary walls of adjacent cells approached actual contact. The effects of sulfate digestion were similar except that in all the woods studied, a very conspicuous swelling of the secondary wall occurred. Sulfite digestion caused about the same effects as the soda digestion, tending to remove the middle lamella. Of the three processes, however, the sulfate digestion approached more closely to complete removal of the middle lamella than the others. Soda and sulfate digestions produced exceedingly fragile sections—indicating more complete removal of the middle lamella—in all woods but cottonwood; in sulfite digestion only the cottonwood sections were fragile. Since the middle lamella is more completely removed in the fragile sections, Bailey concluded that ease of disintegration and commercially successful pulping do not go hand in hand. The middle lamella of Douglas fir was not completely removed by any of the cooking processes used, and straplike segments remained in the corner.

Where three or more cells meet, the resistant segment was insoluble in 72 per cent sulfuric acid but was removed completely by sodium hypochlorite. The ends of these resistant segments were
found on removal to coincide with hiatus in the secondary wall.

Bailey (21) during the mechanical isolation of the lamella noted a definite tendency of the lamella to cleave either approximately in the center or at the union with the secondary wall, indicating a lack of cohesion. This observation correlates very well with that of Carpenter and Lewis (16) who believed that the middle lamella splits on cooking, leaving a lignin sheath on a raw cooked fiber.

The most comprehensive work in this field was carried out by Bixler (1,22) who digested cross sections (20 microns thick) of spruce, loblolly pine, and poplar woods in sulfite, soda, and kraft liquors for varying times at constant liquor concentrations. The digested sections were stained and mounted, and specimens of each digestion were photographed.

The sulfite digestions were made in Carius tubes with sulfite liquor which analyzed 5.6 per cent total, 4.5 per cent free, and 1.1 per cent combined sulfur dioxide. All digestions were made at 150° C.

The alkaline digestions were made in 1/2-inch stainless steel pipes. The soda cooks were made with 6 per cent C.P. sodium hydroxide liquor at 175° C. The sulfate digestions were made at 175° C. with 6 per cent liquor consisting of two-thirds C.P. sodium hydroxide and one-third C.P. sodium sulfide.
To aid in photomicrographic work the sulfite sections were, for the most part, stained with 0.5 per cent solution of Malachite Green and 0.5 per cent Pontamine Black E by a double staining technic. The alkaline sections were in most cases stained with potassium ferri-cyanide-ferric chloride.

To avoid any misunderstanding in his discussion Bixler standardized on the following definitions:

1. All that portion of the fiber wall inside the cambial wall will be referred to as secondary wall.

2. The narrow, lightly stained band surrounding the secondary wall will be referred to as the cambial or primary wall.

3. The material between adjacent cambial walls will be referred to as an intercellular material.

Bixler's work confirmed the picture of mature wood structure presented by Kerr and Bailey (2). The intercellular material was mostly lignin, and amorphous and isotropic. The cambial walls in the wood were mostly cellulose and were birefringent in cross section.

The secondary walls consisted of two parts, the outer part mostly of lignin and the inner portion, comprising most of the secondary wall, mainly cellulose and isotropic in cross section. The sulfite, soda, and kraft digestions attacked the intercellular materials of the 20-micron cross sections and completely removed or gelatinized it. All three types of digestions attacked the secondary walls of the 20-micron cross sections of spruce removed or gelatinized a considerable
portion of the outer layer of these walls, and caused the cambial walls to stand out from them. However, the kraft and soda, in contrast to the sulfite digestions, had a semiselective action on the cross section, dissolving or gelatinizing most of the intercellular material before materially attacking the heavily lignified outer portion of the secondary wall.

During the entire digestions with kraft, soda, and sulfite under the most drastic conditions, Bixler found the cambial wall to be materially unattacked and to enclose completely the secondary wall in all of the digested sections. From the swelling experiments in sulfuric acid he concluded that sulfite digestion had a more drastic effect on both the cambial and secondary walls than either the soda or kraft digestions.

The actions of calcium hypochlorite and chlorine followed by an alkaline wash were found by Bixler to have a similar visual effect on both digested and undigested wood cross sections and were very nearly the same as that of the digestions. They were a little more specific, however, in that although they almost completely delignified the sections, they had a less apparent visible attack on the secondary wall.

Bixler concluded after several experiments on swelling that the constrictions in ballooning of fibers might be definitely associated with the cambial walls and, whether or not cross elements are present
they are not necessary to explain satisfactorily the balloon swelling of sprucewood pulp fibers.

