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Doctor's Dissertation

The Colored Materials of Alkaline Cooking Liquors

by Glenn Curry Kimble

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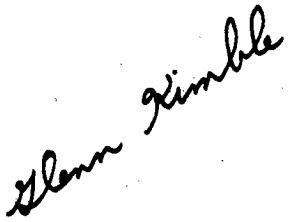
THE COLORED MATERIALS OF ALKALINE COOKING LIQUORS

A thesis submitted by

Glenn Curry Kimble



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I INTRODUCTION

Kraft pulp has in recent years become of increasing importance in many grades of paper which were formerly made of other pulps. The production of high grades of bleached kraft has increased tremendously. With this trend a great interest has developed in the color of unbleached kraft pulp, its bleachability, and in the color of the bleached pulp.

Considerable research has been done on these problems. One phase has been attempts to extract the colored materials from the pulp. Other studies have been made with the thought of relating the color of the pulp to that of the black liquor in which the pulp was cooked. One small fraction of the colored material in kraft black liquor has been investigated chemically by several workers. However, the information available on these subjects is inadequate and confusing.

Before any intelligent approach can be made to these problems, it seems important to know more about the soluble colored materials which are formed from the wood constituents and remain in the black liquor. These materials are so highly colored that all spent alkaline cooking liquors appear black or very dark brown to the eye. The undiluted liquors are so dark that no differences in color can be seen. Perhaps for this reason, the color of these liquors has received much less attention than the color of sulfite liquors. A survey of the literature yields

no information as to the rate at which this color develops during the cook, the wood constituents which form the color, or the relative importance of the various possible sources of color.

A detailed study has been made of the color of sulfite liquors, by correlating optical and chemical analyses of various liquors. The present study of alkaline black liquors was made using the same general techniques.

The object of this work was to determine the source, relative importance, rate of development, and behavior of the colored materials in soda and kraft black liquors. Such information will be of possible value in investigations of alkaline pulp color, pulp bleaching, and optical cook control. It should also contribute to the knowledge of the chemical mechanism of alkaline pulping.

II HISTORICAL REVIEW

A. ALKALINE PULPING AND BLACK LIQUORS

Since alkaline white liquors have only a small amount of color (practically none in soda liquor) it is obvious that the dark color of waste liquors must be produced during the cook by the action of the alkali on the wood constituents. Although the reactions taking place are not fully understood, recent investigations have extended our knowledge of the chemical process to a considerable extent.

The primary object of a cook is to dissolve the lignin and liberate undamaged fibers. This reaction has been studied extensively, both from a pulping standpoint and from the viewpoint of the lignin chemist. In 1911 Klason and Segerfelt (1) spoke of the breakdown of lignin molecules into smaller, alkali-soluble molecules. This dissolved lignin is usually studied by precipitating it from the alkaline liquors with an acid. Holmberg and Wintzell (2) reported that this product was apparently the same whether precipitated by sulfuric, hydrochloric, acetic, or carbonic acid. They also separated this precipitate into two fractions, lignin A, which was insoluble in alcohol, and lignin B, soluble in alcohol.

Later Marshall, Brauns, and Hibbert (3) found that two lignin derivatives are precipitated from the black liquor of a soda cook of spruce: lignin A, which is insoluble and lignin B, which is soluble in dioxane-ether. The ratio of methoxyl groups to acidic hydroxyl groups (methylated by diazomethane) of these fractions and of methanol

lignin prepared from the same wood, indicated that new hydroxyls had been formed, making the highly polymerized lignin complex acidic enough to be alkali soluble. The nature of this profound change in the lignin molecule is not fully understood.

The precipitate formed by acidifying alkaline black liquors does not consist entirely of lignin. Cirves (4) gives an analytical method for kraft liquors in which fats and resins are determined by extracting such precipitates with ether. Brauns and Grimes (5) showed that, in liquors from mild cooks, this precipitate is contaminated by carbohydrate materials, whereas in more drastic cooks the soluble carbohydrates are further degraded and do not precipitate to such an extent on acidification.

Brauns and Grimes (5) stated that, for a normal soda cook, the alkali consumption is about 16 per cent. Of this 16 per cent, approximately 1.5 per cent is used by the acids present as formyl and acetyl groups. Of the remaining 14.5 per cent, from three to four per cent is required for the solution of the lignin. A part of the remaining 11.5 to 10.5 per cent is held by the pulp through absorption, while the major part is used for the dissolution of the carbohydrates. The changes undergone by these carbohydrates require further investigation, but a part at least must be transformed into acidic products.

Research on the alkaline decomposition of pure sugars may indicate some of the possible reactions undergone by the carbohydrates in an alkaline cook. This is not a simple matter. For example, Nef (6)

believed there were at least 116 substances produced by the action of alkalis on hexose sugars. In an earlier article (7) he said that if a pentose or hexose is treated with alkali in the presence of air or other oxidising agent, no trace of saccharinic acid is formed, but monobasic hydroxy acids result. In the absence of an oxidising agent, saccharinic acids are formed through the osone.

Explaining this reaction further, Evans (8) said that the temperature and alkali normality are important factors in the oxidation of sugars. As the alkalinity or temperature of a solution is increased, all the hexose sugars tend to form a 3,4-enediol which will decompose into two molecules of glyceryl aldehyde. It is probable that the speed of oxidation of the fission products is greater than that of saccharinic acid formation under alkaline oxidizing conditions. The glyceric aldehyde is then converted into pyruvic aldehyde, which in turn is changed into lactic acid. At elevated temperatures glucose, fructose, and mannose yield about the same amounts of lactic acid. With maltose, however, little hydrolysis occurs and, therefore, only half as much lactic acid is produced.

Many such decomposition products are found in alkaline black liquors. Many years ago Klason and Segerfelt (1) found saccharinic acids of four and five as well as six carbon atoms in kraft black liquor, identifying meta- and parasaccharinic acid, isosaccharinic acid, and sapinisosaccharinic acid, as well as lactic acid. Hägglund (9) isolated from black liquor about 18 per cent of lactones and oxyacids on the basis of the weight of the wood. He found 55 per cent of this material

to be oxyacids and 45 per cent to be lactones. About five per cent of the oxyacids were lactic acid. He showed that the saccharinic acids present in black liquor consist mostly of five and six carbon chain acids.

Brauns and Grimes (5), by means of two-stage soda cooks on spruce wood, have shown that the carbohydrate materials dissolve more rapidly than does lignin in the early stages of the cook. Then follows a simultaneous dissolution of carbohydrate material and lignin. In the later stages of the cook, when nearly all of the pentosans and hemicelluloses have been removed, more lignin goes into solution.

If a mixture of sodium sulfide and sodium hydroxide is used, the removal of lignin is more rapid and more complete. Hansen (10) concluded from his survey of the literature that the speeding up of the pulping reaction by sodium sulfide is due, very probably, to the action of sodium hydrosulfide on lignin.

Rosin is removed from the wood in the early stages of the cook, according to Wahlberg (11). He said that the "volatile rosin" fraction contains varying quantities of rosin acids, fatty acids, and inert substances, plus a dark color which he attributed (without evidence) to small quantities of lignin compounds. Terpenes undergo no material change, and are recovered in the condensate with methyl alcohol and, in kraft cooks, methyl sulfide, mercaptans, etc. Others (12) state that of the 32.8 kg. of rosin acid per ton of cellulose, 12 kg. appear as "floating resin", 14.4 kg. go into the black liquor,

and 6.4 kg. are lost in the wash water from the diffusers.

It appears, then, that the major organic constituents of alkaline black liquors are fats and resins, lignin, oxyacids and lactones from the breakdown of carbohydrates, and some acetic and formic acids. Summarizing values for kraft and soda liquors which Cirves (4) quotes from Klason, Segerfelt, Rinman, and his own work, an alkaline black liquor contains:

Constituent	Percentage on Basis of Total Organic Matter
Fats and resins	1 - 7
Lignin	50 - 55
Oxyacids and lactones	30 - 40
Acetic acid	Trace - 6
Formic acid	Trace - 6

Thus nearly half of the organic matter is in the form of strong organic acids.

These materials may not all be in true solution. Liander (13) reports that in kraft black liquor about 28 per cent of the organic substances present are in colloidal solution and 72 per cent in true solution, either as such or as the sodium salts. Black liquors are strongly buffered solutions within wide pH ranges. About 50 per cent of the organic substances originally present pass into the filtrate on acidification with a mineral acid.

B. COLORED MATERIALS IN BLACK LIQUORS

The colored materials in alkaline black liquors may be produced by the action of alkali on the extractives, on the lignin, or on the holocellulose fraction of the wood. Bard (14) has shown that extractives, especially tannins, form highly colored liquors in kraft cooks. However, there must be other sources of color, because even a soda cook on extracted wood produces a dark liquor.

It is unlikely that much of this comes from the true cellulose portion, because Bard (14) showed that little darkening occurs when alpha-cellulose is cooked with kraft white liquor.

The colored material may be produced from lignin, although dry, solid alkali lignin compounds, when pure, are not highly colored. Marshall, Brauns, and Hibbert (3) report that alkali lignins A and B were light brown or yellow in color.

Colored solutions can be produced by the action of alkali on sugars, but the chief products of the reactions are not colored in themselves. Reed (15) isolated saccharinic acids from kraft black liquor by precipitating lignin with sulfuric acid, concentrating, precipitating sodium sulfate with alcohol, and concentrating again. He found that the dark color of the filtrate containing the saccharinic acids could be removed by repeated treatment with carbon.

As Bard (14) has shown, the color of kraft pulps is partially dependent on the coloring materials in the black liquor, and several

studies of pulp color and bleaching have been made in which one fraction of the colored material in black liquors was investigated.

Kuettel (16) isolated small amounts of dyes (which he believed to be tannin decomposition products) from kraft waste liquors, and concluded that the principal sources of dye materials in slash pine kraft pulps are the phlobatannins, which are converted by the pulping action into their colored oxidation or condensation products.

Holzer (17) extracted a colored material from kraft black liquor from a cook on pine. He neutralized with hydrochloric acid, filtered, and discarded the dark brown precipitate. The sulfur was settled out of the filtrate, and the colored material precipitated with lead acetate. This precipitate was dissolved, the lead removed with hydrogen sulfide, and the colored material concentrated in vacuo to a dark, red brown, viscous liquid. A similar material was extracted from the pulp with an amyl alcohol-hydrochloric acid mixture and also with sodium hydroxide. By color transmission curves and the change of color with pH, the color appeared to be the same in both cases. These materials gave the usual phlobatannin tests. Since they also contained organic sulfur, Holzer concluded that the color in kraft pulp and black liquor was due to a tannin-base sulfur dye.

However, Graef (18) discounted the sulfur dye theory. He found that kraft coloring matter is not affected by chemicals which solubilize ordinary sulfur dyes. He also indicated that organic and inorganic solvents remove such a small amount of the color from pulp that the extract cannot be called representative of the color. He

believed that phlobaphenes and related compounds were not solely responsible for color of pulps. His work indicates that the presence of sulfur in an alkaline cook does not make the color more resistant to bleaching. He also found that white liquor heated with dextrose produced a solution which gave all the tests Kuettel and Holzer used to identify phlobatannins and phlobaphenes.

Schwartz, McCarthy, and Hibbert (19) have also stated that the difficulties found in bleaching kraft pulp to a high degree of whiteness are not due to the presence of the colored materials isolated from the liquor by Holzer and Kuettel. They believed the difficulties in bleaching kraft pulp are due to the presence of lignin and its degradation products, the latter formed during the processes of cooking and bleaching. This conclusion was based on a more complete investigation of the Holzer "pulp extract" and "black liquor extract". They found that the "pulp extract" had a methoxyl content of 13.6 per cent, whereas kraft lignin isolated from the black liquor had a methoxyl content of 13.3 per cent. They were convinced that there was no apparent need to differentiate between these two preparations. On the other hand, they found that the "black liquor extract" had a methoxyl content of 5.6 per cent. They also found that this same acid-soluble colored material was present in the black liquors from cooks on extracted wood. They believed that this eliminated the possibility that this material was of phlobatannin origin. As a further test they recooked kraft lignin (isolated from black liquor) in alkali. This treatment produced a small amount of an acid-soluble colored material.

When isolated by the Holzer procedure, it had a methoxyl content of 7.2 per cent. The authors therefore believed, "that although carbohydrate impurities may contaminate it, the 'black liquor extract' probably arises from the lignin."

Bard (14), in his study of the effect of tannins on pulping, did some work on this problem. He found that tannins do not form an objectionable sulfur dye, if any at all, when digested with kraft liquor. On addition of tannins to wood being pulped, the same color increase occurs in the soda process as in the kraft process. However, tannin-containing woods do give darker pulps and liquors. Unextracted spruce, which contains little tannin, gives much the same liquor color as extracted spruce. Black liquor color due to tannin obeys Beer's law, whereas the remainder of the color does not.

Bard also made a series of experiments in which alpha pulp was cooked with kraft liquor with the addition of various materials. From these digestions the following information was obtained:

Alpha pulp cooked with kraft white liquor alone is not darkened to any important degree. Addition of lignin, pentosans, or hexosans causes some discoloration of the alpha pulp, but does not produce a color nearly as dark as an unbleached kraft. These materials in combination produce a pulp color only slightly greater than would be obtained from each material acting individually. Tannin, however, in combination with monosaccharides and polysaccharides gives a pulp much darker than would be formed from the components digested individually. The pulp reaches a color typical of kraft pulp from a tannin-containing wood.

Taken as a whole, this information from the literature presents a very sketchy and unsatisfactory picture of the colored materials found in kraft and soda black liquors.

III METHODS, DATA, AND DISCUSSION OF RESULTS

The investigation of the colored materials in a complex mixture of organic and inorganic substances presents many difficulties. Simerl (20) had a similar problem in his study of the sulfite process. Using optical analysis of the cooking liquors and pulps, Simerl used three approaches to the problem:

1. Normal spruce sulfite cooks were made and liquor samples were taken at invervals. By correlating optical and chemical analyses, these periodic samples were used to show the cause of the liquor color and the rates at which the various constituents appeared in the liquor. These samples were also used to show the effect of age, further heating, and pH on the liquor color, and to study the conformity to Beer's law on dilution.

2. Isolated wood components were cooked with sulfite liquor on a small scale. From these experiments, the trends indicated by the examination of periodic liquor samples were verified and more specific information was obtained.

The effect of cooking variables and wood species on liquor color was studied by examination of liquor samples taken from cooks made by the pulping class at The Institute of Paper Chemistry.

The techniques used by Simerl have to be modified considerably for use on alkaline liquors. However, the same general method of attack can be used.

If an isolated wood constituent is cooked in an alkaline white liquor, it behaves in an entirely different way than it would if it were heated in a black liquor with other organic material present. This is shown by Bard's work (14) and by some of the experiments done on this problem. For this reason the experimental work, as far as possible, has been done on black liquors produced under actual cooking conditions.

Chemical investigation of the various fractions of alkaline black liquors was of secondary importance in this problem, and was carried only as far as it was of value in the investigation of color.

SODA BLACK LIQUORS

1. Wood and Cooking Conditions

Spruce was chosen as the species for the preliminary work because of the data available in the literature on composition and cooking. Simerl (20) has compiled a comprehensive survey of the constituents of sprucewood.

The spruce used was grown in the vicinity of Ticonderoga, New York, and received by the Institute on March 4, 1940, as four-foot peeled sticks. It was stored in a dry place open to the air on one side. When used, it was sound and dry.

Disks were cut for ring count and density determinations, and other disks were used for making woodmeal. The remainder of the sticks were chipped to 3/4 inch chips in the semicommercial chipper. The chips

were screened to remove fines, and knots and splinters were removed by hand. After thorough mixing the chips were bagged, each bag containing one digester charge of 4722 grams of oven-dry wood, at a moisture content of 14.15 per cent.

The following figures will characterize the wood used. They are the average values of the five sticks used in this work. Density is given as grams oven-dry weight per cc. oven-dry volume.

Number of rings	62.0
Diameter, inches	6.5
Rings per inch diameter	9.4
Density	0.432

A sample of 40-60 mesh wood was taken for analysis. Ether solubility was determined on the air-dry wood by Institute Method 12. The ether-extracted samples were then extracted with alcohol-benzene by Institute Method 11. Lignin and hot-water solubility were determined on ether- and alcohol-benzene-extracted wood meal by Institute Methods 13 and 10a, respectively. The results are given below on the oven-dry unextracted wood basis.

	Per Cent
Ether solubility	0.71
Alcohol-benzene solubility	0.79
Hot water solubility	2.35
Lignin	26.68

Two cooks, L-1 and L-2, were made in a stainless steel digester with a circulating pump, and an outside heat interchanger heated by steam. In both cooks the following conditions were maintained:

Oven-dry weight of spruce chips--4722 grams

Active alkali ratio--33.3 per cent expressed as NaOH

Sulfidity--0

Water ratio--5.5 grams water per gram oven-dry wood

Maximum temperature--170 degrees C.

Time to maximum--1.5 hr.

Time at maximum--4.0 hr.

The high alkali ratio and the long cooking time were chosen to carry the pulping action as far as possible. By doing this, the periodic liquor samples were made to represent extreme conditions as well as normal cooking schedules. The alkali was actually not as high as the figures indicate, because considerable amounts of unused alkali were removed with the early liquor samples; about 15 per cent of the liquor was removed during the cook.

Liquor samples were taken through a water-cooled coil. Since some liquor was required to flush out the coil each time, the total volume of liquor removed could not be accurately regulated. Therefore, some variation between the cooks could be expected. Samples were taken as shown below:

Cooking Time Hr.	Temperature C.	Volume of Sample Ml.
1/2	144	500
1	164	250
1-1/2	170	250
2-1/2	170	250
3-1/2	170	250
4-1/2	170	250
5-1/2	170	1000

The pulps were washed three times with warm water and screened on a small flat plate screen. Yields were low, as would be expected under these severe conditions. The yields are given below. Lignin was determined in the pulp by Institute Method 428.

Cook	L-1 %	L-2 %
Yield, (oven-dry) unscreened pulp	38.99	39.28
Yield, (oven-dry) screened pulp	39.03	39.39
Screenings on unscreened pulp	0.10	0.27
Lignin in screened pulp, %	-	4.01

Cook L-1 was a preliminary cook, the liquor samples of which were used to find the best methods of optical and chemical analysis. Cook L-2 was made to obtain liquor samples for a program of chemical and optical analysis drawn up on the basis of the work done on the first cook.

2. Optical Analysis of Liquors

The spectral transmittance curves of the liquor samples were determined with the General Electric recording spectrophotometer. In most cases the liquor samples were diluted and a conventional absorption cell used. The method of dilution used to obtain accurate and comparable results will be discussed later. For diluted samples, the absorption cell used was Bimer and Amend No. 31150 with 0.5 cm. thickness.

The samples as drawn from the digester contained small amounts of fiber and dirt. The samples taken early in the cook also precipitated a small amount of organic matter on cooling. To insure uniform results, the liquor samples were all centrifuged for five minutes at 3000 r.p.m. and decanted through a Gooch crucible with an asbestos mat. The transmission as compared with liquor which had been allowed to settle was about 0.5 per cent higher over the entire range. This was determined in a dilution of one volume of liquor to fifty volumes, using distilled water as a diluent. The increase in transmission indicated that a small amount of neutral colored suspended matter was removed. The samples were centrifuged before filtering; otherwise the filters became clogged and the filtration was slow.

a. Theory

In homogeneous transparent substances, the light absorption depends upon the nature of the chromophoric solute, the concentration of solute, and the thickness of liquid absorbing layer. If a layer of 1-cm. thickness transmits a fraction t of the incident light, a thickness

x of the material will transmit the fraction t^x, and the intensity of light transmitted will be $I = I_o t^x$, where I_o is the incident intensity. This may be written $I = I_o e^{-kx}$, where k, the absorption coefficient, equals $(\log_e (I_o/I))/x$. In many cases the absorption coefficient of a solution is proportional to the concentration of the solute. Then the absorption coefficient may be written $k = u_o c$, where c is the concentration and u_o is the absorption coefficient for unit concentration. The transmittance is then given by the equation $T = I/I_o = e^{-u_o cx}$, in which form it is known as Beer's Law. The absorption coefficient, k, can be calculated from the equation $k = (\log_e (1/T))/x$, with T expressed as a fraction (75 per cent equivalent to 0.75), and where x is the thickness of the liquid layer of the cell in centimeters.

Since diluted samples were used for most transmittance measurements, it was necessary to divide the values obtained for the absorption coefficient by the concentration of the liquor in the diluted solution to obtain k for the original liquor. This has been done throughout and the symbol k has been reserved for absorption coefficients on the basis of the original liquor unless otherwise specified. The working equation was very simple. The exponent $(k_d x)$ in the expression $T = e^{-k_d x}$ was read directly from the transmittance curves by means of a scale constructed for this purpose and carefully checked. In this expression x is 0.5 and k_d is the absorption coefficient for the diluted liquor. Then, with $k_d x$ read directly, $k = (k_d x)/(0.5)\ (c_d)$, where c_d is the concentration (as a decimal fraction) of the original liquor in the diluted solution tested. In those cases where undiluted liquor was

used in a thinner cell, $\underline{k} = (\underline{kx})/(\underline{x})(1)$, in which $\underline{kx}$ was read directly from the curves and then divided by $\underline{x}$, the thickness of light-absorbing liquid in centimeters.