In his work with the C stain Bixler showed that it detected differences in a wide variety of treatments. The secondary and cambial walls of digested and bleached 20-micron cross sections stained different colors, and thus the C stain colors obtained with pulp fibers are a composite of the colors of the two walls.

Ritter and Mitchell \((22)\) prepared the hemicellulose fraction of basswood fibers and showed that the ray cells have a different effect on polarized light than the fibers do. Color effects produced by the outer sleeve of the fiber indicate a crystal arrangement crosswise to the fiber. This arrangement tends to restrain abnormal transverse swelling of the fiber.

Grondal \((24)\), in a study of sulfite pulping, has postulated that, during the penetration period, the acid penetrates from tracheids to tracheid, presumably through the bordered pits and, likewise, through the simple pits connecting the wood ray cells to the tracheids. The second stage, from the critical temperature to the maximum temperature, involves the combination of the bisulfite and excess sulfur dioxide with the lignin in the cell walls to form bound lignosulfonic acid and lignosulfonate. The third stage—i.e., the period at maximum temperature—is the period of dissolution of the bound lignosulfonic acid and the hydrolysis of other lignin-sulfur complexes and their
removal by diffusion outward through the chips. The two later stages mentioned can be discerned in the progress of a normal sulfite cook, although the stages intergrade to a certain degree.

Before the chips are thoroughly penetrated, the third stage of the cooking process has already been reached in the large areas of the chips directly exposed to the liquor, and the liquor penetrating the chip must, therefore, contain a considerable quantity of dissolved lignosulfonic acid. As the acid penetrates the chips, it comes in contact with the lignin in the secondary lamellas first, and, thus, it becomes progressively weaker in its action as it diffuses through the cell wall of each tracheid outward toward the middle lamella. By the time the liquor has reached the middle lamella, its activity has decreased so much that the cellulose fibrils in the outermost layers of the secondary lamellas are protected, and they retain their ability to hold the cell wall together. This, naturally, gives a pulp of higher strength.
FACTORS TO BE CONSIDERED IN THE DEVELOPMENT
OF THE MICRODIGESTER

In the design of any piece of experimental equipment, its use requirement must be determined first and then satisfactorily satisfied to allow as broad a utility of the apparatus as possible. The microdigestor, as the name suggests, is to be used in a continuous study of the action of the commercial pulping liquors on the microstructure of wood and, therefore, it must meet the following requirements:

1. It should be acid and alkaline resistant at high temperatures and at concentrations of acid and alkali normally used in commercial pulping processes.

2. It must withstand commercial pulping pressures.

3. Provisions must be made for heating the liquor, and the heater must be easily controlled.

4. Since the rate of pulping is dependent to a high degree on the temperature, a method for measurement of temperature to ±1° C. should be provided.

5. A uniform circulation of the cooking liquor around the wood sample must take place.

6. Since the sample is to be examined continuously throughout
the pulping process, the cell must be provided with windows for viewing and illuminating the sample.

7. The windows must be sufficiently thin to allow the use of a microscope objective with a short working distance to give the necessary magnification for observation of the microstructure of the wood section.

8. The wood sections must be easily mounted in and removed from the microdigestor.

9. The section must be mounted to permit contact with the cooking liquor and prevent fluttering or moving with the circulation of the cooking liquor.

10. Air or gas bubbles must be eliminated from the liquor stream, because their presence would prevent a critical observation and illumination of the wood section.

An apparatus which would meet these requirements would be satisfactory not only for studying the effect of the commercial pulping liquors on the microstructure of wood but also for observing other chemical actions on wood or other types of materials at high temperatures and pressures. Such an apparatus could also be utilized for a continuous microscopic observation of the effects of some of the common wood chemistry reagents on the structure of wood at normal temperatures and at atmospheric pressure.
Evolution of the Design

After considering the requirements listed in the previous section, the first model of the microdigestor was constructed according to the design shown in Figure 59.

A is the body of the microdigestor which rests directly on the microscope stage. It was machined from a piece of Carpenter 8 rolled bar stock having the analysis given in Table III. This is a nonhardening steel.

| Table III |
| Analysis of Carpenter 8 Steel |
| --- | --- |
| Carbon | 0.10 |
| Chromium | 18.00 |
| Nickel | 6.00 |
| Selenium | 0.25 |

B represents the sample chamber and the window for viewing the pulping action on the wood section. An enlarged sketch of this part of the microdigestor is given in Figure 60. Referring to GA, 1 is the collar which screws into the body of the microdigestor and holds the window, 3, in place. This allows the removal of the window for mounting and removing the wood section. A thicokol gasket is placed between the removable collar and the window. Thicokol was chosen because of its resistance to chemicals and temperature.