Color is measured as the spectral transmittance, i.e., the percentage of transmittance of monochromatic light over the wavelength range from 400 to 700 mmu. Practically, however, the transmittance values are converted to absorption coefficients, and the absorption spectrum is used because of the direct proportionality of absorption coefficients to concentration of chromophoric substance in solution. The absorption spectrum is obtained by plotting $\underline{k}$ against wavelength in mmu.

With a solution conforming to Beer's Law, concentration changes may be calculated from the absorption coefficients. When two or more substances are in solution, the monochromatic absorption coefficient is the sum of the several individual absorption coefficients. In a complex solution, such as a black liquor, the relation of absorption coefficients to concentration of chromophoric material is an analytical tool.

Another useful treatment of absorption spectra is the plotting of log $\underline{k}$ against wavelength in mmu. A series of dilutions of a solution obeying Beer's Law will give on such a graph a family of curves of exactly similar shape which may be made to fit each other by translational shifts. This "parallelism" makes possible the identification or differentiation of colored substances at various concentrations.

b. Conformity to Beer's Law on Dilution

Most alkaline black liquors are so deeply colored that useful transmittance curves cannot be obtained in the usual absorption cells without diluting the liquors. The liquors from Cooks L-1 and L-2 required a dilution of at least 50 times to give useful curves when tested in the absorption cell of five mm. thickness. From the foregoing discussion of theory, it is obvious that accurate and comparable measurements of color cannot be made on diluted solutions unless the solutions obey Beer's Law on dilution. It has already been mentioned by Bard (14) that kraft liquors do not obey Beer's Law on dilution with water. This was also found to be true of soda liquors. To make the transmittance measurements truly representative of the colored materials present, it is then necessary to find a diluent in which Beer's Law will be followed or to measure the transmittance of thin liquor films of reproducible thickness.

In order to measure the transmittance of undiluted black liquors, an absorption cell should furnish a liquid layer with a quantitatively reproducible thickness in the range of 0.005 to 0.010 cm. It should also be easy to clean and fill. A pair of cells was built which furnished a liquid layer in the proper thickness range and which could be cleaned and filled conveniently, but the thickness of the liquid layer was not reproducible enough for quantitative work. Successive fillings with one sample showed that the liquid thickness was reproducible only within five or ten per cent.

However, these cells were very useful in the investigation of conformity to Beer's Law with various diluents. By comparing k values obtained with the small cell with those obtained by use of the five mm. cell and diluted solutions, it was possible to follow changes in hue due to dilution over a wide range of concentrations.

A schematic diagram of the cell is shown in Figure 1. A pair of optically flat disks 1-9/16 inches in diameter and 3 to 4/32 inches thick (obtained from the Riggs Optical Company) were separated by two crescent-shaped shims. The shims were cut from 0.002-inch platinum foil with scissors. Before using, the feather edge was removed from the shims by polishing on a glass plate with 600-mesh carborundum. The glass disks were held firmly against the shims by four spring clamps. The clamps were obtained from small fuse holders, such as those used in radios and automobiles. Two of the clamps were soldered to a brass base which served to hold the assembled cell in the spectrophotometer so that it was properly centered. Two cells were made, one of which was filled with distilled water and used in the standard side of the instrument. Extra pairs of glass disks were available for the sample cell to avoid cleaning and drying before every test.

In using the cell, the shims and glass disks were cleaned by scrubbing with sodium bicarbonate to remove deposits, then washed in fresh cleaning solution and thoroughly rinsed in distilled water. The parts were air dried. A warm blast from an electric hair drier was used to speed the drying if necessary. The parts were handled with tweezers as far as possible to avoid greasy finger prints.

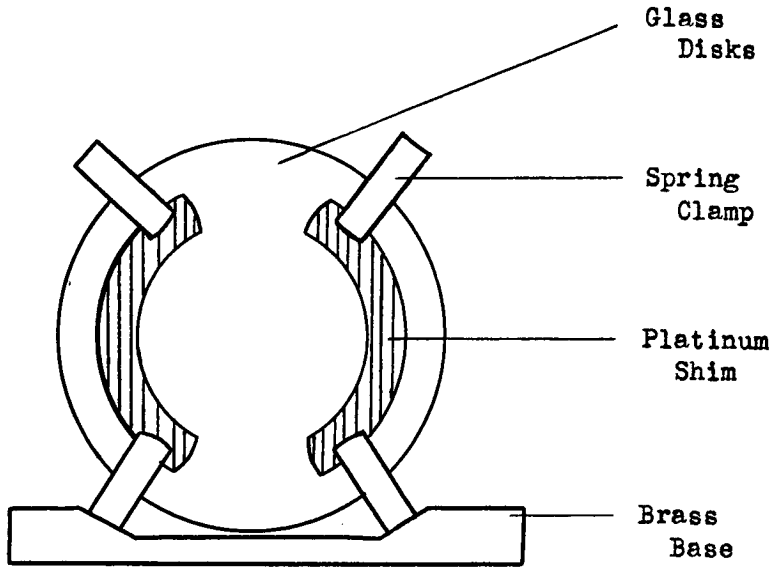


Figure 1

THIN FILM ABSORPTION CELL

To fill the cell, the shims were put in position at the edges of one of the glass disks, and the other disk placed over them. The two top clamps were placed to hold the disks together at one end of the shims. The disks were held upright and a few drops of the liquid to be tested were placed on the crack between the disks with a dropper. The liquid immediately spread between the disks by capillary attraction. The unclamped bottoms of the disks were then pushed gently in and out. This caused the bottom edge of the liquid film to move up and down, which removed small visible air bubbles. When a smooth unbroken film had been formed between the disks, they were pushed into the bottom clamps, which were attached to the base. The excess liquid formed a drop at the bottom of the disks and could be removed with a blotter. The remainder of the liquid would be held as a smooth film for some time by capillary attraction, although it began to draw in from the edges by evaporation after the first few minutes.

This cell was used as follows: A transmittance curve was run and the values of kx determined at various wavelengths. Since x (thickness of the liquid layer) was not exactly reproducible, a value for x was taken which would make k determined in the small cell equal to k as determined in the 5 mm. cell on a diluted solution. This was done at one wavelength (500 mmu.) and the x value found was used to find k at the other wavelengths. Then a comparison of k values at different wavelengths would show immediately if the absorption curve had been distorted (the "hue" changed) by dilution.

The 5-1/2-hour liquor from Cook L-1 was used to investigate the conformity of soda black liquor to Beer's Law. Dilutions were made with distilled water to contain 0.25, 0.5, 2, 4, and 10 per cent of black liquor. Transmittance curves were run, using the five mm. cell. The k values obtained are shown in Table I. It can be seen that above 500 mmu. k increases with increasing dilution, whereas at the shorter wavelengths it decreases. This indicates that a serious change in hue was caused by dilution. Even at 460 and 500 mmu., where k is most uniform, a 10 to 12 per cent variation in k is found over the dilution range used.

Black liquors act as indicators, with a very marked color change near the neutral point. It seemed possible that the pH change on dilution with water might account for the change in hue. A 0.1 molar sodium carbonate solution was used instead of distilled water in an attempt to maintain a higher pH. The exact pH obtained was not determined, since a glass electrode pH meter does not give good results at such high pH. The results of diluting with sodium carbonate solution (Table II) show that a change in the shape of the absorption spectrum takes place on dilution which is almost the same as when water was used. There is some improvement, however.

Since using a mild alkaline solution improved the results but did not provide a satisfactory diluent, a normal solution of sodium hydroxide was tried. These results (Table III) show that over the range of 460 to 540 mmu. k varies very little with dilution. Over a liquor concentration range of 0.25 to 10 per cent, absorption at

TABLE I

VALIDITY OF BEER'S LAW WITH SODA BLACK LIQUOR ON DILUTION WITH WATER, COOK L-1, 5 1/2-HOUR LIQUOR

Liquor %	Absorption Coefficient, k Wavelength--mμ 420	460	500	540	600	680
0.25	280	152	96	72.0	43.2	24.0
0.50	280	152	100	72.0	43.1	24.0
1.0	290	150	98	66.0	41.6	24.0
2.0	332	155	96	65.0	39.2	25.0
4.0	---	161	90	56.4	34.5	19.5
10.0	---	---	88	53.2	30.0	16.0
100.0	468	176	99	59.8	31.5	14.4

TABLE II

VALIDITY OF BEER'S LAW WITH SODA BLACK LIQUOR ON DILUTION WITH 0.1 MOLAR SODIUM CARBONATE, COOK L-1, 5 1/2-HOUR LIQUOR

Liquor %	Absorption Coefficient, k Wavelength--mμ 420	460	500	540	600	680
0.25	312	160	100	72.0	42.4	27.0
0.50	304	160	100	70.0	41.6	26.0
1.0	306	158	98	66.0	40.8	24.0
2.0	332	157	98	64.0	38.1	23.0
4.0	---	170	99	62.0	37.0	17.0
10.0	---	---	---	58.4	33.0	17.6
100.0	468	176	99	59.8	31.5	14.4

TABLE III

VALIDITY OF BEER'S LAW WITH SODA BLACK LIQUOR ON DILUTION WITH 1 NORMAL SODIUM HYDROXIDE, COOK L-1, 5 1/2-HOUR LIQUOR

Liquor %	Absorption Coefficient, k Wavelength--mmu. 420	460	500	540	600	680
0.25	408	179	100	58.8	31.9	18.4
0.50	402	172	100	59.6	35.0	19.6
1.0	404	172	100	61.0	34.0	18.6
2.0	---	177	98	60.8	34.1	18.6
4.0	---	178	97	60.4	33.0	17.4
10.0	---	---	---	61.4	31.6	17.6
100.0	468	176	99	59.8	31.5	14.4

these wavelengths is directly proportional to the concentration of the black liquor. Therefore, it can be assumed that k at 500 mmu. can be used as a measure of color intensity. It appears that the error in measuring k caused by dilution is less than 3 per cent. Since comparisons will not ordinarily be made of solutions so widely different in concentration, much better accuracy than this can be expected.

Comparison of the k values obtained by dilution and those obtained in the small cell show that there is still some distortion of the absorption curve near 400 and near 700 mmu. However, the change on dilution with sodium hydroxide is much less that that with other diluents. It must be kept in mind that at these wavelengths instrumental

sensitivity is lowest, and that the comparison of an undiluted liquor with a 400 to 1 dilution is rather severe.

On the whole, dilution with sodium hydroxide furnishes a quite accurate method of investigating the shape of the absorption curve of black liquors and the concentration of the colored materials in black liquor. Because of this information, normal sodium hydroxide solution was adopted as a diluent. In the remainder of the work on soda liquors k was determined from dilutions made with sodium hydroxide or on solutions which had been made up to one normal in sodium hydroxide at the volume tested.

c. Effect of Age on Soda Liquor Color

The color of the samples changed with time, and even after several weeks an equilibrium was not reached. Figure 2 illustrates this for the half-hour liquor sample from Cook L-2. These curves represent transmittances of this sample at different ages when freshly diluted with normal sodium hydroxide. They show that the transmittance decreased during the first week. After 12 days the trend had been reversed. At this time the curve (not shown) was nearly the same as the three-day curve. The transmittance continued to increase until, after 47 days, the color was much lighter than it was immediately after the cook.

The 5 1/2-hour liquor showed the same effect, except that it continued to darken for a longer time. After 12 days the hue changed slightly, but the depth of color was not greatly altered. Figure 3

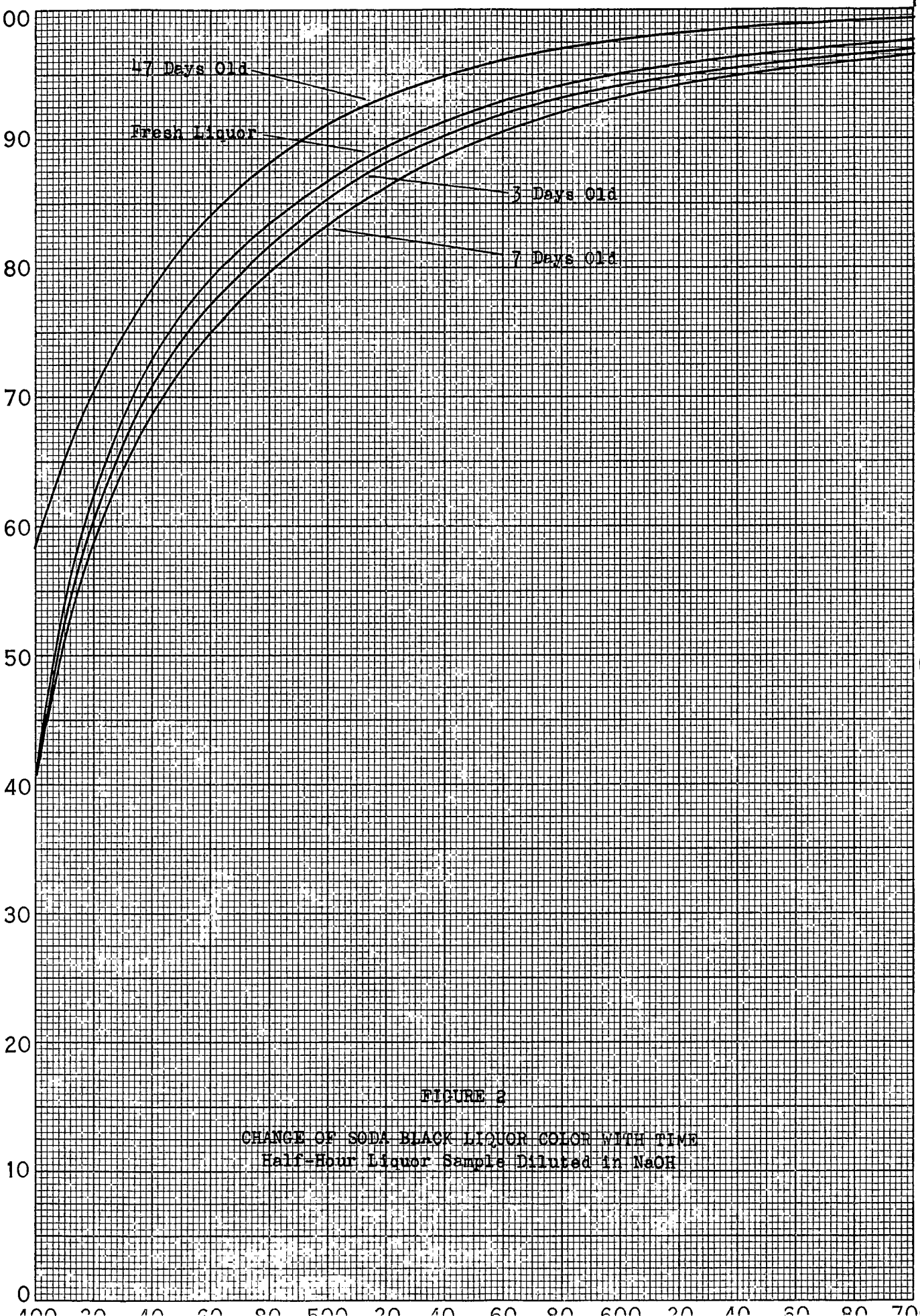


FIGURE 2

CHANGE OF SODA BLACK LIQUOR COLOR WITH TIME
Half-Hour Liquor Sample Diluted in NaOH

TEST NO._____ BY_____
DATE_____

GENERAL ELECTRIC
RECORDING SPECTROPHOTOMETER

INSTRUMENT NO._____

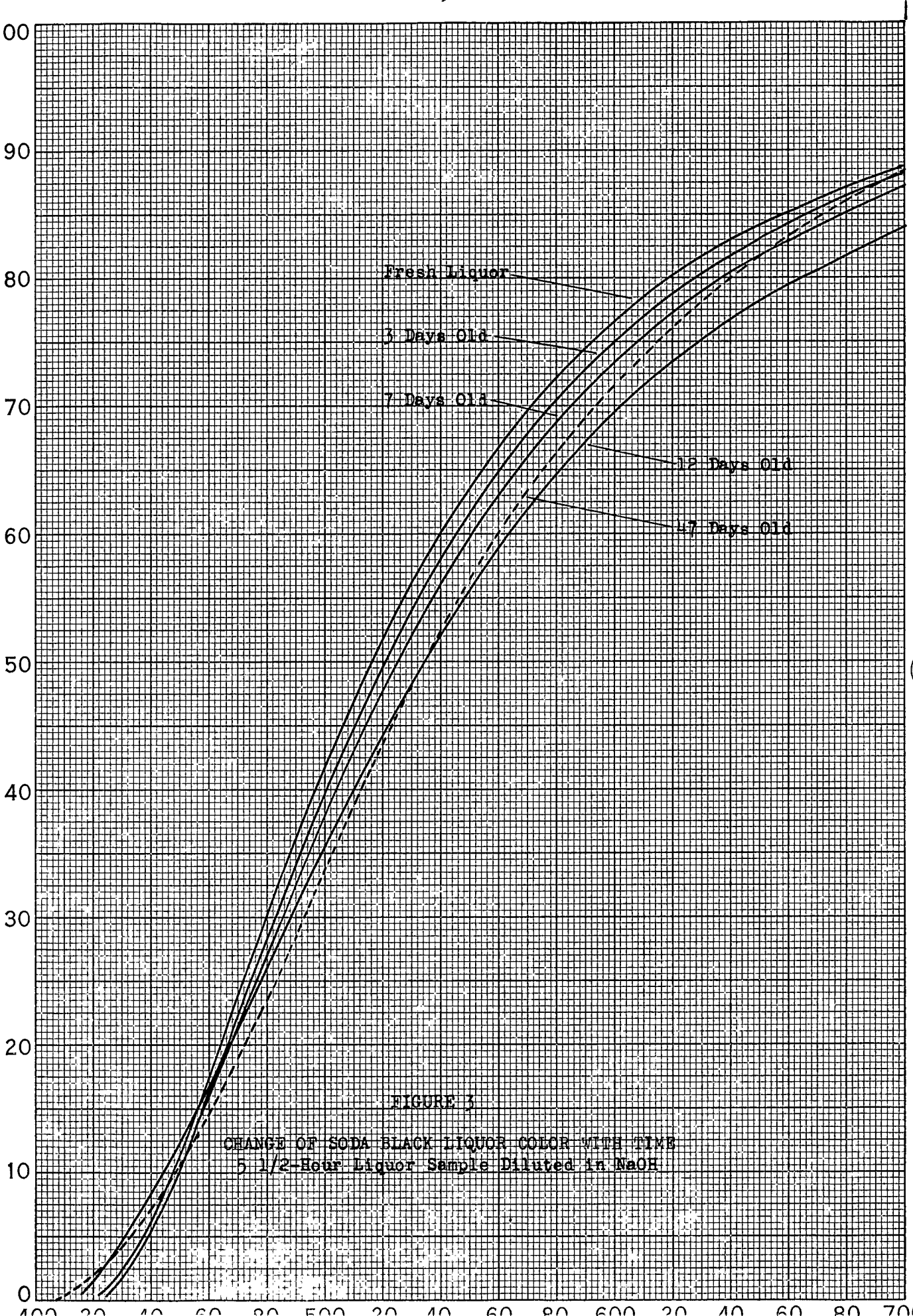


FIGURE 3

CHANGE OF SODA BLACK LIQUOR COLOR WITH TIME
5 1/2-Hour Liquor Sample Diluted in NaOH

shows transmittance curves for this liquor taken 40 minutes, three days, seven days, twelve days, and forty-seven days (broken line) after the cook.

Unfortunately, all of the tests could not be run on fresh liquors, and there are probably some discrepancies due to the change of the color with time. Whenever comparisons of different samples or different liquor fractions were made, this was minimized as far as possible by comparing transmittance curves taken at nearly the same time.

The change in color of the solutions after dilution was found to be even more rapid. An investigation of this effect was made and will be presented in detail in a later section. This study also aided in reducing errors due to color change with time.

3. Chemical Analysis of Liquors

The determination of the organic constituents in alkaline black liquors is a complex problem and complete or accurate methods have never been developed. The methods used in the analysis of these liquors are patterned after those used by Grimes (21) in his study of alkaline pulping.

a. Total Solids

A ten ml. sample was pipetted into a tared porcelain crucible and weighed at once. The crucible was heated on a steam bath until the liquor was sticky, then left overnight in a vacuum desiccator over sodium

hydroxide. The crucible was dried in an oven at 105° C. and weighed in a weighing bottle. The oven drying was carried out for five hours or more until nearly constant weight was reached. Although the excess free sodium hydroxide in the samples was difficult to dry, this method seemed to give logical and reproducible results.

b. Ash

Nearly all of the inorganic matter in the liquors was sodium, as the hydroxide or as organic salts. Sodium could be determined with sufficient accuracy by weighing as the sulfate.

The residue from the total solids determination was smoked off with a burner, moistened with sulfuric acid, and put in a cold muffle furnace. The muffle was heated and the crucible held at red heat for two hours. The crucible was cooled, moistened again with sulfuric acid, and the heating repeated. Two hours at red heat was found to be sufficient to give constant weight. The sodium sulfate was weighed and converted to sodium hydroxide by calculation.

c. Total Organic Matter

Total organic matter was calculated by subtracting ash (as sodium hydroxide) from total solids.

d. Acid-Insoluble Organic Matter

The liquor samples were pipetted into centrifuge jars and diluted to 75 ml. with water. The size of the sample varied from 10 to 100 ml., depending on the lignin content of the liquor. Larger

samples were required of the liquors from the early part of the cook to insure an accurate analysis and enough precipitate for the methoxyl determinations. Samples over 50 ml. were divided between two jars for the first precipitation.

Each diluted sample was made acid with six normal hydrochloric acid, stirred thoroughly, and centrifuged. The supernatant liquor was filtered through an A-2 porous bottom porcelain crucible, using suction. The decanted liquor was replaced with distilled water and the precipitate stirred again. After centrifuging, the wash water was decanted as before. This was repeated until the first liquor and four portions of wash water were collected in the suction flask. In all cases, the last wash was colorless. If necessary a drop or two of hydrochloric acid was added to prevent colloid formation. This acid-soluble fraction was diluted to a volume 20 times that of the black liquor sample. In making up to this volume, enough strong sodium hydroxide was added to neutralize the acid and make the final volume one normal in alkali. This solution was used for determining transmittance of the acid-soluble fraction of the liquor.

Meanwhile, the precipitate was transferred to a crucible, where it was washed with water until the filtrate was neutral to litmus paper. This required a week or more, but it was necessary to prevent the formation of a dark horny substance on drying. After thorough washing the precipitate would dry to a brown, crumbly powder.

When the washing was finished, the precipitate was dried in a vacuum desiccator over sodium hydroxide. Finally, it was dried at

105° C. to constant weight (two hours) and weighed in a weighing bottle.

e. Acid-Soluble Organic Material

The acid-soluble organic material was estimated by subtracting acid insoluble from total organic. This can be nothing better than an approximation. Most of this fraction has been identified by other investigators (1) as colorless organic acids, and it is obvious that the total weight of material in this fraction could have no relation to color. The color actually found in the acid-soluble fractions of the periodic samples substantiates this conclusion.

f. Methoxyl Content

The methoxyl content of the dried precipitates and of other preparations was determined by the Institute Method 18.

g. Potentiometric Titrations

A ten-ml. black liquor sample was pipetted out and diluted to 500 ml. in a volumetric flask. Of this, 100 ml. were taken for titration. Therefore, a two-ml. liquor sample was titrated in an initial volume of 100 ml. A complete potentiometric curve from pH 12 to pH 4 was determined with tenth normal standard acid, using a Cameron pH meter. It was standardized against potassium biphthalate buffer.

Strong alkali was calculated from the acid required to pH seven. Total alkali was calculated from the acid required to pH four.

4. Course of the Soda Cook

Figures 4 and 5 show the transmittance curves of the periodic liquor samples (diluted 1 volume to 50 with normal sodium hydroxide) of Cooks L-1 and L-2, respectively. The curves of log $\underline{k}$ against wavelength which were derived from these transmittances are shown on Figures 6 and 7. The chemical analyses are given in Table IV and V and presented graphically in Figures 8 and 9.

If it is kept in mind that maximum temperature was not reached until the end of 1 1/2 hours, Figures 8 and 9 show that the pulping action was extremely rapid during the first part of the cook. In general, the analyses confirm the results of Brauns and Grimes (5), with the carbohydrates (which comprise most of the acid-soluble organic material) going into solution more rapidly than the lignin during the first part of the cook.

Lignin was estimated from the amount of acid-insoluble material and the methoxyl content of this precipitate. This was done by assuming a methoxyl content of 14.7 per cent for alkali lignin, except for the 5 1/2-hour liquor. Apparently the low methoxyl content of this precipitate is not representative of the lignin. According to Brauns and Grimes (5) lignin may be partially demethylated after severe cooking. They also found lower methoxyl on the acid precipitates after severe cooking. For this sample, 14.45 was used as an approximation. This value is underlined in the table.

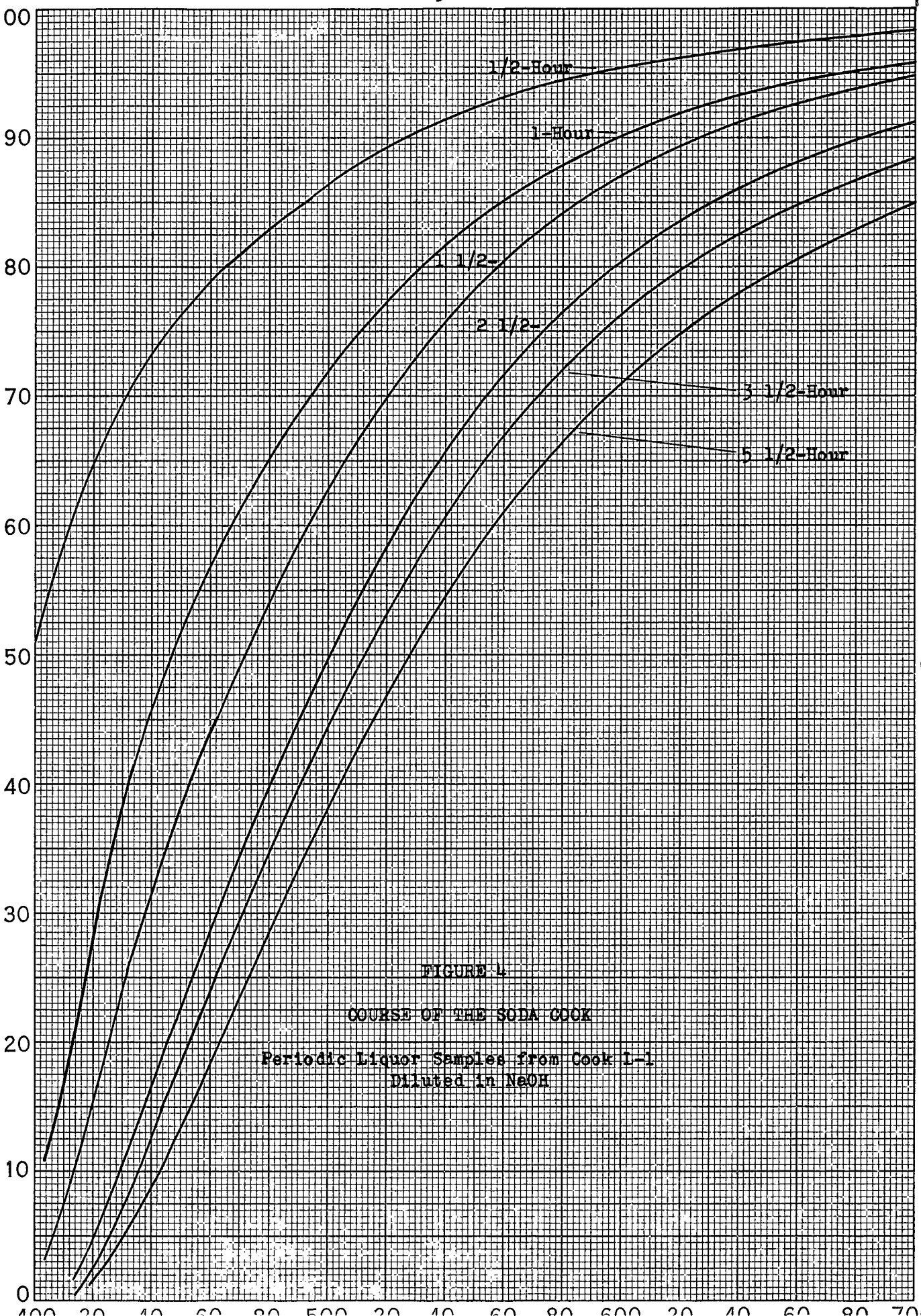


FIGURE 4

COURSE OF THE SODA COOK

Periodic Liquor Samples from Cook 1-1
Diluted in NaOH

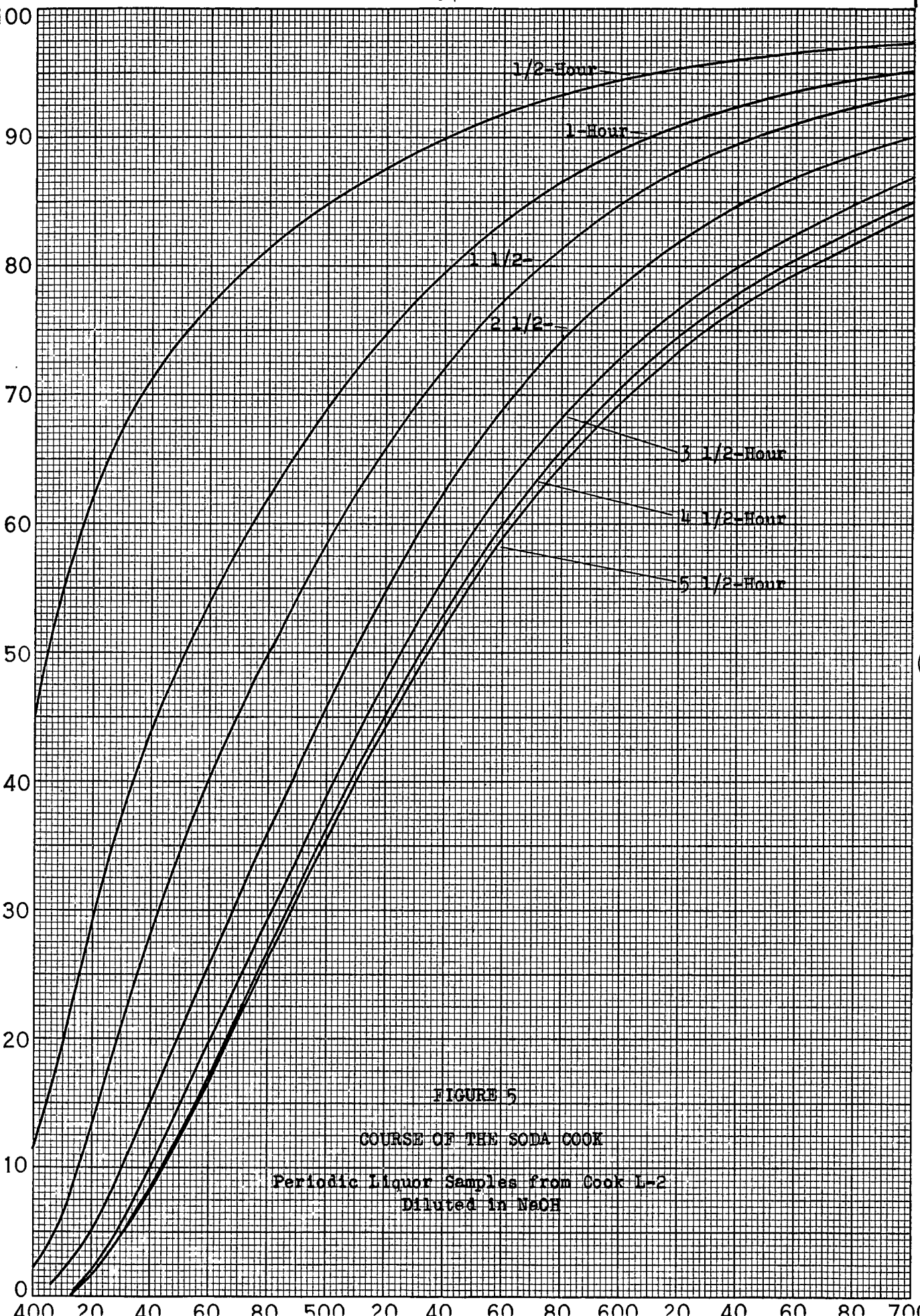


FIGURE 5

COURSE OF THE SODA COOK

Periodic Liquor Samples from Cook L-2
Diluted in NaOH

FIGURE 6

SPECTRAL ABSORPTION OF PERIODIC LIQUOR SAMPLES FROM COOK L-1

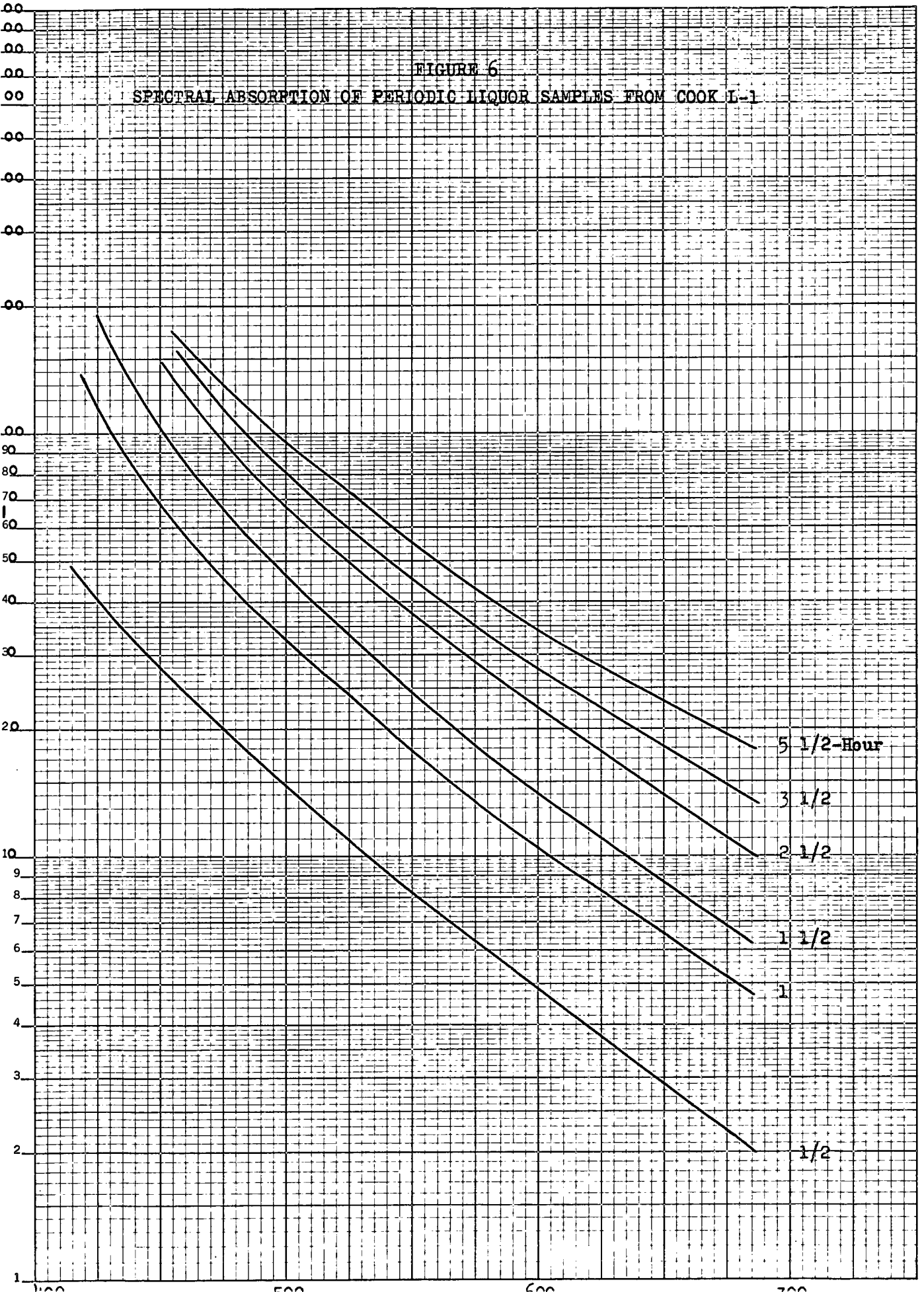


FIGURE 7

SPECTRAL ABSORPTION OF PERIODIC LIQUOR SAMPLES FROM COOK L-2

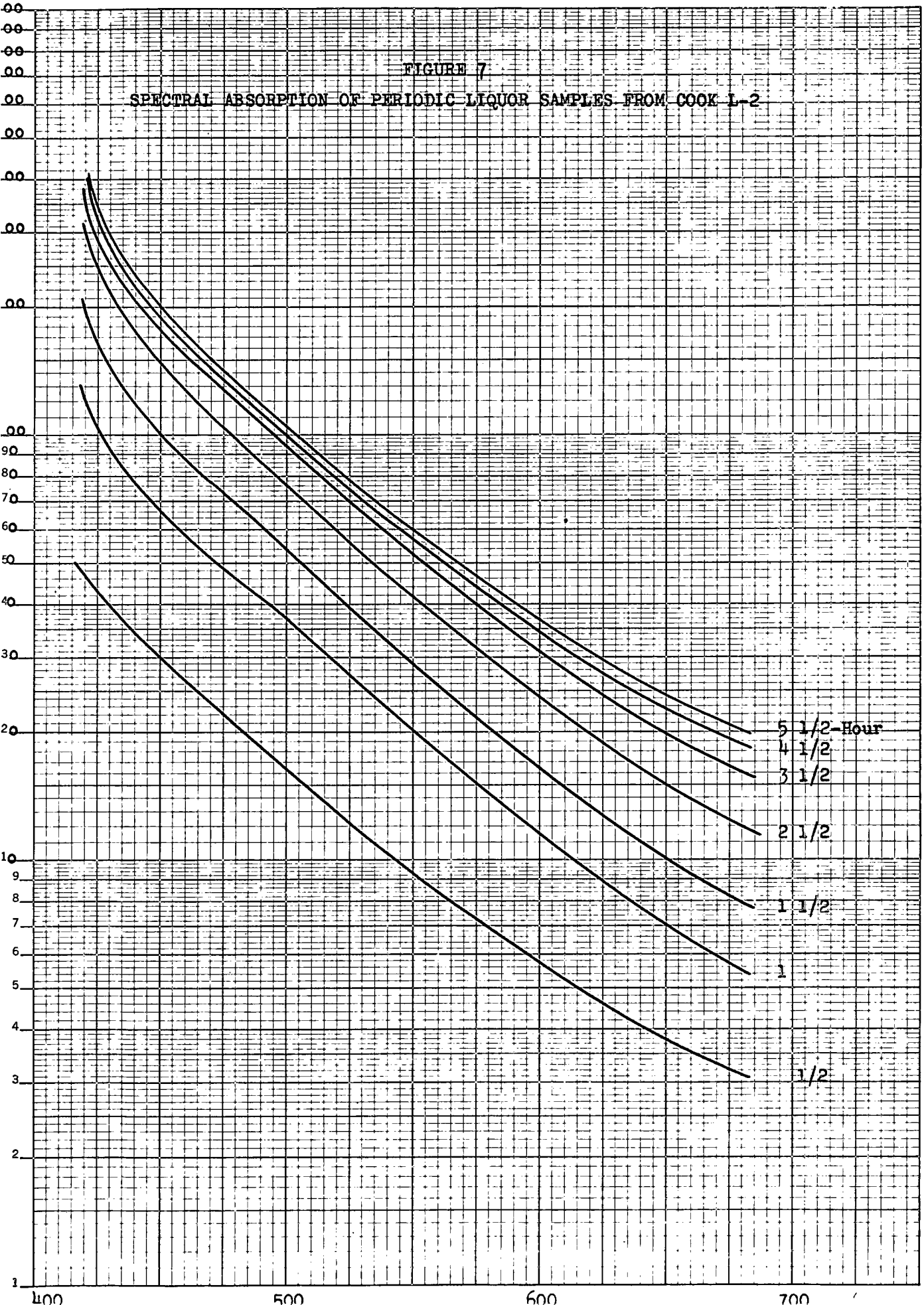


TABLE IV

ANALYSIS OF LIQUOR SAMPLES FROM COOK L-1

All concentrations in grams per liter

Cooking time in hr.	1/2	1	1 1/2	2 1/2	3 1/2	4 1/2	5 1/2
Strong alkali as NaOH	53.0	48.3	44.9	40.6	39.0	37.8	37.2
Total alkali as NaOH	60.6	57.1	56.0	53.7	53.1	51.0	53.9
Total solids	91.6	106.8	128.1	147.3	154.1	158.1	172.2
Ash as NaOH	64.7	62.2	62.2	62.8	64.4	62.2	67.3
Total organic matter	26.9	44.6	65.9	84.5	89.7	95.9	104.9
Acid insoluble	2.5	11.3	25.6	42.3	45.3	45.7	49.7
Acid soluble organic	24.4	33.3	40.3	43.2	44.4	50.2	55.2
k at 500 mmu	14.8	33.0	46.7	70.1	81.4	83.6	97.5

TABLE V

ANALYSIS OF LIQUOR SAMPLES FROM COOK L-2

All concentrations in grams per liter

Cooking time in hours	1/2	1	1 1/2	2 1/2	3 1/2	4 1/2	5 1/2
Strong alkali as NaOH	46.4	40.8	36.1	33.3	32.0	31.0	28.6
Total alkali as NaOH	55.0	50.5	50.0	46.2	46.2	45.8	44.7
Total solids	90.3	104.4	132.7	153.0	166.3	166.8	170.6
Ash as NaOH	63.9	60.7	65.0	64.6	64.1	64.1	64.8
Total organic matter	26.4	43.4	67.7	88.4	102.2	102.7	105.8
Acid insoluble	2.8	12.6	26.2	43.4	49.3	48.5	49.8
Acid soluble organic	23.6	30.8	41.5	45.0	52.9	54.2	56.0
Methoxyl in acid insoluble, %	10.61	13.42	13.63	14.31	14.33	14.48	13.63
Estimated lignin	2.0	11.5	24.3	42.4	48.1	47.7	48.7
Acid insoluble less lignin	0.8	1.1	1.9	1.1	1.2	0.8	1.1
k at 500 mmu	16.5	37.0	54.5	77.5	94.3	102	104