The windows, 3, are of a special design and were manufactured
by the Bausch and Lomb Optical Company. Their design is shown in Figure 60B. The wood section is clamped between the two glasses in the manner shown in Figure 60B, and the liquor allowed to circulate both above and below it. The bottom glass is cemented to the body of the microdigestor with DeKotinsky cement at $\frac{1}{4}$ (Figure 60A) in the diagram.

Referring again to Figure 59, $C$ represents the thermometers mounted on both ends of the microdigestor. These have a range from 0 to 250° C. divided into 1-degree intervals. They are sealed into the cases with litharge and glycerin.

The circulating line, $D$, is made from standard 1/8-inch stainless steel pipe having the normal 18-8 composition. The bends were made in the pipe by carefully bending it around objects having diameters equal to those of the bends. The union, $E$, was provided for ease in removing the line for cleaning.

The liquor is heated by an electric heater, $F$, which was wound with 40 feet of No. 20 nichrome wire. The temperature of the liquor is controlled by means of two adjustable external resistances connected in series and capable of carrying 5 amperes. Since the heating is done on only one leg of the circulating line, convection causes sufficient circulation.

An Ashcroft pressure gauge with a stainless steel diaphragm is connected by means of a gooseneck at the point labeled $G$. The
FIGURE 60
ENLARGED VIEW OF THE REACTION CHAMBER
gooseneck serves as an air chamber for the air and gas that escape from the liquor as it is being heated by the electric heater.

The microdigestor is filled at the line G. After filling, the line is capped as shown in the diagram. If the filling is done with care and frequent shaking, the air can be liberated into the gooseneck and thus bubbles are prevented from going through the sample chamber, B.

Attempts to use this first microdigestor showed that it was quite unsatisfactory in many respects. Its deficiencies are listed below:

1. The glasses as shown in Figure 60B would not withstand over 40-lb./in.² pressure and, as a result, the temperature of the liquor could not be brought up to that used commercially.

2. The wood section fluttered with the circulation of the liquor to such an extent that it could not be observed with the microscope. This was caused by having circulation both above and below the wood section.

3. The DeKotinsky cement used to seal the bottom window in the body of the microdigestor was thermoplastic and softened at 125° C., causing leaks to occur between the bottom window and the body.

4. Air bubbles were entrapped in the liquor stream, entered the sample chamber, and caught on the wood section, destroying the
microscopic detail of the wood elements. However, when the apparatus,—
i.e., the microdigerster and the microscope,—were set at an angle
of 10 degrees to the horizontal with the gooseneck and pressure gage
at the high end, this difficulty was nearly eliminated.

5. The Carpenter 3 stainless steel was not resistant to
sulfite acid under the cooking conditions used. This decomposition
of the steel caused the liquor to turn green and decreased the light
transmission through the liquor in the sample compartment. At the same
time, the presence of the metallic ions in the liquor caused an auto-
oxidation and reduction of the sulfite liquor with a deposition of
free sulfur on the wood section, completely destroying its detail.

6. The circulation caused by convection was adequate, but
it varied in rate as the temperature changed. At the higher temperatures,
the circulation was too rapid. A method of controlling the circulation
therefore, was necessary.

In an attempt to alleviate these deficiencies, a new micro-
diggerster body was designed and constructed. This is shown in Figure 61.

The body of the microdigerster, A, was made from Ryerson 316
stainless steel, having the analysis shown in Table IV.
TABLE IV

ANALYSIS OF RYTONON 316 STEEL

<table>
<thead>
<tr>
<th>Per cent</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.10 (maximum)</td>
</tr>
<tr>
<td>Chromium</td>
<td>15.00 to 15.00</td>
</tr>
<tr>
<td>Nickel</td>
<td>1.50</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2.00 to 3.00</td>
</tr>
</tbody>
</table>

This type of stainless steel was recommended as resistant to sulfite acid under the cooking conditions to be used. Since there was a large amount of lathe work on this piece, it was heat treated before using.

The collar, C, used for holding the top glass was changed slightly in its design to allow the use of an 8-mm. objective for observing the wood section. The original design would allow the use of only a 16-mm. objective.

The holes, G, for the inlet and exit of the liquor were enlarged; this effected a decrease in the velocity of the liquor for the same volume of liquor circulating.