FIGURE 8

CONCENTRATION OF CHEMICAL COMPONENTS AND COLORING MATTER IN SODA BLACK LIQUOR

Cook L-1

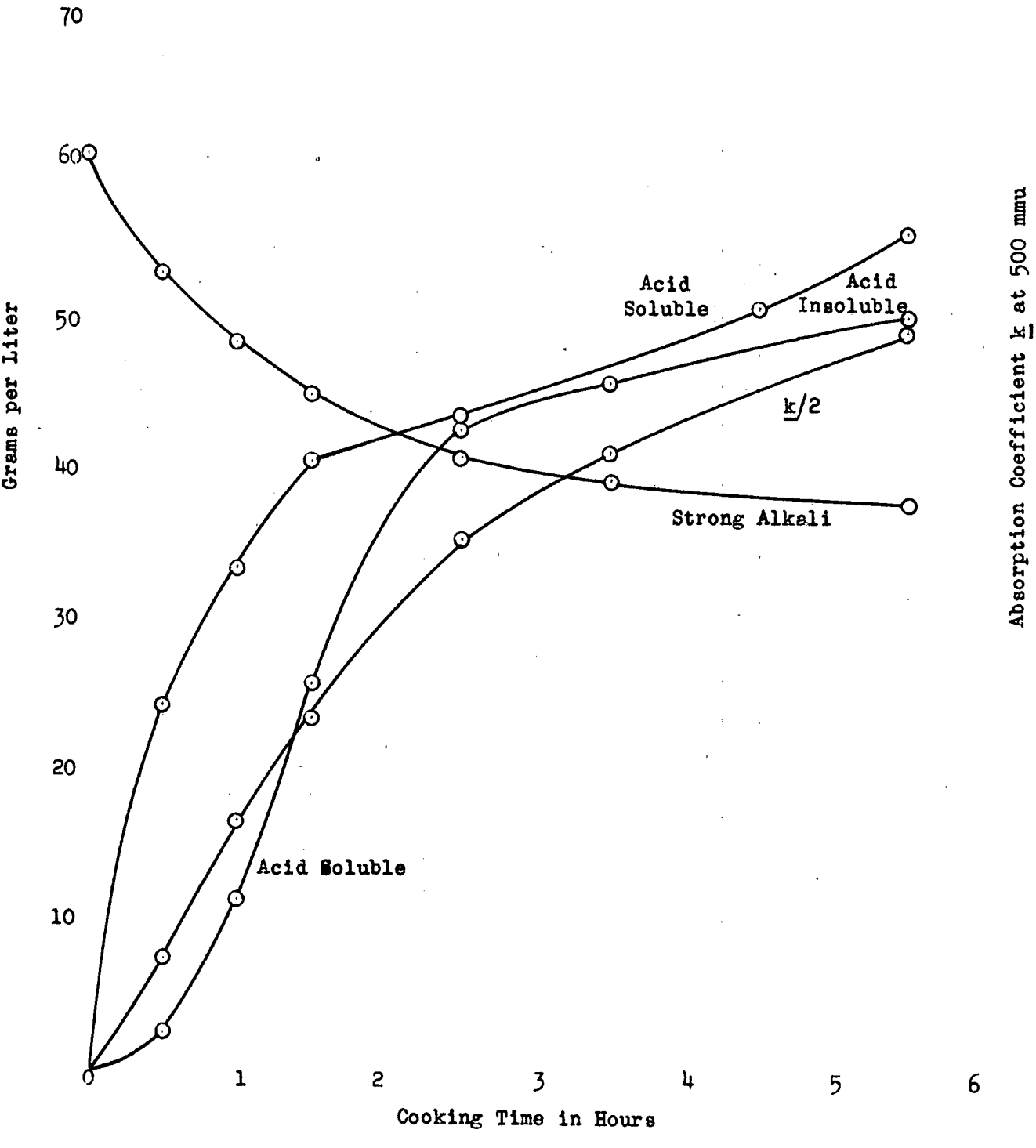
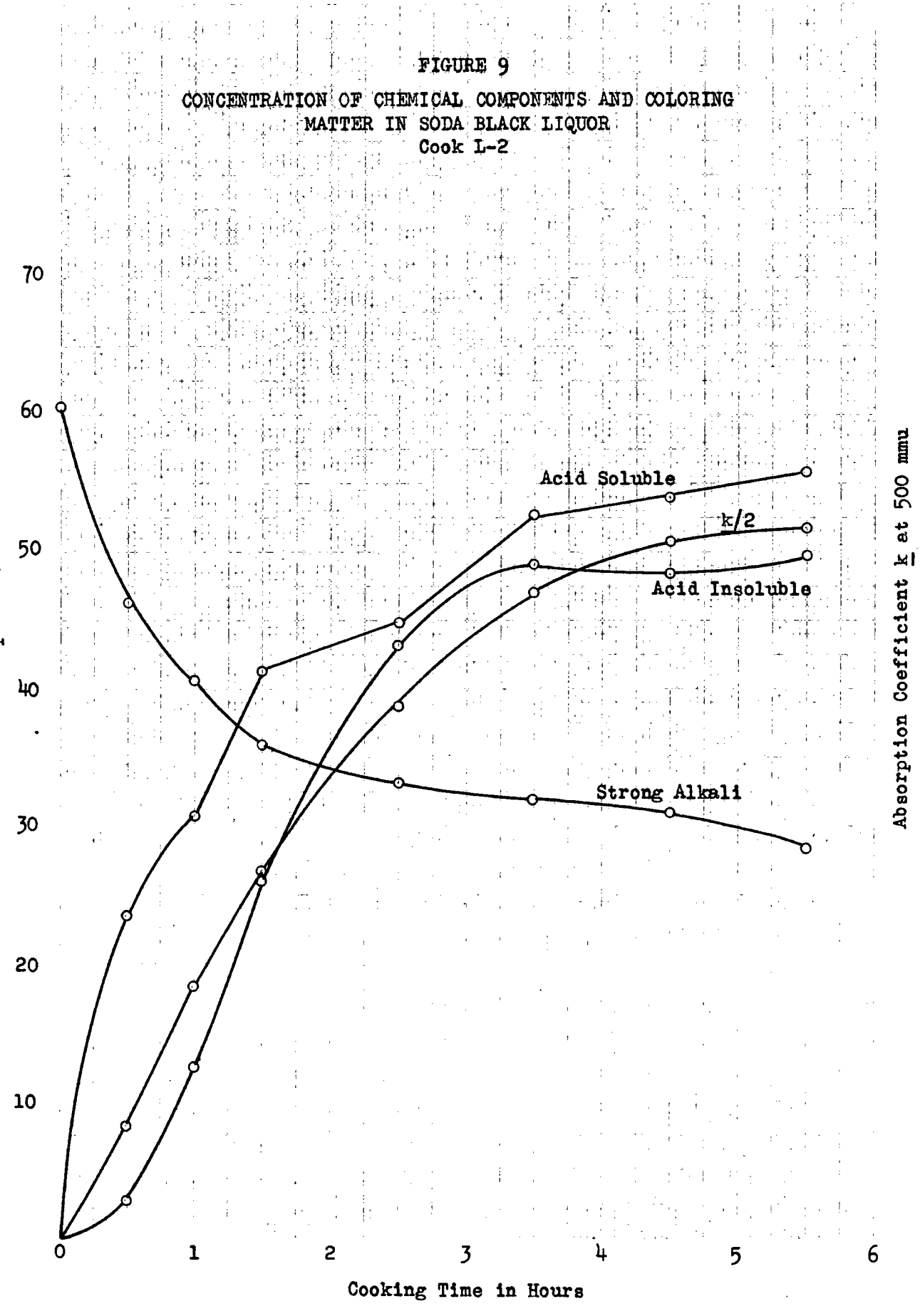


FIGURE 9

CONCENTRATION OF CHEMICAL COMPONENTS AND COLORING MATTER IN SODA BLACK LIQUOR
Cook L-2



The color increased in a smooth curve with time. The log k curves show that there was no marked change in the shape of the absorption spectrum (hue) from hour to hour. Since this is true, k at 500 mmu. is a measure of color which can be used in comparisons of the various liquors.

The complete potentiometric titration curves showed much the same results as Brauns and Grimes (5) in regard to the relative amounts of alkali used by the lignin and the carbohydrates and as to the buffering action of the acids formed from the carbohydrates. This is made quite clear when the black liquor titrations are compared with the titrations made on solutions of purified lignin in sodium hydroxide. Since these data are not pertinent to this problem, they are not reproduced here.

5. Heating of Isolated Liquor

Several of the periodic liquor samples were heated further in order to investigate the effect of heating on the color and chemical analysis. The samples were pipetted into stainless steel tubes of about 110 ml. capacity. The tubes were capped loosely with stainless steel caps to minimize volume changes due to distillation from the liquor outside the tubes. The tubes were then placed in a small autoclave which was about two-thirds full of soda white liquor. The autoclave was sealed, brought up to 170° C. and held there for three hours with a gas flame. Air cooling to 100° C. required about two hours. At this time the autoclave was opened and the tubes removed.

Each tube was emptied into a beaker and washed with distilled water. Liquor and washings were made up to twice the volume of the original sample. These solutions were sampled for optical and chemical analysis.

Blanks were run on sodium hydroxide. No color was found in these or in the liquor surrounding the tubes. The black liquors became much darker on such treatment. There was a possibility that the oxygen in the air trapped in the autoclave had some effect on this change. There was about 1 1/2 liters of air over the six tubes. To investigate this, a comparison cook was made on the 5 1/2-hour liquor in a stainless steel bomb heated in a wax bath. Before heating, oxygen was removed by three evacuations, each followed by the introduction of nitrogen. In this cook the color change was about half that found by the use of the autoclave. However, the new color formed had the same spectral absorption curve in each case. It seems permissible to assume that the samples heated in the autoclave give results which will show how the soluble constituents in the liquor change on further heating.

The 1/2, 1 1/2, 3 1/2, and 5 1/2-hour samples from Cook L-2 were reheated for three hours at 170° C. as described before. Table VI contains the analyses of these reheated liquors and those of the original liquors. Table VII gives the absorption coefficients at several wavelengths of the original and reheated liquors.

In all cases a small decrease is noted in the amount of acid-insoluble material after heating the isolated liquors. However, the methoxyl

TABLE VI

EFFECT OF HEATING ISOLATED LIQUORS
ANALYSIS OF LIQUORS FROM COOK L-2

All concentrations in grams per liter

Cooking time—hr.	1/2		1 1/2		3 1/2		5 1/2	
Further heating—hr.	0	3	0	3	0	3	0	3
Strong alkali as NaOH	46.4	45.0	36.1	33.8	32.0	29.2	28.6	26.3
Total alkali as NaOH	55.0	53.6	50.0	47.4	46.2	45.6	44.7	44.0
Total solids	90.3	87.6	132.7	124.6	166.3	164.1	170.6	173.3
Ash as NaOH	63.9	59.7	65.0	58.5	64.1	64.6	64.8	65.1
Total organic matter	26.4	27.9	67.7	66.1	102.2	99.5	105.8	108.2
Acid insoluble	2.8	2.6	26.2	22.0	49.3	45.0	49.8	47.5
Acid soluble organic	23.6	25.3	41.5	44.1	52.9	54.5	56.0	60.7
Methoxyl in acid insoluble, %	10.61	10.90	13.63	13.64	14.33	14.07	13.63	13.66
Estimated lignin	2.0	1.9	24.3	20.4	48.1	43.1	48.7	46.5
Acid insoluble less lignin	0.8	0.7	1.9	1.6	1.2	1.9	1.1	1.0

TABLE VII

EFFECT OF HEATING ISOLATED LIQUORS
OPTICAL ANALYSIS OF LIQUORS FROM COOK L-2

$\underline{k}$ at various wavelengths

Cooking time--hr.	1/2		1 1/2		3 1/2		5 1/2	
Further heating--hr.	0	3	0	3	0	3	0	3
mμ								
420	47.4	51.5	202	254	390	---	410	---
460	26.5	26.8	92	122	164	208	180	268
500	16.5	16.1	54.5	74.5	94.3	121	104	164
540	10.2	10.8	32.2	48.1	58.3	77.2	65.0	110
600	5.8	6.0	16.5	28.1	31.3	44.8	36.9	65.3
680	3.1	4.1	8.0	15.1	16.0	24.8	20.1	35.0

content is not appreciably changed. A small amount of alkali is consumed by further heating, probably due to the formation of additional acids from the carbohydrates in solution. No marked changes in the analyses are apparent.

The color darkened a great deal in all except the 1/2-hour sample. It can be seen that the color is increased more by heating the isolated liquor than it is by further cooking in the presence of the pulp. The cause of this increase in color on heating is not apparent from the chemical analyses. Other experiments will clarify this point.

6. Preparation of Purified Lignin

The 2 1/2-hour liquor sample from Cook L-2 contained 43.4 grams per liter of acid-insoluble material, yet it had not undergone such severe heating as the later samples. For this reason it was chosen for use in preparing a purified alkali lignin. It seems logical that such a preparation would be representative of lignin as found in black liquor.

In general, the purification procedure was that used by Marshall, Brauns, and Hibbert (3) in preparing alkali lignin A.

A 150-ml. sample of black liquor was placed in centrifuge jars, precipitated with hydrochloric acid, and the precipitate washed four times by centrifuging with water. It was further washed until free of acid by repeatedly stirring with water and filtering on a Büchner funnel with hardened filter paper.

When the precipitate was acid free, the moist cake was dissolved in about 70 ml. of purified dioxane. Water was removed by distilling under reduced pressure, adding dry dioxane, and repeating until the distillate would not wet potassium carbonate crystals. The dioxane solution was then centrifuged and filtered through a fritted glass crucible to remove the precipitate.

The amount of precipitate was not very great, and after washing was colorless. This precipitate (which should consist mostly of carbohydrates) was washed with dioxane and water and dissolved in alkali. The alkaline solution was only very faintly yellow. This carbohydrate fraction from 150 ml. of liquor gave such a slight color when dissolved in 50 ml. of sodium hydroxide that it was useless to run a transmittance curve. However, it should be remembered that at this point in the cook most of the carbohydrates were in the acid-soluble fraction.

A five-ml. portion of the dioxane solution was poured through a filter paper into a dropping tube which added it dropwise to about 80 ml. of purified absolute ether in a centrifuge jar. During the addition the ether was agitated by an electric stirrer. The lignin separated as a sandy precipitate. It was a very light yellow-brown--almost cream colored--although the acid precipitate was almost chocolate brown before purification. The ether precipitate was centrifuged and the ether decanted. Fresh ether was added, and the precipitate stirred. The precipitation was repeated until all the dioxane solution had been used.

After every third addition of dioxane solution, the precipitate was washed by centrifuging with fresh ether. When all the dioxane had been added, the precipitate was washed twice with ether and finally allowed to stand overnight with ether. The final ether washes were colorless. The others were light yellow.

All the ether used in precipitating and washing was filtered through filter paper and saved. This light yellow solution should contain acid-insoluble extractives and a small fraction of lignin designated as lignin B by Marshall, Brauns, and Hibbert (3). It was concentrated by distilling under reduced pressure. The ether and dioxane were removed by adding water and continuing the distillation. When this was done a precipitate appeared, partly as a yellow suspension and partly as a very dark sticky material. This precipitate dissolved in alkali, and was made up to 250 ml., one normal in alkali. It was estimated that this material was then in solution at about half its concentration in the black liquor. It was subjected to optical analysis both before and after further heating.

The lignin precipitate was finally washed twice with petroleum ether by centrifuging, allowed to stand overnight with petroleum ether, centrifuged, decanted, and dried for a week in a vacuum desiccator over concentrated sulfuric acid. The yield was five to six grams. The procedure was by no means quantitative, since mechanical losses were high.

Four grams of the product were dissolved in normal sodium hydroxide to a final volume of 100 ml. This solution, 40 grams of purified

lignin per liter, was tested by the optical and chemical analyses used on the black liquors. Methoxyl determinations were run on the product before dissolving.

When the light colored purified lignin was dissolved in alkali, it gave a very dark colored solution. Transmittance was determined after further dilution with sodium hydroxide. It was precipitated from the strong solution with acid as in the analytical procedure. This precipitate was brown in color, lighter than the precipitate from the black liquor, but darker than the purified lignin.

The solution of purified lignin was heated for three hours at 170° C. by the procedure used for the liquors. The color became much darker. On acid precipitation only 79.2 per cent was recovered, based on the purified lignin in the solution before heating. This precipitate was very dark in color.

The methoxyl contents determined were as follows:

Precipitate from black liquor	14.31%
Purified lignin	14.65%
Purified lignin precipitated from NaOH	14.16%
Purified lignin heated 3 hours in NaOH, then precipitated	15.34%

The increase in methoxyl content on heating indicates that the material made soluble in acid by this heating must have had a lower methoxyl content, somewhere around 12 per cent. The discussion of acid-soluble color will show that this contributed very little color to the acid-

soluble fraction, however. Comparison of results of heating black liquor and of heating this purified lignin solution indicate that lignin reacts differently when it is not protected by the other organic matter.

Values for the absorption coefficients of these special liquors are given in Table VIII. They show that the lignin accounts for a large part of the liquor color. They also show that the ether-soluble material changes in hue somewhat but does not darken very much when heated. The lignin solution, however, darkens greatly. This would account for the darkening of the black liquors on heating.

7. Acid-Soluble Color

This fraction of black liquor has been of particular interest to other investigators. Kuettel (16), Holzer (17), Graef (18), and Schwartz, McCarthy, and Hibbert (19) have worked with this fraction from kraft liquors. They obtained a colored extract by precipitating with acid, filtering, and precipitating the colored material from the filtrate with basic lead acetate. This was further purified and tested. Kuettel and Holzer maintained that this material was the same as a colored material they extracted from kraft pulp and, therefore, held that it was partly responsible for pulp color and the difficulty found in bleaching kraft pulp. They identified it as a sulfur dye of tannin or phlebotannin origin. Graef, however, found that the identification tests were inconclusive and that there was no adequate evidence to show that this liquor extract was related to pulp color. Schwartz,

TABLE VIII

PREPARATION OF PURIFIED LIGNIN
ABSORPTION COEFFICIENTS OF PRODUCTS IN ALKALINE SOLUTION

$\underline{k}$ at several wavelengths

mμ	420	460	500	540	600	680
Purified lignin, one gram per liter	5.88	2.82	1.612	0.952	0.47	0.195
Purified lignin, one gram per liter, after 3 hr. at 170° C.	8.76	4.06	2.44	1.608	0.94	0.488
Original 2 1/2 hr. liquor	300	135	77.5	47.0	24.2	12.0
Purified lignin, calculated to liquor basis by methoxyl content	249	119	68.4	40.4	19.9	8.3
Ether soluble in precipitate	24.0	11.4	5.56	2.76	1.36	0.6
Ether soluble after 3 hr. at 170° C.	22.6	10.1	5.88	3.60	2.04	0.84

et al., maintained that this acid-soluble colored material is mainly lignin which has been partially demethylated and made soluble in acid by the cooking action. Since previous workers have covered this fraction from a chemical standpoint, the present work was confined mostly to a study of its color.

As described in the analytical procedure, the acid filtrate and four washes were combined and made one normal in sodium hydroxide at a definite volume related to the volume of liquor sample. After the first four washes, the filtrates were colorless and only very slightly acid. The transmittances determined were thus quantitatively representative of all the colored material in the liquor which was soluble at pH values up to slightly under seven. In the acid state the solutions were a light yellow. They darkened considerably when made alkaline. The solutions were made alkaline and the transmittances determined as soon as possible after the precipitations.

In the following tables the k values have all been calculated to the original liquor basis and can be compared directly with values in other tables. Since the values are nearly the same for many samples, it would be confusing to compare them graphically. The absorption coefficients at various wavelengths are given in Table IX. In order to show the relative importance of color in this fraction, Table X has been compiled. This shows k at 500 mmu for the acid-soluble fractions, for the whole liquors, and the difference, or the color due to the acid-insoluble fraction. In these tables the fractions obtained from the alkali-lignin solution before and after heating have been calculated to the basis of a liquor containing 40 grams of lignin per liter.

TABLE IX

ACID-SOLUBLE COLOR OF SODA BLACK LIQUORS

$\underline{k}$ at several wavelengths

mμ	420	460	500	540	600	660
1/2-hr. sample	20.6	16.3	5.9	3.9	1.9	1.1
1-hr. sample	25.2	12.8	6.7	3.8	1.8	1.0
1 1/2-hr. sample	25.6	11.4	6.3	3.9	2.0	1.0
2 1/2-hr. sample	24.4	10.3	5.6	3.2	1.6	1.0
3 1/2-hr. sample	26.0	10.6	5.6	3.5	1.7	1.0
4 1/2-hr. sample	24.0	9.2	4.9	3.0	1.5	0.8
5 1/2-hr. sample	24.4	9.2	4.5	2.8	1.4	0.8
1/2-hr. reheated	14.7	6.1	3.0	1.6	0.8	0.4
1 1/2-hr. reheated	24.6	9.2	4.4	2.7	1.2	0.7
3 1/2-hr. reheated	24.6	9.3	4.6	2.8	1.3	0.8
5 1/2-hr. reheated	23.6	8.0	3.6	2.1	0.8	0.4
Purified lignin 40 g./liter	2.4	0.8	0.16	---	---	---
Purified lignin 40 g./liter, heated	9.3	3.2	1.6	0.8	0.3	0.08

TABLE X

RELATIVE IMPORTANCE OF ACID-SOLUBLE COLOR IN SODA BLACK LIQUORS

$\underline{k}$ at 500 mmu

	% of total in acid soluble	Acid soluble	Acid insoluble	Whole liquor
1/2-hr. sample	36	5.9	10.6	16.5
1-hr. sample	18	6.7	30.3	37.0
1 1/2-hr. sample	12	6.3	48.2	54.5
2 1/2-hr. sample	7.2	5.6	71.9	77.5
3 1/2-hr. sample	5.9	5.6	88.7	94.3
4 1/2-hr. sample	5.0	4.9	97.1	102
5 1/2-hr. sample	4.5	4.5	99.5	104
1/2-hr. reheated	19	3.0	13.1	16.1
1 1/2-hr. reheated	5.9	4.4	70.1	74.5
3 1/2-hr. reheated	3.8	4.6	116.4	121
5 1/2-hr. reheated	2.2	3.6	160.4	164
Purified lignin 40 g./liter	0.25	0.16	64.4	64.5
Purified lignin 40 g./liter heated	1.6	1.6	96.0	97.6

This makes the values directly comparable with those obtained from the black liquors, since they had about this lignin content.