The windows, E, are standard Pyrex glass, 1.6 mm. thick, ground optically flat on both sides. (This design provided for a shoulder against which the windows could rest.) Thickol gaskets, G, were placed below and above the windows to allow a tight seal. Stainless steel rings, D, 1/16-inch thick were placed on top of the Thickol gasket, against which the top collar, B, and the bottom collar, C, could be turned without wrinkling the gaskets and putting uneven strains on
The sample holder used in this design is shown in Figure 62. Since the wood sections used are only 20 microns thick, it was felt that penetration was not a major problem, and contact of the liquor with the wood section on only one side would be sufficient. If one side of the wood section were pressed against the top window, the liquor would pass only the other side, and the tendency for the wood section to flutter would be materially reduced. To accomplish this, a spiderweb was constructed from stainless steel of 18–8 composition, 1/16-inch thick. By bending the legs at an angle with the vertical, as shown in Figure 62, the spider acts as a spring pushing the wood section against the top glass. Figure 62 shows the wood section mounted in the sample chamber of the microdigestor. The liquor comes in contact with the wood section through the hole in the body of the spider 3/16 in. in diameter. The section is also illuminated through this hole.

The newly designed body was connected with the same circulating line and the fittings as shown in Figure 59. Most of the difficulties encountered with the old design had been alleviated, but the corrosion of the steel still persisted. Since the apparatus contained approximately 50 ml. of cooking liquor, the small volume of cooking liquor was exposed to an unusually large area of stainless steel, and any appreciable corrosion caused the liquor to be colored dark green. At the same time, the presence of iron in the liquor caused the auto-
FIGURE 62
SAMPLE HOLDER FOR THE MICRODIGESTER
oxidation and reduction of the sulfur in the liquor and, thus, a precipitation of free sulfur on the wood section.

The windows would withstand a pressure of 100 lb./in.\(^2\) and did not leak. The fluttering of the sample was no longer noticeable, and the enlarged holes leading into the sample chamber reduced the velocity of flow of the cooking liquor to a satisfactory rate at the high cooking temperatures.

The coloration of the cooking liquor, together with the precipitation of the sulfur on the wood section, prevented the use of this design for visually observing the effect of the pulping liquors on the microstructure of the wood elements. As has been mentioned, the ratio of the surface of metal exposed to the sulfite liquor to the volume of the pulping liquor was abnormally high, and it was felt that this might be causing the corrosion of the stainless steel. An increase in volume of liquor would also reduce the concentration of the dissolved metallic ions and, therefore, the intensity of the dark green color caused by their presence. A reduction in the concentration of the dissolved metallic ions might also reduce the auto-oxidation and reduction on the sulfite liquor to a point where it would no longer seriously interfere with the visual observation of the wood section.

It was recognized that the increased liquor volume would increase the liquor to wood ratio. However, in the original design,
the liquor to wood ratio was considerably greater than that used in industry, and it would seem virtually impossible to make any satisfactory design wherein the liquor to wood ratio would approximate commercial conditions.

To obtain the larger volume, the microdigestor body, as shown in Figure 61, was connected in parallel with one of the experimental digesters in the pulping laboratory of The Institute of Paper Chemistry. This digester was lined with stainless steel and equipped with an indirect heater and a centrifugal pump for the circulation of the liquor from the bottom of the digester through the heat exchanger into the top of the digester. The volume of the digester, including the circulation line, is 47 liters. A schematic drawing of this assembly is given in Figure 63.

With this assembly, the liquor is heated by the heat exchanger indicated in the diagram. The liquor comes from the bottom of the experimental digester into the centrifugal pump and through the heat exchanger. At the top of the heat exchanger the liquor is divided, part going into the experimental digester and the remainder though the microdigestor. To insure circulation through the microdigestor, an orifice 1/8-in. in diameter and 1 in. long is placed in the inlet line to the experimental digester, increasing the head loss in this line.

The rate of circulation through the microdigestor is con-
FIGURE 63
SCHEMATIC DRAWING OF THE MICRODIGESTER ASSEMBLY

- pressure gauge
- relief line
- experimental digester
- heat exchanger
- microdigestor
- 1/4" 12-3 pipe
- 1/2" 12-3 pipe
- centrifugal pump
- blow valve
trolled by the valves placed before and after it. Since the circulation through the microdigester must necessarily be slow, the heat loss from the top of the heat exchanger to the microdigester was large, and the temperature drop was excessive. To prevent this the line was insulated with standard 1/4-in. pipe covering.

Since the volume of the liquor in the experimental digester is 17 liters and the rate of circulation through the microdigester is slow, the liquor passing through the microdigester is virtually fresh during the entire cook.

This assembly was tried and found to overcome the difficulty of liquor coloration and the precipitation of sulfur which came from the corrosion of the steel in the original design.

A photograph showing this assembly is given in Figure 64.

APPLICATIONS OF THE MICRODIGESTER

The purpose of designing the microdigester was to provide an apparatus which would allow a continuous observation of the same wood section throughout a complete cooking process. The body of the microdigester, as shown in Figure 61, was designed to permit its being placed on the stage of a microscope. Therefore, by concentrating a light beam from a standard illuminator on the wood section through the bottom window of the microdigester and through the hole in the sample holder, the action of the pulping liquor on the wood section
FIGURE 64
THE MICRODIGESTER ASSEMBLY
could be observed through the microscope. The magnification that can be used is limited by the thickness of the glass in the top window. The thinnest glass that would successfully withstand the pressure requirements was 1.6 mm. thick and, since this is the working distance required for an 8-mm. objective, 21 diameters was the greatest magnification that could be obtained by the objective. With a normal 10 x eyepiece the total magnification will not allow the observation of the cambial or primary wall but will easily differentiate the middle lamella from the secondary walls.

Visual observation is a valuable tool for the study of the action of pulping liquors on wood structure, but this action is very slow and therefore, it is difficult for the observer to actually see it as it occurs. At the same time, some record of the changes would be very valuable for a detailed study of this action.

Photography offers two alternatives for recording the action of the pulping liquors on the wood structure. The first is to take still photomicrographs of the section at definite known intervals during the cook and compare them to see how and when the action occurs. Since the same field is being viewed during the entire cook, it is very easy to compare the photographs. The second alternative is to take cinemicrographs of the wood section throughout the cook. The speed of taking the moving pictures may be reduced to a point where the action is visible when projected at the normal rate of 16 frames per second. Enlargements of individual frames of the moving pictures
would give still pictures for a more detailed study of the action.
The moving pictures have the advantage, however, of giving the definite chronology of the action of the liquor on the various elements of the wood section.

Applications of the Microdigestor to Sulfite Pulping

Sulfite cooks were made on spruce cross and radial sections. These were followed with both photomicrographs and cinephotomicrographs. The methods used in these cooks and the photographic technics used will be described in the following sections.

Sulfite Cooking Procedures

Forty-seven liters of soda-base sulfite liquor having a total sulfur dioxide content of \( \frac{1}{4} \) per cent and a combined content of 1 per cent, as determined by the Palmrose iodate method, were placed in the experimental digester, and the digester closed to prevent the loss of any sulfur dioxides. It may be pointed out that an attempt was made to use a calcium-base sulfite liquor, but there was a precipitation of calcium sulfite in the microdigestor and on the wood section, making the observation of the changes in the section very difficult.

A 20-micron section of sprucewood, cut on a Bausch and Lomb sliding microtome, was placed on the top window of the microdigestor, and the window was placed in the microdigestor in such a way that the wood section was between the top window and the sample holder as
shown in Figure 62B. The valves on either side of the microdigestor were opened and the pump started. The temperature of the liquor was raised to 100° C. in two hours, along a straight line curve by means of the steam heat exchanger in the experimental digester. The liquor temperature was kept at 100° C. for the duration of the cook. This temperature was taken at the outlet of the microdigestor with a thermometer mounted in the assembly at this point.

The reason for the selection of 100° C. as the maximum temperature was that there was a 30° temperature drop between the liquor in the experimental digester and the microdigestor, even though the pipes leading to the microdigestor were insulated with asbestos pipe covering. Therefore, the temperature in the experimental digester was 130° C. whereas that in the microdigestor was 100° C. The pressure of a sulfite acid, having a composition of 5 per cent total and 1 per cent combined sulfur dioxide at 130° C. is approximately 100 lb./in.². Since the pressure in the microdigestor is the same as that in the experimental digester, the windows of the microdigestor are withstand- ing as great a pressure as they were designed for, and thus, the maximum temperature that can be attained in the microdigestor is 100° C. A booster heater was placed on the inlet side of the digester to raise the temperature to that of the liquor in the experimental digester. However, local overheating under the heater caused an evolution of gas bubbles which passed through the sample chamber and destroyed the illumination for microscopic observation.
FIGURE 67
AFTER 2 HOURS

FIGURE 68
AFTER 3 HOURS
FIGURE 65
BEFORE COOKING

FIGURE 66
AFTER 1 HOUR
Since the liquor to wood ratio and the penetration of the liquor into the wood section are so far removed from commercial conditions, following commercial cooking schedules would mean very little more than the schedule used in this work. Action does start on the wood section at a temperature as low as 50° C.