These data show that the acid-soluble color is formed early in the cook, reaching a maximum after one hour (when the temperature was 164° C.). Apparently no new color is formed by further cooking, and the color already formed is either destroyed or becomes insoluble in acid, since it decreases slowly either with further cooking or with heating of the isolated liquor.

Schwartz, McCarthy, and Hibbert (19) have proposed that the coloring matter in this fraction of kraft liquor is lignin partially demethylated and made soluble in acid by the cooking action. The argument against this, in a soda cook, is as follows: It is not reasonable that such a reaction would occur under the mild conditions at the first of the cook, and then be reversed under severe conditions. It is true that purified lignin produces a small amount of acid-soluble color when heated in alkaline solution. However, this apparently does not occur when black liquor is heated, since acid-soluble color then decreases in every case. The lignin is evidently protected by the other organic material.

Two other sources can be suggested for this color. One is the extractives. It is true that the extractives which are removed from the wood are dissolved rapidly during the first part of the cook and are partially soluble in acid. They undoubtedly account for part of this color. The other source is carbohydrates or hemicellulosic

material. It is entirely possible that some of this color is the result of the action of alkali on this wood fraction. However, this is apparently not a very significant factor in liquor color. It should be noted that at the end of the cook all the acid-soluble color accounted for only about five per cent of the liquor color.

5. Fading after Dilution

It has been mentioned before that the black liquors changed in color with time. After darkening for a few days, the color began to decrease. It was found that this action was much faster in the diluted solutions. Therefore, the study of color change with time was made on these diluted solutions. The 50 to 1 dilutions in normal sodium hydroxide were aged and the transmittance curves repeated at intervals. Other experiments showed that the color changes in either water or sodium hydroxide and in dilutions ranging from eight to one up to 400 to 1 were all comparable. Higher dilution increased the rate of change somewhat at first, but the same general effect was obtained. Since the 50 to 1 dilutions in normal sodium hydroxide were available and the results were comparable with other data, these were used.

Table XI shows the decrease in k which was found after one week of aging the diluted solutions. The first section of the table shows the purified lignin solution and the purified lignin solution which had been heated further. The 5 1/2-hour sample is also included, since most of its color is due to lignin. The table shows

TABLE XI

LOSS OF COLOR OF SODA BLACK LIQUOR FRACTIONS
ON STANDING ONE WEEK IN DILUTED SOLUTION

Decrease in k at several wavelengths

mμ	420	460	470	500	540	600	680
Purified lignin, 40 g./liter	-6	-1	0	4.4	5.6	4.0	2.6
Purified lignin, 40 g./liter Heated	-10	-5	1	9.5	13.2	12.0	9.6
5 1/2-hr. liquor	10	0	1	7.0	9.4	8.0	7.0
Acid-soluble from heated lignin solution	-0.1	0	0.40	0.40	0.14	0.04	---
1/2-hr. liquor	9.9	9.4	8.5	7.6	5.0	3.8	2.2
1/2-hr. acid soluble	3.56	2.98	2.72	2.12	1.84	1.04	0.72
5 1/2-hr. acid soluble	3.20	1.08	1.02	0.84	0.56	0.16	0.08
Ether soluble	1.6	1.7	1.8	1.24	0.68	0.40	0.24
5 1/2-hr. reheated, acid soluble	0.8	0.3	0.24	0.23	0.19	0.07	0.01

that lignin really only undergoes a change in hue, becoming redder. At wavelengths below 470 mmu the absorption coefficient increases with aging (note the negative values in the table), above 470 the absorption decreases, whereas at 470 the absorption stays nearly constant with time. It should be noted that the acid-soluble color from the reheated lignin solution showed somewhat the same change.

The last section shows the decrease in absorption coefficient of liquors and liquor fractions which contain little or no lignin. The acid-soluble color, the ether-soluble color from the precipitate, and the early liquor samples all show a marked decrease in absorption over the whole visible range. The decrease is quite high over that range where lignin showed practically no change. This indicates that the color in these fractions is of a different nature than the lignin color. It also means that the small amount of acid-soluble color produced by heating purified lignin in alkaline solution is different from the acid-soluble color found in the black liquor samples, even that sample which was cooked 5 1/2 hours and then heated three hours longer outside the digester. This can be seen by a comparison of Figure 10 and Figure 11, in which the logarithms of the positive values (color lost) from Table XI have been plotted against wavelength.

Since lignin shows practically no change in absorption coefficient at 470 mmu, whereas the other liquor color shows a marked change, the change in absorption at this wavelength can be used to investigate the fading of nonlignin color. Even though lignin is

FIGURE 10

COLOR LOST BY SODA BLACK LIQUOR FRACTIONS ON AGING

DECREASE IN k IN SEVEN DAYS

Nonlignin Fractions

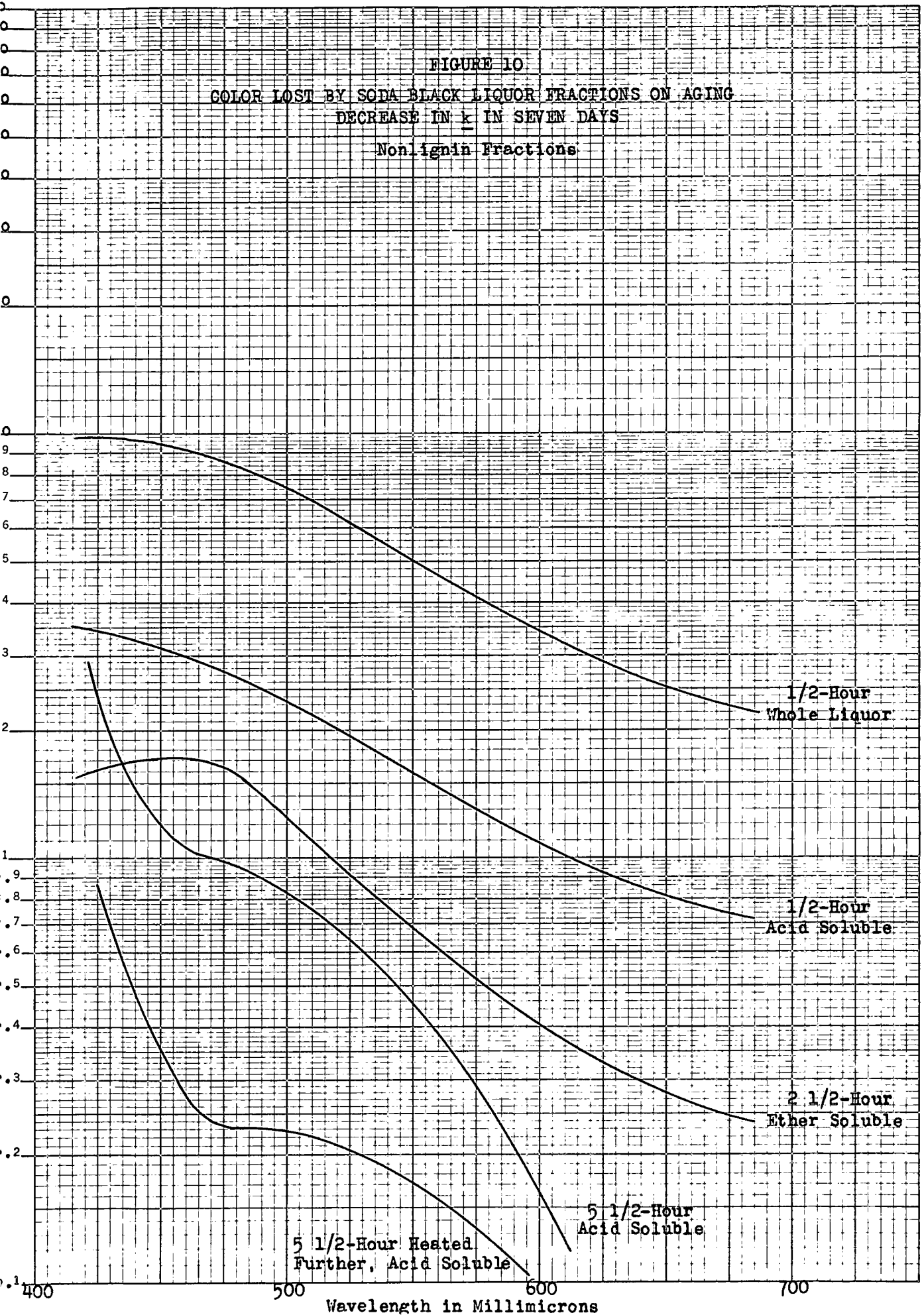
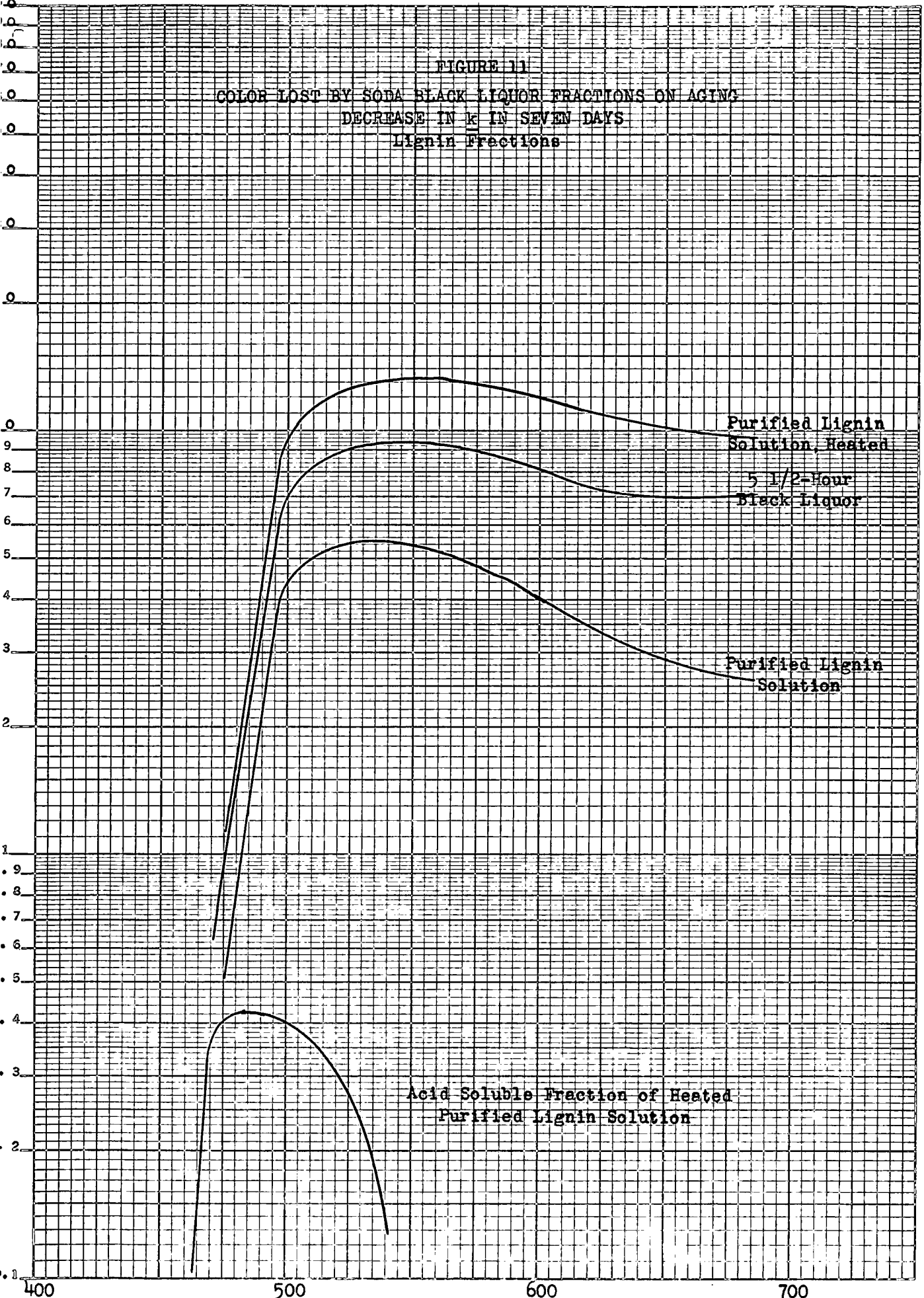


FIGURE 11

COLOR LOST BY SODA BLACK LIQUOR FRACTIONS ON AGING

DECREASE IN $\bar{k}$ IN SEVEN DAYS

Lignin Fractions



present in the solution, it will have little effect on the change in coefficient at 470 mmu. $\underline{k}$ values at this wavelength have been compiled in Table XII and plotted in Figure 12 for the periodic liquor samples after various aging times. These curves show that the color loss is most rapid during the first week, and that after three weeks there is little further change. They also show that the early liquor samples fade markedly but, except for comparatively minor changes, the later samples do not.

Since the color change seems to be nearly over after three weeks, the change in this period has been used in Table XIII as a measure of this fugitive color. This table shows the decrease in $\underline{k}$ at 470 mmu in three weeks for the periodic samples and for the acid-soluble fractions. It also gives the percentage of the original $\underline{k}$ lost in this period. This treatment shows more clearly than before that the early liquor samples must contain some unstable colored material which is not present after 2 1/2 hours cooking (or one hour at maximum temperature). A part, but not all, of this unstable color is in the acid-soluble fraction. A small amount is left in this fraction throughout the cook. The effect of this is no doubt covered by the relatively dark color of the later samples. However, it is plain that most of this unstable color formed early in the cook is either stabilized or destroyed.

This table also shows that, besides the fugitive color, the acid-soluble fraction contains a very stable colored material which appears even before maximum temperature is reached and which does not

TABLE XII

CHANGE IN COLOR OF SODA BLACK LIQUORS ON STANDING IN DILUTED SOLUTION

$\underline{k}$ at 470 mmu

Days aging	0	7	21	35
Cooking hr.				
1/2	23.1	14.2	11.7	10.9
1	53.8	42.5	37.8	35.2
1 1/2	79	72.5	69	67.5
2 1/2	117	116	117	117
3 1/2	141	138	141	145
4 1/2	151	149	151	152
5 1/2	154	151	153	153

FIGURE 12

CHANGE OF COLOR OF SODA BLACK LIQUORS ON STANDING IN DILUTED SOLUTION

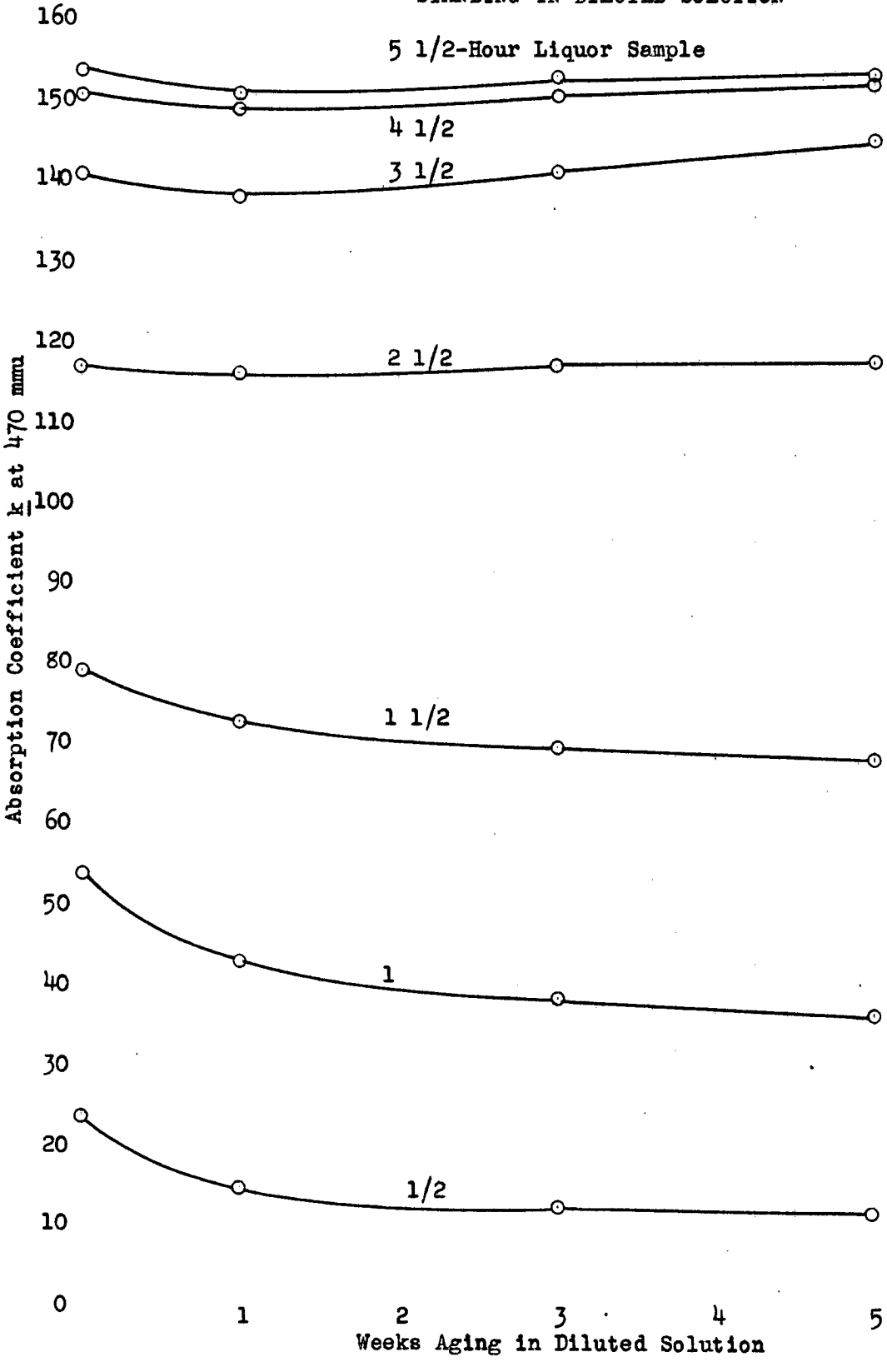


TABLE XIII

CHANGE IN COLOR OF SODA BLACK LIQUORS ON STANDING THREE WEEKS IN DILUTED SOLUTION

$\underline{k}$ at 470 mμ

Cooking hrs.	Whole Liquors				Acid-Soluble Fractions			
	Fresh	After three weeks	Decrease	Lost %	Fresh	After three weeks	Decrease	Lost %
1/2	23.1	11.7	12.4	54	9.2	4.8	4.4	48
1	53.8	37.8	16.0	30	9.8	6.8	3.0	32
1 1/2	79	69	10.0	13	10.8	6.6	4.2	39
2 1/2	117	117	0	0	8.8	6.5	2.3	26
3 1/2	141	141	0	0	8.8	6.5	2.3	26
4 1/2	151	151	0	0	7.9	6.0	1.9	24
5 1/2	154	153	1	0.6	7.6	6.0	1.6	21

change thereafter. After these acid-soluble fractions had been aged for three weeks, the curves were almost identical from 400 to 700 mmu for all the periodic samples from 1 to 5 1/2 hours cooking.

It might also be mentioned that, in determining the weight of acid-insoluble material, these first three samples (which contain unstable color) were different in behavior from the others. The precipitates were lighter in color. They showed a strong tendency to become colloidal and required frequent additions of acid to prevent this during centrifuging.

9. Correlation of Optical and Chemical Analyses

From Tables VIII and IX, it can be seen that the color in the 2 1/2-hour liquor has been divided into three fractions: acid-soluble, ether-soluble in the precipitate, and ether-insoluble or lignin. One other fraction, the dioxane-insoluble fraction of the precipitate, was found to have practically no color. If the color of these materials has not been altered by the chemical treatment received in the separations, the absorption coefficients of the fractions can be plotted against concentrations to show the relationships involved.

Table XIV repeats the absorption coefficients at several wavelengths for each of these fractions. These coefficients are added and the sums compared with the values found for the whole liquor without any chemical treatment. These values are plotted against

TABLE XIV

THE COLOR OF THE SEPARATED FRACTIONS OF THE 2 1/2-HOUR SODA BLACK LIQUOR

$\underline{k}$ at several wavelengths

Wavelength mmu	420	460	470	500	540	600	680
Acid soluble	24.4	10.3	8.8	5.6	3.2	1.6	1.0
Ether soluble in precipitate	24.0	11.4	9.5	5.56	2.76	1.36	0.6
Lignin	249	119	104	68.4	40.4	19.9	8.3
Whole liquor calculated	297.4	140.7	122.3	79.5	46.4	22.9	9.9
Whole liquor obtained	300	135	117	77.5	47.0	24.2	12.0

wavelength (as logarithms) in Figure 13. The curve obtained by adding the three fractions is remarkably close to that obtained directly from the whole liquor. It is safe to conclude that the absorption values obtained for these fractions are representative of the colored materials as they occur in the liquor.