All the cooks were made with 100° C. as the maximum temperature. The circulation was kept as slow as possible by only cracking the valve on the inlet side of the microdigestor. The cooks were continued until the section became so weak that it would not remain in focus.

**Photomicrographic Methods of Following the Cooking Action of Sulfite Liquor**

A Bausch and Lomb photomicrographic camera with a fixed bellows length of 250 mm. was used for all the photomicrographs presented in this section. The photographs were taken on Wratten N plates with the Wratten 45 filter, and the exposure times were determined by means of the Instascope exposure meter, which has been calibrated by Graff (25). The magnification was 210 diameters. The negatives were developed for nine minutes at 65° F. in developer D760.

Figures 65 to 70 are photomicrographs of a spruce cross section, 20 microns thick, taken at the indicated intervals during cooking by the sulfite process. Figure 65 shows the section before the cook was started; Figure 66, after one hour's cooking time; Figure 67, after two hours; Figure 68, after three hours; Figure 69,
after four hours; and Figure 70, after eight hours. The maximum
temperature of this cook was 100° C., and the strength of the sodium-
base liquor was 5.0 per cent total and 1.0 per cent combined sulfur
dioxide.

A study of these photomicrographs shows that the springwood
is attacked first, and to a much greater extent, than the summerwood.
After one hour's cooking time, the springwood tracheid walls have
begun to swell and, in a few cases, the walls have started to split
at the middle lamella. Apparently the wood ray cells at the point
of junction with the tracheids are the most susceptible to attack.
After the cook has progressed for two hours, the springwood tracheids
show a considerable swelling of the secondary walls and a tendency
for these cells to split apart and become individual. The swelling of
the summerwood tracheid walls is also noticeable at this point. In
some cases the summerwood tracheids have started to split at the middle
lamella.

After three hours' cooking, the section became quite fragile
and, as seen in Figure 65, the springwood tracheid walls have split
and striated at the middle lamellas in all cases. The swelling of
the summerwood tracheid walls is very noticeable at this point, and
these cells have become quite changed from their original shapes.
Since the section is held against the top glass with no support under
the part of the section in the field of the microscope, it has the
tendency to drop as the strength of the section decreases; such
FIGURE 73
AFTER 2 HOURS

FIGURE 74
AFTER 3 HOURS
parts as drop go out of focus. The depth of focus of an objective decreases as its magnification is increased and, thus, to avoid this difficulty the magnification of the objective must be decreased. A magnification of 200 diameters is, however, as low as should be used in order that the resolution may be sufficient for a study of the cell wall detail. Therefore, one cannot keep the section entirely in focus as the cook proceeds.

The cell walls have swelled continuously throughout the first three hours of cooking, but from the third hour on, the middle lamella is attacked to a greater extent, and the rate of the cell wall swelling decreases. As the middle lamella is attacked, the cells become separated and appear as individual units. This is shown in Figures 69 and 70.

Figures 71 to 75 are photographs of a spruce radial section, 20 microns thick, as it is being cooked by the sulfite process using a sodium-base liquor having a total sulfur dioxide content of 5.0 per cent and a combined content of 1.0 per cent. The maximum temperature was again 100° C.

Figure 71 is a photomicrograph of the original section before cooking; Figure 72, after 1 hour's cooking; Figure 73, after 2 hours; Figure 74, after 3 hours; and Figure 75, after 5 hours.

These photographs show the swelling of the cell walls to some extent and, in some cases, a tendency for the trachoid cells
to split one from another. However, they do not show the effects of the cooking liquor as well as the cross sections for the cooking action on the radial section is apparently much slower than it is on the cross section. The reason for the difference in appearance of the section in Figure 75 is that the photomicrograph is slightly out of focus. This makes the bordered pits appear swollen in comparison with those in the preceding figures.

It should be pointed out that these photomicrographs are not included for the purpose of proving the effect of the pulping liquor on the wood section but merely to show that the technic of taking still pictures at intervals during the cook may be used in further experimental work with the microdigestor. The major difficulty encountered in this technic is that of using the sufficiently high magnification required for a detailed study of the wood section without having a large portion of the section being studied out of focus.

**Cinephotomicrographic Methods of Following the Cooking Action of Sulfite Liquor**

The cinephotomicrographs were taken with a Cine-Kodak special movie camera which was used with a Bausch and Lomb cinephotomicrographic unit. A photograph of the setup is given in Figure 76. The apparatus consisted of a mount for the Cine-Kodak special camera, an optical connector and observation eyepiece, a Bausch and Lomb student microscope, and a Bausch and Lomb illuminator having an
FIGURE 76
CINEPHOTOMICROGRAPHIC UNIT
adjustable diaphragm and focus. The optical connector is fitted on the Cine-Kodak special camera in place of the photographic lens and, by means of the prism included in it, reflects about 90 per cent of the light from the microscope to the camera; the remaining 10 per cent of the light passes into the observation eyepiece to allow continuous observation and focusing, even though pictures are being taken.

Apparatus for taking single frames at definite time intervals

The pulping action on the wood section is very slow and thus, taking pictures at a normal rate—i.e., 16 frames per second—would be a waste of film and the action when projected would be too slow to follow. On the other hand, the time between exposures cannot be too long, for, when projected, the pictures would be jumpy and difficult to observe. After observation of the cooking action and some experimentation, it was decided that one frame every ten seconds would be the best rate for making the exposures. When projected at a normal rate of 16 frames per second, the action would be speeded up by a factor of 160. Since the equipment on hand did not provide for this, an actuator was designed to operate the Cine-Kodak special camera at the required rate—i.e., 1 frame every 10 seconds. The Cine-Kodak special camera is equipped with a single frame release button. When the camera is set to take 16 frames per second, the single frame release button will operate the camera at a speed of 8 frames per second—i.e., will take 1 frame in 1/8 second. Therefore,
by tripping the single frame release every 10 seconds, one frame would be exposed at this time interval, and each frame would have an exposure of 0.0625 second. Figure 77 gives the design of an apparatus which will accomplish this requirement.

Referring to Figure 77, A represents a synchronous motor and reduction gear combination having an output speed of 1 r.p.m. A nonconducting disk, B, made of Bakelite is connected to the motor shaft. Six contactors are imbedded at equal distances in the circumference of the disk, and hence in one revolution contact is made six times at intervals of 10 seconds with the contactor finger, C. When a contact is made, a relay is operated which sends current to the solenoid, D. The solenoid then pulls the steel core, E, into an equilibrium position and thus forces the brass rod, F, against the lever, G. The lever G pushes down on the single frame release button H, exposing one frame.

D represents the Cine-Kodak special camera; G, the camera support; G, the lever fulcrum; J, the frame for the actuator and K, the support to hold the core and rod in place when no current flows in the solenoid.

The actuator is suspended from the camera support to reduce vibration that might be caused by the operation.
Determination of the correct exposure

The only means of varying the exposure of the Cine-Kodak special camera when it is operating at a given number of frames per second and with a given light intensity, are provided by the three different openings of the shutter sector and the four different values of the neutral screens in the connecting headpiece between the microscope and the Cine-Kodak special camera. In this work, the light intensity was set to give a reading of $K$ in the Instoscope when it was placed, by means of an adapter on the microscope. A test roll of film, Cine-Kodak Super X panchromatic, was taken while varying the openings of the shutter sector and the neutral screens in the connecting headpiece. The actuator was used with the camera set at 16 frames per second. Examination of this film showed that when a Wratten 45 filter was used, a correct exposure was obtained with the shutter sector fully open and the neutral screen set at 0.

Determination of the optimum magnification

The optimum magnification for the Cine-photomicrographs depends on the following points: (1) the resolution required to give sufficient detail for intelligent observation of the projected pictures; (2) the area of the wood section that is to be photographed; (3) the amount of vibration of the apparatus and the movement of the section—i.e., the allowable magnification is reduced as the vibration and movement of the section increases, for the greater the magnification the less is the depth of focus, and the more difficult it is to obtain
uniform pictures (vibration and movement of the section are especially undesirable when long intervals elapse between successive frames); and (4) the grain size of the developed film. If the film is grainy, it prevents a large magnification during projection.