The data in Tables V and X show that there is no possible connection between the color in the acid-soluble fraction and the total weight of organic matter in this fraction. Since it is known that the bulk of this organic matter consists of colorless acids and carbohydrates, no relationship would be expected. The color in this fraction is due to a small amount of extractives and possibly also to some colored product formed in small quantities by the action of alkali on carbohydrates. This is in sharp contrast to the behavior of sugars in the acid solution in a sulfite cook.

In this liquor sample (2 1/2-hour) lignin accounts for about 86 or 87 per cent of the total color. In samples taken near the end of the cook, it accounts for more than 90 per cent of the color.

If we consider the relationship between the lignin content of the black liquors and the color due to the acid-insoluble material, we can make some interesting calculations. This has been done in Table XV. In order to show also the unstable color which disappears with time, these calculations have been made both for fresh and aged liquor samples, using $\underline{k}$ at 470 mmu as a measure of color. As explained in the previous section, at this wavelength $\underline{k}$ is constant with time

FIGURE 13

SPECTRAL ABSORPTION OF THE SEPARATED FRACTIONS OF THE 2-1/2-HOUR SODA BLACK LIQUOR

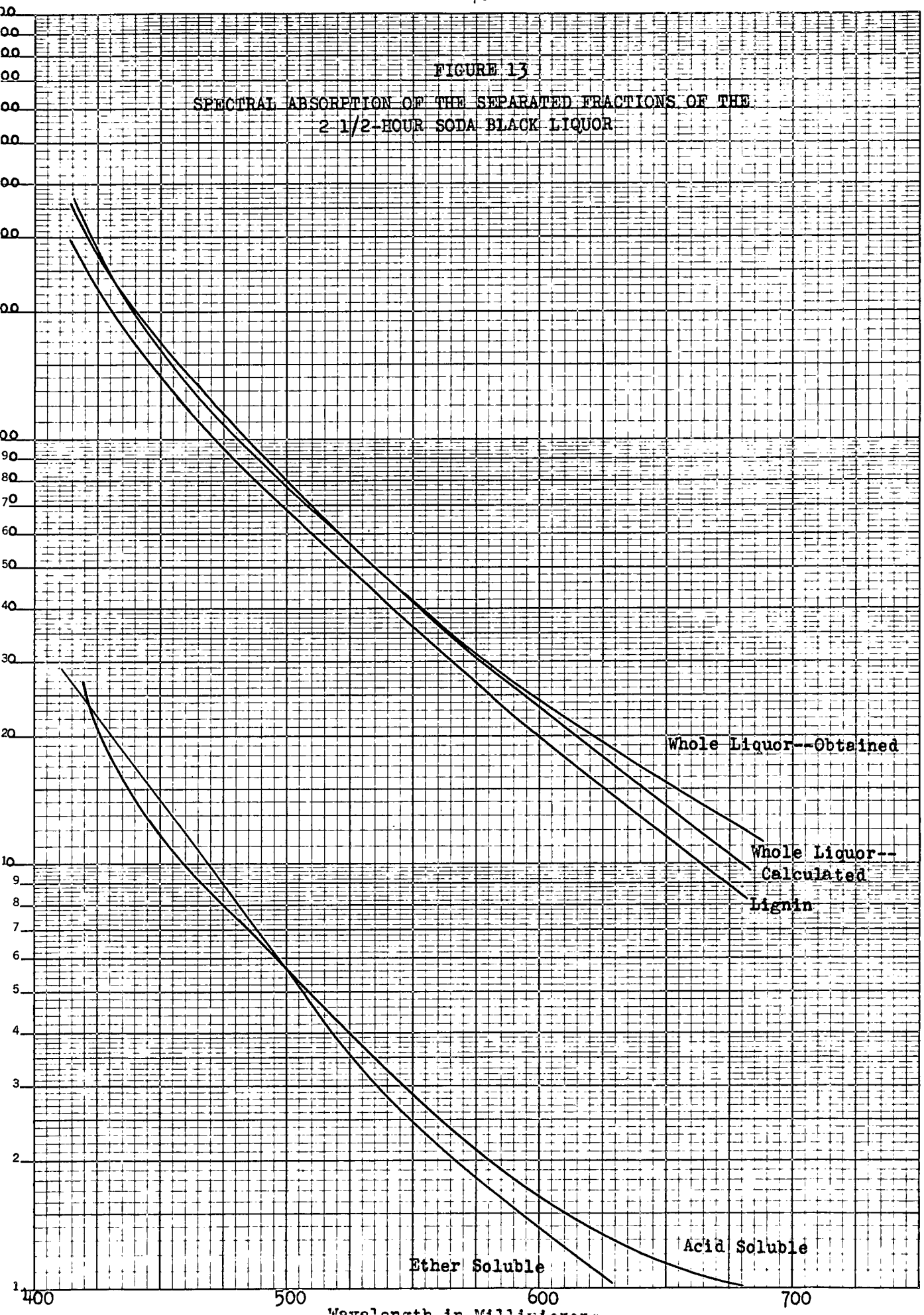


TABLE XV

COLOR OF SODA BLACK LIQUOR FRACTIONS AS A FUNCTION OF LIGNIN CONTENT

$\underline{k}$ at 470 mm

Cooking hr.	Lignin g./l.	$\underline{k}$ lignin (calc.)	Fresh dilutions			Aged dilutions		
			Total	Acid soluble	Precipitate (diff.)	Total	Acid soluble	Precipitate (diff.)
		(1)	(2)	(3)	(4)	(5)	(6)	(7)
1/2	2.0	4.9	23.1	9.2	13.9	11.7	4.8	6.9
1	11.5	28.2	53.8	9.8	44.0	37.8	6.8	31
1 1/2	24.3	59.5	79	10.8	69	69	6.6	62
2 1/2	42.4	104	117	8.8	108	117	6.5	110
3 1/2	48.1	118	141	8.8	132	141	6.5	134
4 1/2	47.7	117	151	7.9	143	151	6.0	145
5 1/2	48.7	119	154	7.6	146	153	6.0	147

for lignin, but does vary as the unstable color disappears.

Seven columns of $\underline{k}$ values have been calculated. In the first column, it has been assumed that the lignin color does not change with cooking, and the absorption coefficient of the purified lignin from the 2 1/2-hour sample has been used to calculate the theoretical absorption of the lignin in each liquor sample. This is not a valid assumption, but has been used merely as a reference line in Figures 14 and 15.

Column two in Table XV contains the values obtained from transmittance curves taken immediately after dilution of the original liquor samples. They represent all of the color in the liquors. Column three contains similar values for the acid-soluble fractions. Column four was obtained by subtracting three from two, and therefore, represents the remainder of the color, or that of the acid-insoluble material.

Columns five, six, and seven were obtained in a similar manner, using samples which had been aged in the diluted form. It can be seen from the preceding section that these samples should represent all the stable color and contain practically none of the fugitive color.

The values for the unaged liquors have been plotted in Figure 14, those for the aged samples in Figure 15. In both cases the dotted lines with no data points are the calculated lines for the lignin absorption, assuming no change in lignin color with cooking.

It is obvious from both figures (especially Figure 15) that, after 2 1/2 hours of the cook, the color due to the precipitate increases

FIGURE 14

COLOR OF SODA BLACK LIQUOR FRACTIONS AS A FUNCTION OF LIGNIN CONTENT

Fresh Solutions

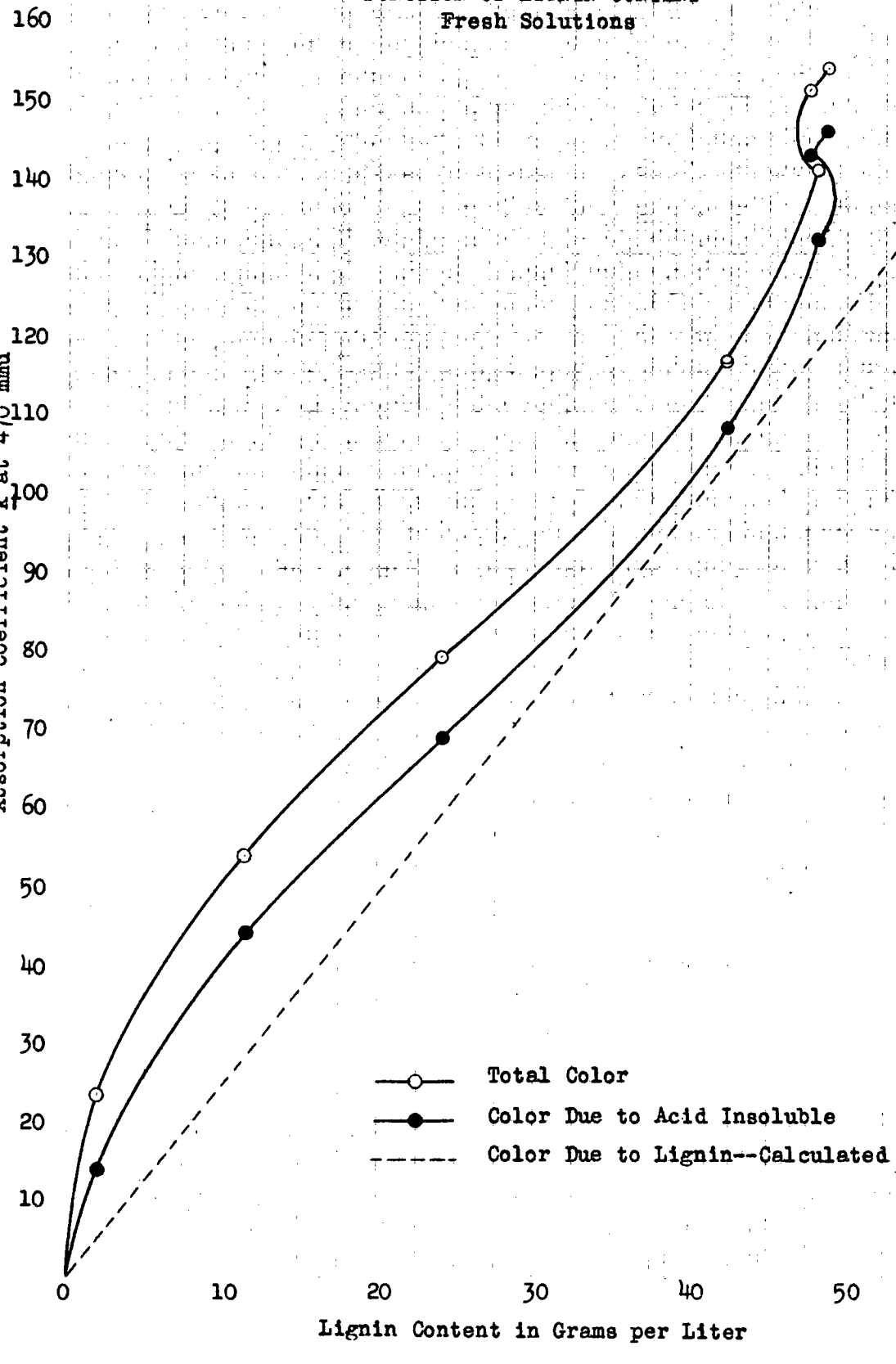
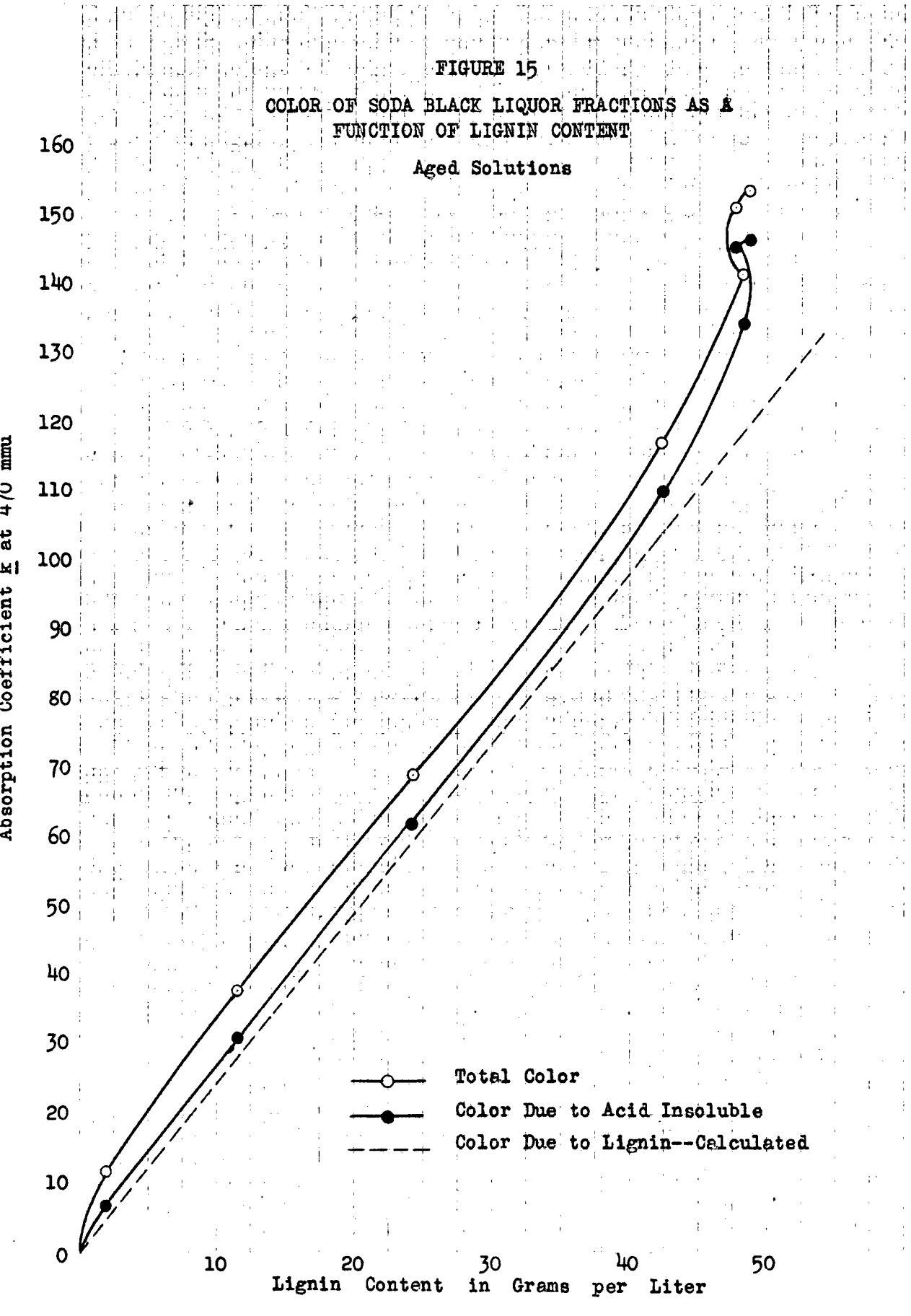


FIGURE 15

COLOR OF SODA BLACK LIQUOR FRACTIONS AS A FUNCTION OF LIGNIN CONTENT

Aged Solutions



much faster than the calculated color due to lignin. There is a marked increase in this acid-insoluble color between 3 1/2 and 5 1/2 hours when the lignin content is nearly constant. It has been shown that acid-soluble color decreases with cooking in this part of the cook, and always decreases on heating the isolated liquors. It has also been shown that the ether-soluble part of the acid-insoluble material does not change much on heating, a solution of purified lignin in alkaline solution, however, darkens very markedly on heating. The last column of Table XVI (obtained by a method similar to that used for Table XV) shows that the increase in acid-insoluble color which occurs on heating an isolated liquor is quite dependent on the lignin content of the liquor, although also somewhat related to total time at maximum temperature. From these facts, it is safe to conclude that the increase in liquor color near the end of the cook is due to a darkening of the lignin already in solution by the action of heat on the alkaline solution. Possibly such a reaction accounts for the darkening of over-cooked alkaline pulps. At any rate, the darkening of the liquor seems to be the result of a change in the dissolved lignin.

Further examination of Figure 15 shows that during the first 2 1/2 hours of the cook the color from the acid-insoluble material, as determined experimentally, is very nearly the same as the calculated color due to lignin. It should be slightly higher on account of acid-insoluble extractives, designated as "ether soluble" in the treatment of the 2 1/2-hour liquor. The curve shows that the observed acid-insoluble color is slightly higher than the calculated lignin color over this range. The difference is small and nearly constant.

TABLE XVI

CHANGE IN THE COLOR OF SODA BLACK LIQUOR CAUSED BY HEATING ISOLATED LIQUOR AS A FUNCTION OF LIGNIN CONTENT

Cooking hr.	(from Table XV) Original Liquor		$\underline{k}$ at 470 mμ			
	Lignin g./l.	$\underline{k}$ precipitate	Total	After 3 hr. heating: Acid soluble	After 3 hr. heating: Precipitate (diff.)	Increase caused by heating: $\underline{k}$ precipitate
1/2	2.0	13.9	23	5	18	4
1 1/2	24.3	69	107	8	99	30
3 1/2	46.1	141	185	7	178	37
5 1/2	48.7	153	235	6	229	76

In Figure 15, the total color has also been plotted. Since the unstable color has been removed by aging, the total color is higher than the acid-insoluble color by a constant amount throughout the entire cook. It seems reasonable that the very stable color found in the acid-soluble fraction and in the ether-soluble part of the acid-insoluble fraction is caused by stable extractives which are dissolved during the first hour of the cook. Evidence has already been presented to show that it is not a product of lignin.

When compared with Figure 15, Figure 14 shows clearly the development of the unstable color during the first 1 1/2 hours of the cook, and its destruction by further cooking or by aging of the liquor samples. This parallel suggests that the color is actually destroyed by cooking rather than stabilized.

KRAFT BLACK LIQUORS

1. Wood and Cooking Conditions

Examination of kraft black liquors from similar cooks on spruce, jack pine, and loblolly pine shows that the difference in species causes very little difference in color. However, for any one of these woods, the kraft and soda black liquors are very different. Since this is true, sprucewood was used for this part of the study of kraft black liquors. Kraft black liquors from spruce are not very different from those of other commonly used woods, and in this case the comparison with soda black liquors is more direct. Further discussion of these points will be given later in the comparison of kraft and soda liquors.

Cook L-4 was made on the same sprucewood used for the Soda Cooks L-1 and L-2. The initial active alkali ratio was reduced to 27 per cent. of which one third (calculated as sodium hydroxide) was sodium sulfide. The procedure and all other conditions were the same as for soda cooks. The following yields were obtained:

	Cook L-4
Yield, oven-dry screened pulp, %	45.74
Yield, oven-dry unscreened pulp, %	46.00
Screenings in screened pulp, %	0.46
Lignin in screened pulp, %	3.54

Although the yield is six per cent higher, this pulp was cooked to a slightly lower lignin content than the soda pulps. In view of the importance of lignin in liquor color, the kraft liquors obtained from this cook will serve quite well in comparing the two alkaline processes.

2. Optical Analysis of Liquors

The same theoretical considerations, treatment of data, and experimental procedures were used for the kraft black liquors as for the soda black liquors. Since the kraft liquors were darker, higher dilutions were usually necessary. This does not affect the validity or accuracy of the absorption coefficients, because the coefficients are all calculated to the same basis.

a. Conformity to Beer's Law on Dilution

The black liquor from a kraft cook (No. 205) on loblolly pine was used to investigate the conformity of kraft black liquor to Beer's Law. The description of this cook will be found in Section C. Dilutions were made with distilled water to 0.2, 0.5, 2.0, and 4.0 per cent black liquor. Transmittance curves were run, using the five mm. cell. The undiluted liquor was tested in the thin film cell. The k values are shown in Table XVII. These figures show that dilution with water causes a serious change in hue similar to that observed for soda black liquor. Table XVIII shows similar data for dilutions with normal sodium hydroxide. Unlike soda black liquors, kraft liquors do not follow Beer's Law when this solution is used as a diluent (Table XVIII). Dilution with normal sodium hydroxide caused a large increase

TABLE XVII

VALIDITY OF BEER'S LAW WITH KRAFT BLACK LIQUOR (COOK205) ON DILUTION WITH WATER

Wavelength mmu	420	460	500	540	600	680
			Absorption coefficient k			
Liquor %						
0.2	374	202	122	80.0	46.0	27.0
0.5	310	160	97	56.0	31.6	16.8
2.0	480	177	91	52.8	26.0	11.6
4.0	---	192	90	51.2	25.0	10.6
100	426	173	90	53.5	25.8	11.2

TABLE XVIII

VALIDITY OF BEER'S LAW WITH KRAFT BLACK LIQUOR (COOK 205) ON DILUTION WITH ONE NORMAL SODIUM HYDROXIDE

Wavelength mmu	420	460	500	540	600	680
			Absorption coefficient k			
Liquor %						
0.2	504	248	140	83	44.0	23.0
0.5	532	244	140	84	42.8	20.0
2.0	---	226	119	71	36.0	16.0
4.0	---	---	110	64	31.4	13.7
100	521	212	110	65	30.5	13.7

in absorption coefficient. It would be impossible to make quantitative comparisons of colored materials under such conditions.

The kraft white liquor used in the experimental kraft cooks was made from commercial sodium hydroxide and sodium sulfide. It had the usual yellow color. Transmittance curves showed that this color was negligible when compared with the total liquor color. However, if used as a diluent in making a 100 to 1 dilution, the effect would be 100 times as great and would seriously affect the resulting transmittance. Therefore, a special white liquor was made for use as a diluent. Analytical grade sodium hydroxide and sodium sulfide were dissolved separately, cooled, and mixed to give the desired concentrations. The mixture was allowed to stand a few days and the precipitated iron sulfide filtered out. The resulting kraft white liquor was entirely colorless. Such a white liquor was the diluent in the solutions used to obtain the absorption coefficients shown in Table XIV. These data show that kraft black liquor follows Beer's Law very closely when diluted with colorless kraft white liquor. The agreement is close enough for this work, and much better than any results which could be obtained by using water or a sodium hydroxide solution.

All the following work on kraft black liquors was done using the colorless kraft white liquor as a diluent at the concentration of the white liquors used in making the cooks. In a few cases, it was necessary to make some fractions up to this concentration by adding to the neutralized liquor fraction a smaller volume of stronger white liquor.

TABLE XIX

VALIDITY OF BEER'S LAW WITH KRAFT BLACK LIQUOR (COOK 205) ON DILUTION WITH KRAFT WHITE LIQUOR

Wavelength mmu	420	460	500	540	600	680
			Absorption coefficient k			
Liquor %						
0.2	502	206	108	61	30.0	11.0
0.5	496	210	108	63	29.6	12.8
2.0	---	206	103	62	30.0	12.8
4.0	---	202	104	61	29.8	12.4
100	502	204	106	63	30.4	13.2

b. Effect of Age on Liquor Color

The kraft black liquors did not change as much with age as did the soda liquors. In no case did any of the liquors decrease in color. A slight darkening was observed. For example, the transmittance of a 100 to 1 dilution of the half hour liquor at 500 mmu dropped from 90 per cent to 88 per cent in 25 days. Other samples showed similar changes. This made it possible to do the experimental work on these liquors with little error from changes in color with time. The 5 1/2-hour sample was the only one showing any great change. This sample was analyzed optically and chemically both before and after

the change occurred. The results showed that the lignin had darkened. However, the age of the liquor samples can be discounted as a source of error in the following work.

The diluted solutions were also allowed to age for three weeks and the transmittance determinations repeated. In marked contrast to the soda liquors, little change occurred. There were small, irregular variations which seemed to have no significance.

3. Chemical Analysis of Liquors

The analytical procedures used for the soda black liquors were revised somewhat for use on kraft liquors. The major change was the addition of an ether extraction of the acid-insoluble material in order to obtain more information about this precipitate.

a. Ether-Soluble Organic Material

The liquor sample was treated with hydrochloric acid and the precipitate washed by centrifuging, following the same procedure used in the analysis of soda black liquors. After the last water wash in the centrifuge jar, the acid-soluble fraction was removed from the suction flask and set aside for further analysis. The wet precipitate was covered with ethyl ether and stirred vigorously. When this was done the precipitate changed in character. It was evidently wetted by the ether rather than by the water. It lost its gelantinous nature and became granular. The small amount of water which had been held by the precipitate appeared in a separate layer. The mixture was centrifuged and the ether and water decanted through the porous bottom

crucible into the suction flask. This was best done by first decanting into a beaker and then pouring the two liquid layers through the filter separately.

The precipitate was covered with about 50 ml. of ether and allowed to stand for an hour or two, with occasional stirring. The ether became yellow as the resins and ether-soluble lignin dissolved. Then the ether was decanted through the filter. This extraction was repeated three or four times until the solvent no longer became colored. Finally, the precipitate was left overnight in ether to insure complete extraction. This ether was also decanted through the filter. The combined ether extracts were removed from the suction flask. The small volume of water was removed in a separatory funnel and the ether solution quantitatively divided into two parts. One aliquot was reserved for the transmittance determination. The other was evaporated on a steam bath. The residue was dried at 105° C. and weighed. This residue, insoluble in acid but soluble in ether, is designated as ether-soluble organic material.

b. Lignin

After the final ether extraction, the precipitate was washed with water into the porous bottom crucible. It was further washed until the filtrate was no longer acid to litmus. Since the precipitate was not gelatinous, it was easily washed and filtered. Finally, the precipitate was dried at 105° C. and weighed. On drying, there was no tendency to char or form a hard cake. The dried residues were of

the same color and general appearance as those which had been washed only with water. The same procedures used for soda black liquors were used here in determining methoxyl content and estimating lignin.

c. Carbohydrates

The acid-soluble fraction mentioned before was also divided into two parts. One was used for determining the total acid-soluble color. The other, while still acid, was extracted in a separatory funnel with ether. This ether extract was relatively unimportant and was used only for color investigations. The weight of organic matter was very small and was not determined in most cases. After this extraction, the remaining water layer contained a large amount of organic material. The bulk of this consisted of carbohydrate degradation products. In order to get a general idea of the rate at which these products were appearing in the liquor, the solution was evaporated on a steam bath, and the residue was dried to constant weight at 105° C. It was then carefully ashed to constant weight just at red heat to avoid loss of sodium chloride. The loss in weight on ashing was used as a rough measure of the amount of carbohydrates present in the acid-soluble fraction. There was undoubtedly some loss of carbon dioxide and furfural on oven-drying with hydrochloric acid present. Therefore, these values are arbitrary and not comparable with those obtained for the soda cooks.

4. Course of the Kraft Cook

a. Color

Figure 16 shows the transmittance curves of the periodic liquor samples (diluted 1 volume to 100 with colorless kraft white liquor) of Cook L-4. The curves of log $\underline{k}$ against wavelength which were derived from these transmittances are shown in Figure 17. The latter curves show little change in shape from hour to hour. Since this is true, absorption coefficient $\underline{k}$ at 500 mmu is a measure of color which can be used in comparisons of the various liquors. These values are plotted against cooking time in Figure 18. The color increased in a smooth curve with time.

b. Carbohydrates

The chemical analyses are given in Table XX and plotted in Figure 18. As mentioned in the procedures, the measure of carbohydrates is only approximate. However, it can be seen from Figure 18 that, as expected, the carbohydrates came out very rapidly during the first part of the cook. After one hour at maximum temperature (2 1/2 hours total cooking time) there was very little increase in the carbohydrate content of the liquor. As Brauns and Grimes (5) have also shown, the carbohydrates are dissolved more rapidly than lignin during the first part of the cook.

c. Ether-Soluble Organic Material

This fraction contains the resin acids and some fats and waxes. However, it also contains some ether-soluble lignin. The methoxyl contents of some of these residues were determined and found to vary between 11.0 and 12.0 per cent. This indicates that the major

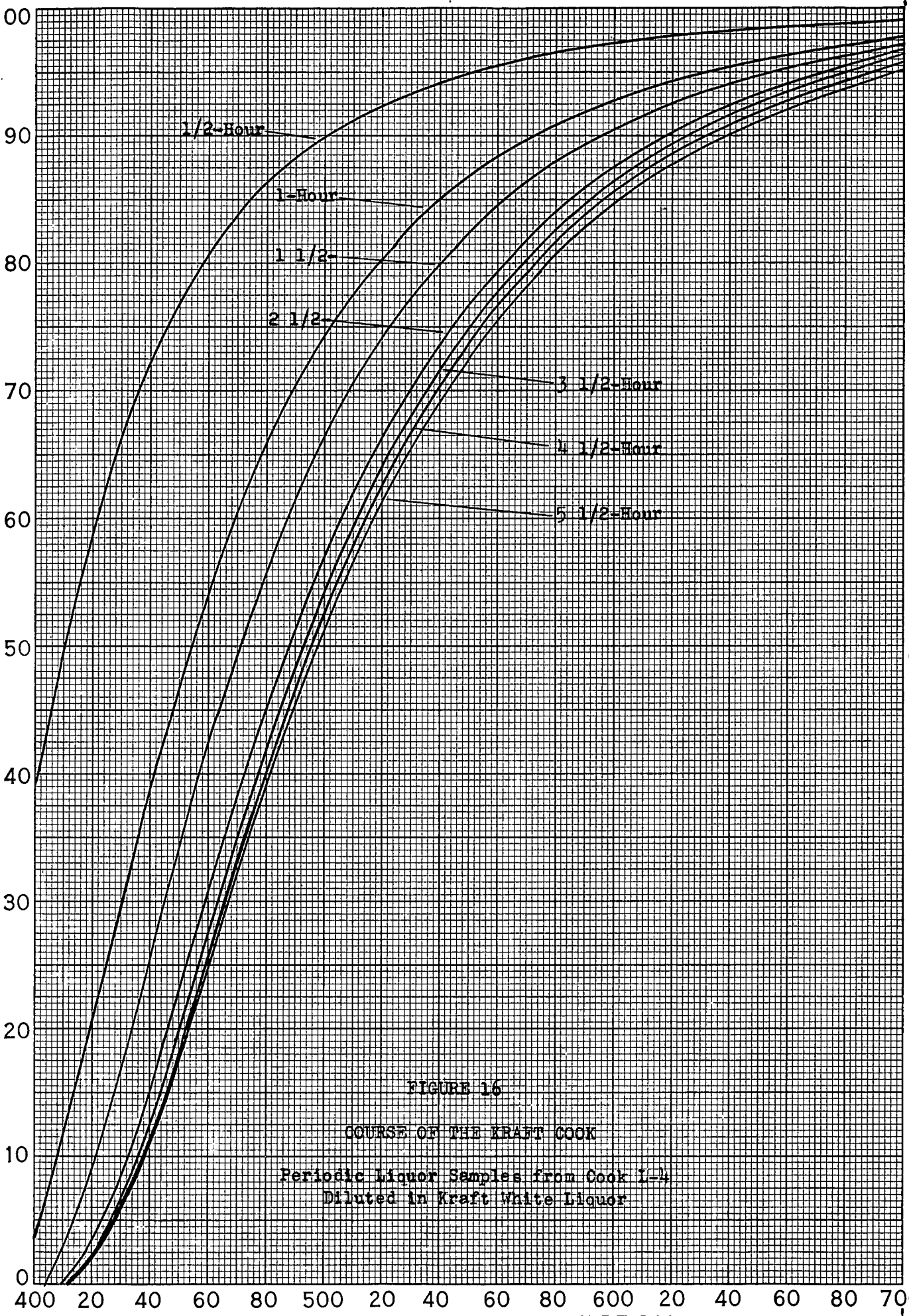


FIGURE 16

COURSE OF THE KRAFT COOK

Periodic Liquor Samples from Cook L-4
Diluted in Kraft White Liquor

TEST NO._____BY_____

DATE_____

GENERAL ELECTRIC

RECORDING SPECTROPHOTOMETER

INSTRUMENT NO.

P-62581

FIGURE 17

SPECTRAL ABSORPTION OF PERIODIC LIQUOR SAMPLES
COOK L-4

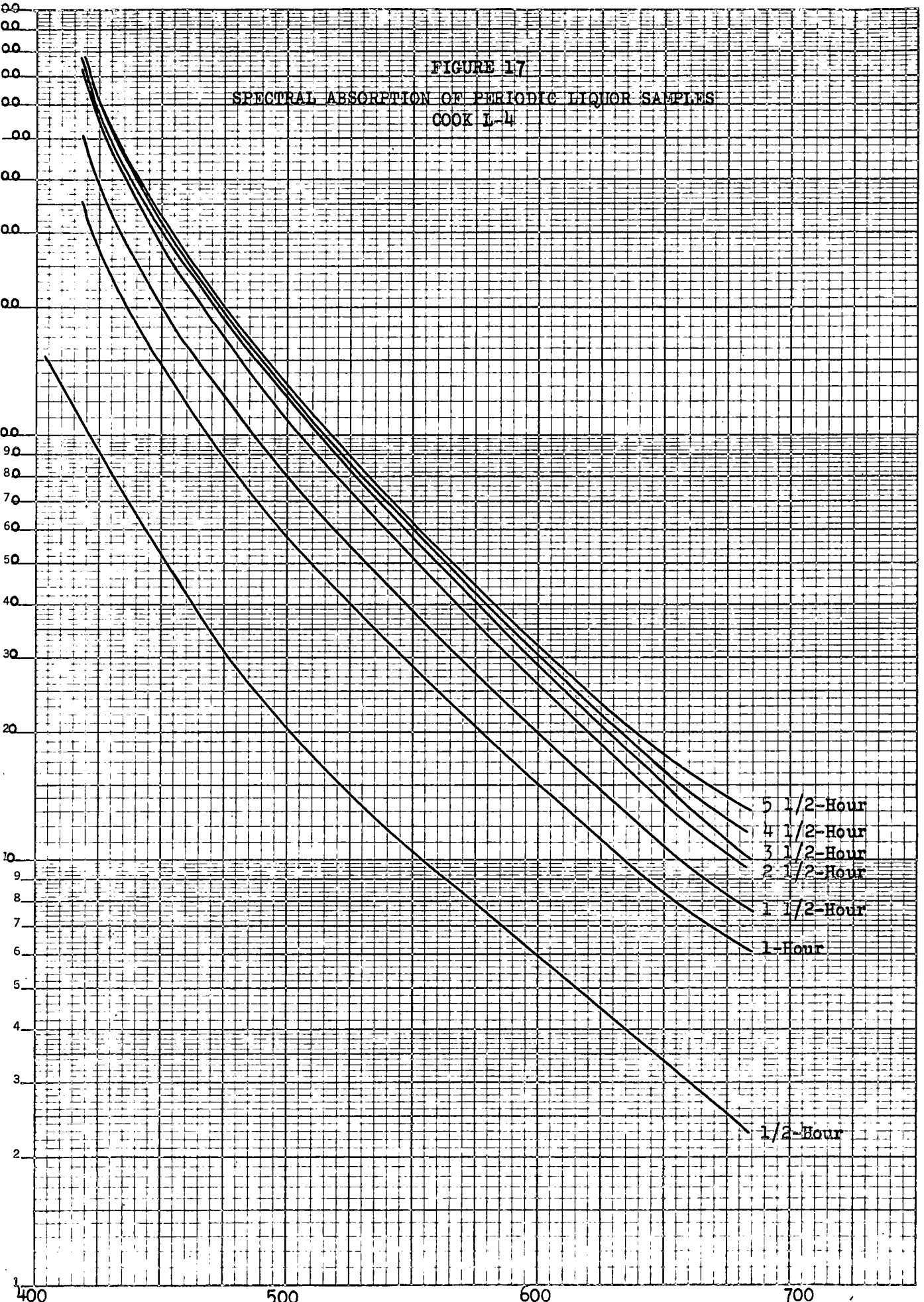


FIGURE 18

CONCENTRATION OF CHEMICAL COMPONENTS AND COLORING MATTER IN KRAFT BLACK LIQUOR

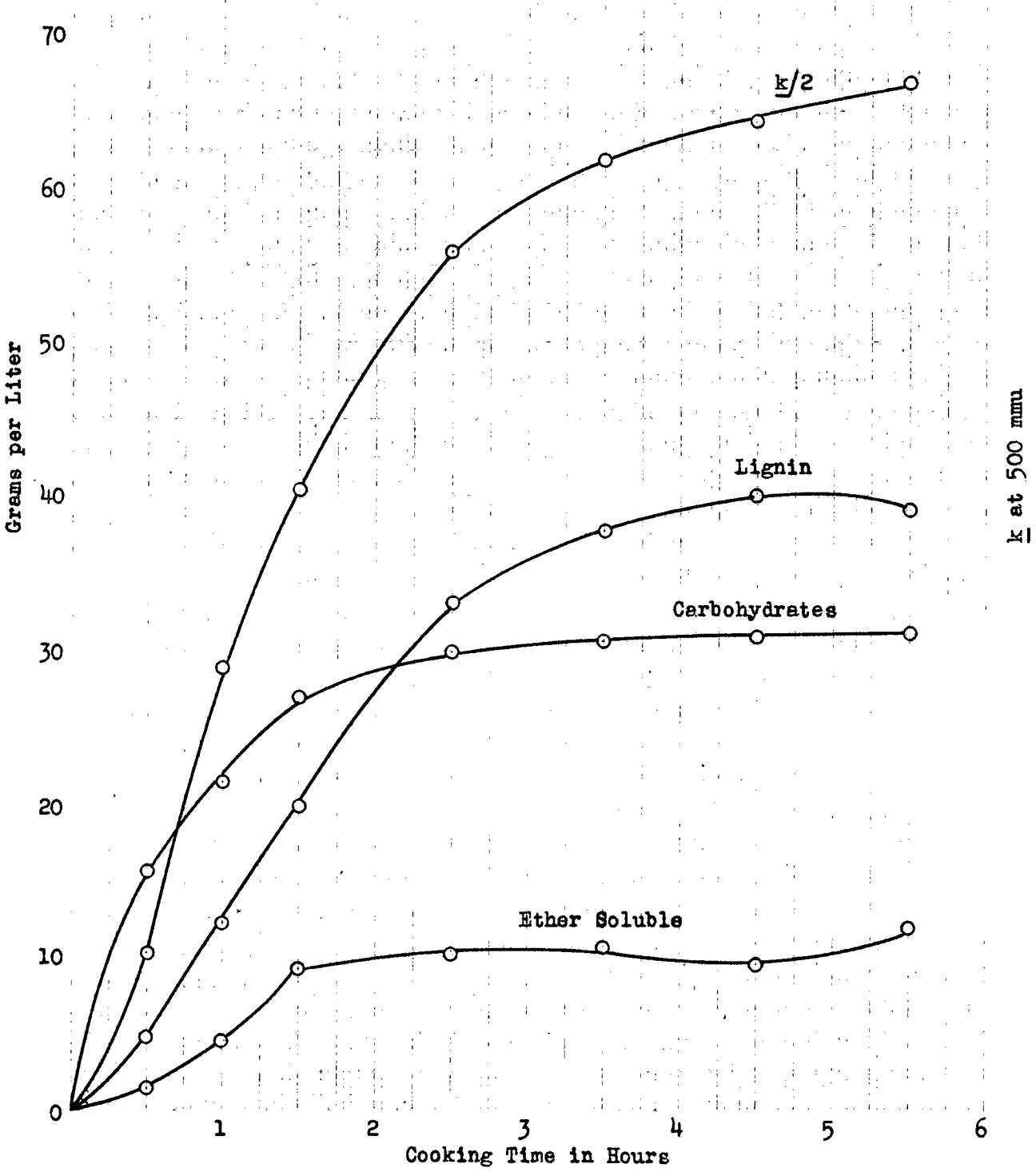


TABLE XX

ANALYSIS OF LIQUOR SAMPLES FROM COOK L-4

All concentrations in grams per liter

Cooking time in hr.	1/2	1	1 1/2	2 1/2	3 1/2	4 1/2	5 1/2
Carbohydrates	15.6	21.6	27.2	30.0	30.8	31.0	31.1
Ether-soluble organic material	1.72	4.76	8.75	10.4	10.9	9.87	12.1
Acid and ether insoluble	7.36	16.5	21.4	34.5	38.4	40.2	39.2
Methoxyl in acid and ether-insoluble, %	9.57	13.00	13.42	13.95	14.22	14.40	13.42
Estimated lignin	4.9	14.9	20.0	33.4	37.8	40.2	39.2
$\underline{k}$ at 500 mmu	21	58	81	112	124	129	134

part is lignin. Figure 15 shows that a large part of this material comes out during the first part of the cook, with only a slight increase during the last four hours. This may mean that the lignin in this fraction is different from the ether-insoluble lignin and is removed from the wood faster, or it may be that, at this stage of the cook, lignin can be degraded to become ether soluble (because the alkali is stronger) before the other organic buffering materials have been dissolved. Later experiments give more information on this point.

d. Lignin

In estimating the lignin content of the acid- and ether-insoluble material, the methoxyl content of pure thiolignin was assumed as 14.42 per cent. This was the figure obtained for the purified thiolignin made from the 2 1/2-hour black liquor. It also agrees with the values obtained by Ahlm (22). As in the soda cook, the methoxyl content of the final liquor sample was low and 14.42 per cent was used in calculating the lignin value. This value is underlined in Tables XX and XXI.

Figure 15 shows that lignin dissolves rapidly during the first part of the cook, even more rapidly than in the soda cook. This is still more noticeable if the lignin contained in the ether-soluble fraction is considered. The lignin content of the liquors increases slightly between 3 1/2 and 4 1/2 hours. The apparent decrease in lignin during the last hour is doubtless due to the failure of the analytical method as the lignin becomes degraded. This effect is even more pronounced when isolated liquor samples are heated.

5. Heating of Isolated Liquor

Soda black liquors were reheated with air above the tubes in the autoclave. One further test was made in which a liquor sample was heated in a small autoclave after removing oxygen by successive evacuations followed by introduction of nitrogen. To avoid any possible reaction because of the presence of oxygen, the latter method, as described in the soda liquor section, was used for all of the kraft liquor samples.

Samples of the 1/2-, 1 1/2-, 3 1/2-, and 5 1/2-hour liquors were heated for three hours at 170° C. The chemical analyses are compared with the analyses of the original liquor samples in Table XXI. The change in color is indicated by the absorption coefficients in Table XXII. These data show that heating a liquor sample in the absence of pulp produces a darkening of the liquor in all except the 1/2-hour sample, which contains very little lignin. The lignin is changed. After heating it has a lower methoxyl content, and cannot be completely recovered by this analytical method. This accounts for the apparent drop in lignin content of the liquor during the last hour of the regular cook. This degradation of lignin is seen to be much more severe when isolated liquor samples are heated than it is for an equivalent time in the digester with pulp present.