Test strips were taken using a 16-mm. objective and a 3x projection eyepiece, a special objective having a magnification of 16x and a 3x projection eyepiece, and the combination of an 8-mm. objective and the 3x projection eyepiece. Examination of these strips showed that, with the amount of vibration present, the pictures taken with the 8-mm. objective and the 3x eyepiece were very jumpy and, thus, it was hard to follow the cooking action. The magnification on the film, with this combination, was 63 diameters. Also, at this high magnification, the depth of focus is small and any movement of the wood section between exposures causes a change in focus from frame to frame. The special objective with the 3x eyepiece gave a magnification of 48 diameters. The pictures taken with this combination were much better than those taken with the previous but still had a tendency toward unsteadiness during projection. The pictures taken with the 16-mm. objective and 3x eyepiece were the most satisfactory and the changes in the wood section could be followed. A complete cook of a spruce cross section was photographed using this combination, and the film is filed at The Institute of Paper Chemistry at Appleton, Wisconsin. The cinephotomicrographs show the same trends as did the still photographs.
Application of the Microdigestor to Alkaline Pulping

Cooks were made on spruce cross sections with kraft liquor having a total chemical content expressed as sodium hydroxide of 4 per cent. The sulfidity was 33.3 per cent. These cooks were unsuccessful, however, because the alkaline liquor attacked the windows of the microdigestor and left a film of a silicate-like material at the point of attack. This film destroyed any chance of observing the wood section.

The Pyrex windows were replaced with windows ground from Jena 0-20 glass which is stated by the manufacturer to be alkali resistant but they, too, were attacked by the alkaline liquor with the formation of the translucent film on the surface in contact with the liquor.

Before the microdigestor can be applied to a study of the action of alkaline liquors on wood, a transparent material that is alkali resistant and will meet the specifications as regards temperature and pressure must be found. The photographic methods already described under sulfite pulping can be used for the alkaline pulping studies.
SUMMARY

A microdigestor has been developed which can be used for the study of the action of acid pulping liquors on the microstructure of wood. It will stand commercial pulping temperatures and pressures and is sufficiently small to fit on a microscope stage. The observation windows are thin enough to allow the use of an objective which will give a maximum magnification of 200 diameters. The wood section is so mounted that the liquor is in contact with it and yet fluttering caused by the circulation of the cooking liquor is prevented.

Preliminary cooks were made with the microdigestor and the progressive action of the cooking liquor on the wood sections was recorded by photomicrographs and cinemicrophotomicrographs. An apparatus for the actuation of the single frame release button of the Cine-Kodak special camera at 10-second intervals was designed and successfully used. The correct exposure was determined for the Cine-Kodak Super X panchromatic film. The optimum magnification for cinemicrophotomicrographs was found to be 30 diameters, obtained with a 16-mm. objective and a 3x eyepiece.

Photomicrographs were taken of a spruce cross section and a spruce radial section while they were being cooked with sulfite liquor. Cinemicrophotomicrographs were also taken of a spruce cross section during a sulfite cook and are filed at The Institute of Paper Chemistry.
at Appleton, Wisconsin

In comparison with the other technics used for the study of the effect of cooking liquors on the microstructure of wood, the microdigester offers the distinct advantage of being able to follow the action of the liquor on the same wood section throughout the complete cook. However, the magnification that may be used is limited, by the thickness of the windows in the microdigester, to approximately 200x. In order that a critical study of the effect of pulping liquors on the microstructure of wood might be made a magnification of 500x is required. At the present time no stains are known that could be used in the technic involving the microdigester. In the previous work the use of stains have been extremely valuable in determining the effect of the liquors on the wood cell structures.

PROPOSED FUTURE WORK

The object of this work was to develop a microdigester which could be used for the continuous observation of the change in microstructure of wood effected by commercial pulping liquors under normal pulping conditions. The microdigester has been developed and cooks of an exploratory nature have been successfully carried out to show that this piece of apparatus can be used in research pertaining to pulping and wood chemistry. This apparatus can be used, then, for studying the effects on the microstructure of wood of sulfite liquor,
of nitric acid, of alcohols (those used for pulping) and, if the proper glass is found, of alkaline liquors.

One advantage of the microdigestor is that liquor can be removed by displacement without disturbing or moving the wood section. Thus, the wood section could be pulped and the pulping liquor displaced with water and finally the water with chlorine water or a solution of hypochlorite. This would allow the study of the pulping action and the bleaching action on the same part of the same section.

Reactions with the components of wood which are carried out at room temperatures and atmospheric pressure can also be studied in the microdigestor. Therefore, a study of the effect of extracting agents, of the preparation of the Gross and Bevan fraction, of the preparation of the holocellulose fraction, and of many other reactions common to wood chemistry can be carried out. These studies can be made continuously and followed by either photomicrographs or cinephotomicrographs.
LITERATURE CITED