The absorption coefficients quoted for the original liquors in Table XXII are slightly higher than those quoted elsewhere. The values in this table are taken from transmittance curves run at the

TABLE XXI

EFFECT OF HEATING ISOLATED LIQUORS
ANALYSIS OF LIQUORS FROM COOK L-4

All concentrations in grams per liter

Cooking time--hr.	1/2		1 1/2		3 1/2		5 1/2	
Further heating--hr.	0	3	0	3	0	3	0	3
Ether-soluble organic material	1.72	4.14	8.75	8.1	10.0	11.6	12.1	13.6
Acid and ether-insoluble	7.36	1.68	21.4	14.7	38.4	34.7	39.2	37.9
Methoxyl in acid and ether insoluble, %	9.57	9.09	13.42	13.33	14.22	13.34	13.42	12.58
Estimated lignin	4.9	1.06	20.0	13.6	37.8	32.1	39.2	35.0

TABLE XXII

EFFECT OF HEATING ISOLATED LIQUORS
COLOR OF LIQUORS FROM COOK L-4

Absorption coefficient k

Cooking time--hr.	1/2		1 1/2		3 1/2		5 1/2	
Further heating--hr.	0	3	0	3	0	3	0	3
mmu								
420	112	73	455	540	800	---	740	---
470	41	28.8	144	169	220	258	260	322
500	26	18.6	84	104	128	160	173	216
540	15	11.8	46	62	70	95	108	137
600	8	6	20	30	31	48	56	76
680	2.2	2	7.4	12	12.4	21.4	27	38

time the liquors were reheated. This was done some time later than the analytical work and the liquors had darkened slightly.

6. Preparation of Purified Thiolignin

The 2 1/2-hour black liquor was used to prepare purified thiolignin by the procedure used by Ahlm (22). This is the same procedure used in preparing alkali lignin from soda black liquor, except that the product of the first ether-dioxane precipitation is further purified by dissolving in dioxane and precipitating again in ether. Ahlm has shown that this treatment removes all carbohydrates and free sulfur.

The carbohydrates insoluble in dioxane were removed from the dioxane solution by centrifuging and filtering. The precipitate was washed with dioxane and water; it was white and produced no color when dissolved in kraft white liquor. This indicates that in kraft liquors, as in soda liquors, the carbohydrates insoluble in acid are not a source of liquor color.

The transmittance of the ether-dioxane soluble material was found by extracting an aliquot of the filtered ether-dioxane solution with kraft white liquor in a separatory funnel. This left the ether layer colorless.

A solution in kraft white liquor was made containing 13.6 grams of purified thiolignin per liter. A portion of this was heated for three hours at 170° C. in the absence of oxygen. These two

solutions of thiolignin (original and reheated) were then submitted to all the optical and chemical tests used on the black liquors. The sulfur content of the thiolignin was not determined. Ahlm (22) has investigated this thoroughly. Since it was impractical to purify all the precipitates to remove free sulfur so that valid sulfur determinations could be made, it was not possible to follow the sulfur content of the lignin through the cook.

The following methoxyl contents were obtained:

	Per Cent
Precipitate from black liquor	13.95
Purified thiolignin:	
Original	14.42
Precipitated from white liquor solution	14.33
Heated three hours in white liquor, then precipitated	13.27

The precipitations of the white liquor solutions with acid gave the following results:

	Grams	Per Cent
Thiolignin in solution	0.6900	100
Original solution:		
Acid and ether insoluble	0.6436	93.3
Acid and ether soluble	------	6.7
Reheated solution:		
Ether soluble	0.1362	19.7
Acid and ether insoluble	0.4980	72.2
Acid soluble	------	8.1

These figures show that, after the ether-dioxane precipitation, the analytical method recovered 93.3 per cent of the thiolignin, the remaining 6.7 per cent going into the acid- and ether-soluble fractions or being lost mechanically. However, after cooking the purified lignin in white liquor, only 72.2 per cent could be recovered, about 20 per cent becoming ether soluble and eight per cent acid soluble or lost. Thus it appears that, if black liquors are heated in the absence of the pulp, lignin is degraded faster than in an actual cook. Further, if lignin is cooked in white liquor with no other organic material present, the degradation is still faster. The change in the lignin is evidenced by increased solubility in acid and ether and by a drop in methoxyl content. This illustrates the errors which can be made by trying to apply the results of a cook of a purified material to the entirely different situation found in an actual cook on wood.

Table XXIII shows the absorption coefficients of these preparations in white liquor solution compared with those of the original 2 1/2-hour black liquor and the ether-soluble material obtained by the analytical method. The fraction removed by the ether extraction in the analytical procedure has almost exactly the same absorption spectrum as the fraction soluble in ether-dioxane. The weights obtained were also nearly the same. The data also show that heating the alkaline solution of thiolignin darkened it considerably.

TABLE XXIII

PREPARATION OF PURIFIED THIOLIGNIN
COLOR OF PRODUCTS IN WHITE LIQUOR SOLUTION

Wavelength mmu	420	470	500	540	600	680
			Absorption coefficient k			
Purified thiolignin, one g./l.	10.95	3.65	2.35	1.45	0.717	0.290
After 3 hr. at 170° C.	15.38	5.29	3.52	2.25	1.22	0.521
2 1/2-hr. liquor	604	192	112	61	26	9.8
Purified thiolignin, calculated to liquor basis by methoxyl content	336	122	78.5	48.4	24	9.7
Ether-dioxane soluble, liquor basis	---	47.2	25.6	13.6	5.9	2.1
Ether soluble, from liquor analysis	177	46.8	26.5	14.7	7.6	3.5

7. Color of Separated Liquor Fractions

The total acid-soluble color in kraft black liquor was determined in the same manner as in the soda liquor, except that the solutions were made up with sodium hydroxide and sodium sulfide to white liquor concentrations rather than with sodium hydroxide alone.

Only half of the acid filtrate was used for this determination. The other half, while still acid, was extracted with four portions of ether in a separatory funnel, during which it was apparent that a definite fraction was being removed. The first two ether extracts were highly colored, the third only slightly colored, and the last invariably colorless. The ether solution was in turn extracted with colorless white liquor. When this alkaline liquor was shaken with the yellow ether solution, the colored material immediately became a dark brown and went into the aqueous layer. No color whatever remained in the ether layer. Evidently the ether-soluble material was an acid-base indicator and also acidic in nature, since it was so readily soluble in alkali.

The extraction of the ether-soluble material from the acid-insoluble fraction has already been described under the analytical procedure. The aliquot of this ether solution which was reserved for optical analysis was put in a separatory funnel and extracted with white liquor. The color change and extraction of colored material was the same as described above for the ether extraction of the filtrate. Three portions of white liquor were used for each sample, although one or two removed all the color.

All of the procedures above were kept on a strictly quantitative basis so that the absorption coefficients could be calculated to the original liquor basis. The transmittance curves were determined as soon as possible after the solutions were made. The absorption coefficients are listed in Table XXIV.

From the weight of acid- and ether-insoluble material and the methoxyl content of this precipitate, it was estimated that the 2 1/2-hour liquor contained 33.4 grams of lignin per liter. The solution of purified thiolignin contained 13.6 grams per liter. From the ratio of these two values, the absorption coefficients obtained in analysing the thiolignin solution before and after heating were calculated to the same basis as the 2 1/2-hour liquor. These values are shown in Table XXV.

If the color determinations were accurate and if none of the fractions changed in color during the chemical treatments in the separations, it should be possible to add the absorption coefficients of the three major fractions to obtain the same absorption spectrum as was obtained directly for the whole liquor. If the sum is taken of total acid-soluble color and of color soluble in ether but insoluble in acid (Table XXIV), this will give all the color except that due to lignin. For the 2 1/2-hour liquor, we can obtain values for lignin from Table XXV. If this fraction is added to the previous sum, the following values are obtained for the absorption coefficients of the 2 1/2-hour liquor:

TABLE XXIV

COLOR OF SEPARATED FRACTIONS OF KRAFT BLACK LIQUORS
COOK L-4

Wavelength mmu		420	470	500	540	600	680
Liquor Fraction	Cooking hr.	Absorption coefficient k					
Original whole liquors	1/2	105	35	21	12	6	2.4
	1	338	101	58	33	15	6.4
	1 1/2	490	141	81	45	20	8.0
	2 1/2	664	192	112	61	26	9.8
	3 1/2	760	210	124	67	29	10.4
	4 1/2	780	222	129	70	31	12.0
	5 1/2	780	226	134	74	32	13.6
Reheated whole liquors	1/2	73	29	19	12	6	2.0
	1 1/2	540	169	104	62	30	12.0
	3 1/2	---	258	160	95	48	21.4
	5 1/2	---	322	216	137	74	38.0
Total acid-soluble from original liquors	1/2	34.4	12.1	6.8	3.2	1.4	0.4
	1	49.2	15.8	8.4	4.0	1.6	0.4
	1 1/2	58.0	16.6	8.5	4.0	1.5	0.4
	2 1/2	58.4	16.0	8.5	4.1	1.6	0.4
	3 1/2	54.0	14.4	7.8	3.7	1.5	0.4
	4 1/2	50.8	13.2	7.2	3.5	1.5	0.4
	5 1/2	53.2	13.4	7.2	3.4	1.4	0.36
Total acid-soluble from reheated liquors	1/2	40.4	12.1	6.0	3.3	1.8	1.0
	1 1/2	69.2	17.0	8.8	4.8	2.4	1.2
	3 1/2	66.4	15.0	8.0	4.0	1.6	0.5
	5 1/2	57.6	16.2	8.8	4.8	2.4	1.6
Ether-soluble in acid insoluble from original liquors	1/2	18	5.6	3.3	1.8	0.8	0.3
	1	71	21.4	12.0	6.4	2.9	1.2
	1 1/2	--	43.6	24.6	13.6	6.4	3.2
	2 1/2	177	46.8	26.5	14.7	7.6	3.5
	3 1/2	152	42.8	24.8	13.6	6.3	2.6
	4 1/2	144	41.2	23.6	13.4	6.4	2.7
	5 1/2	144	43.6	25.0	14.4	6.5	2.4

TABLE XXIV (Continued)

Wavelength mmu		420	470	500	540	600	680
Liquor Fraction	Cooking hr.	Absorption coefficient k					
Ether-soluble in acid insoluble from re-heated liquors	1/2	40	16.8	10.8	6.2	2.9	1.2
	1 1/2	--	56.0	32.6	18.4	8.7	3.3
	3 1/2	--	51.2	29.4	16.5	7.7	3.2
	5 1/2	104	35.2	21.2	11.8	5.6	2.2
Ether soluble in acid soluble from original liquors	1/2	20.0	6.6	3.5	1.7	0.8	0.33
	1	31.3	9.7	5.0	2.4	1.1	0.32
	1 1/2	36.1	10.3	5.3	2.6	1.1	0.48
	2 1/2	39.4	11.4	6.1	3.3	1.5	0.70
	3 1/2	33.6	9.8	5.6	3.3	1.6	0.64
	4 1/2	36.0	10.2	5.5	3.1	1.4	0.53
	5 1/2	38.7	9.9	5.0	2.7	1.2	0.48
Ether soluble in acid soluble from re-heated liquors	1/2	27.5	6.8	3.1	1.4	0.6	0.30
	1 1/2	48.0	12.5	6.1	3.5	1.6	0.67
	3 1/2	42.4	11.5	6.6	4.0	1.9	0.80
	5 1/2	27.2	6.8	3.8	3.2	1.5	0.45

TABLE XXV

COLOR OF SEPARATED FRACTIONS OF THIOLIGNIN SOLUTIONS

Calculated to same basis as 2 1/2-hr. liquor

Wavelength mmu	420	470	500	540	600	680
			Absorption coefficient k			
Before heating:						
Whole solution	366	122	78.5	48.4	24.0	9.7
Total acid soluble	5.2	2.4	1.50	1.01	0.58	0.43
Ether soluble in acid insoluble	21.3	7.8	1.77	2.71	1.36	0.53
After heating:						
Whole solution	513	177	117.7	75.1	40.7	17.4
Total acid soluble	30.9	11.2	7.55	4.65	1.92	0.97
Ether soluble in acid soluble	15.0	3.9	2.47	1.50	0.54	0.40
Ether soluble in acid insoluble	62.4	21.5	13.68	8.28	4.07	1.90

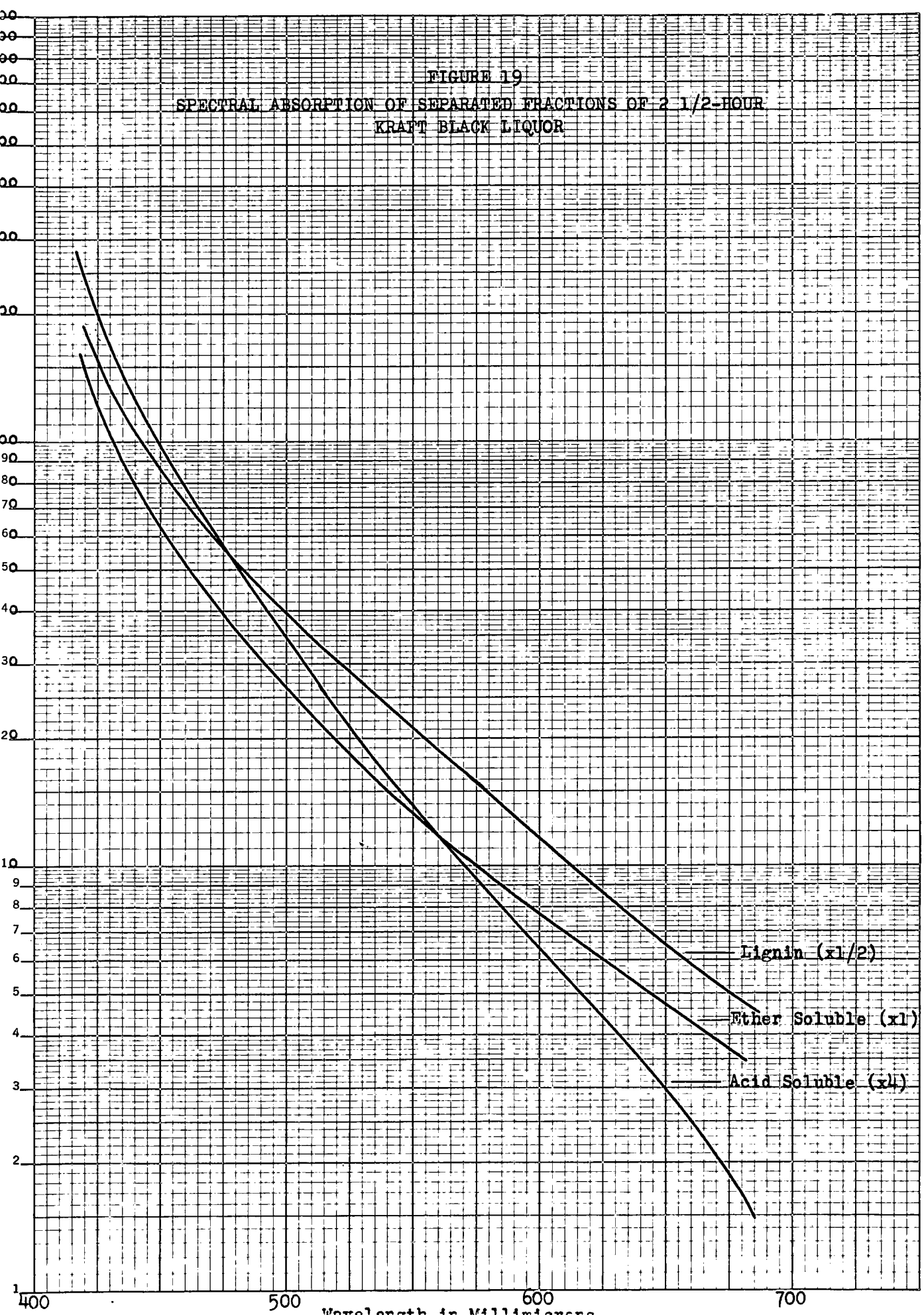
Wavelength--mmu	420	470	500	540	600	680
Sum of fractions	601	185	113	67	33	13.6
Direct determination	664	192	112	61	26	9.8

These results show that, during the chemical separation, one or more of the fractions has changed somewhat in hue, with the theoretical absorption coefficient-wavelength curve becoming less steep. The coefficients evidently remained very nearly constant at 500 mmu. Although these values do not agree as well as those which were obtained for the soda liquors, the disagreement is not serious. The values obtained at the lowest and highest wavelengths are subject to several errors, such as the slight deviations from Beer's Law and low instrumental sensitivity. At any rate, quite comparable absorption coefficient values are obtained at wavelengths near 500 mmu.

Absorption coefficients at one wavelength can be used as a comparative measure of color only if all of the fractions have parallel log k-wavelength curves. If the k values in Table XXIV are plotted on a semilog scale against wavelength, it is seen that each fraction gives a family of nearly parallel curves throughout the cook. The ether-soluble and acid-insoluble curves are nearly parallel to the lignin curves. However, the acid-soluble fractions have much steeper curves than the others. This is illustrated for the 2 1/2-hour liquor in Figure 19. Because only the shape and slope of the log k-wavelength curves are of interest in this comparison, some of the values have been multiplied by factors in order to make the comparison more easily seen.

FIGURE 19

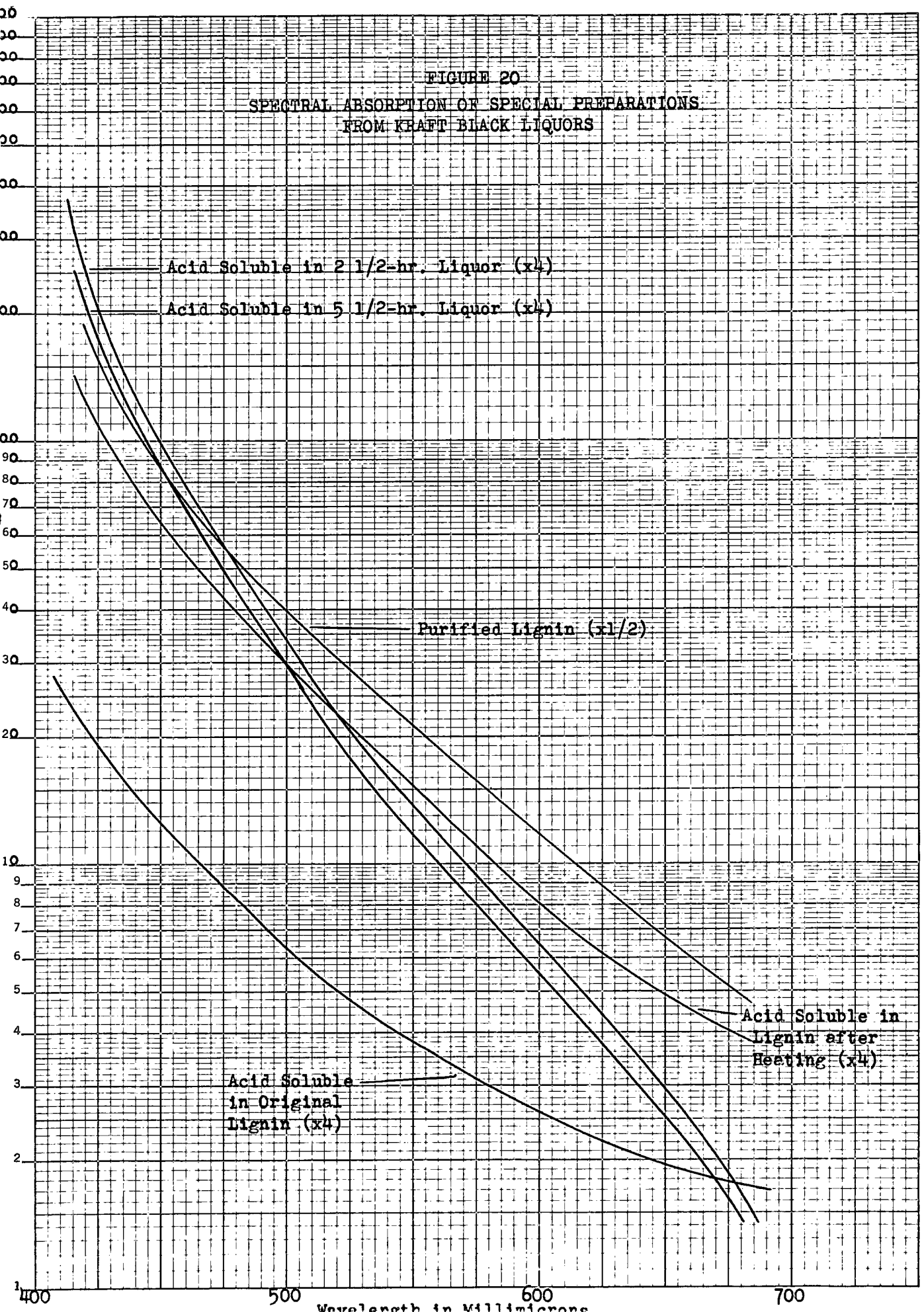
SPECTRAL ABSORPTION OF SEPARATED FRACTIONS OF 2 1/2-HOUR KRAFT BLACK LIQUOR



Since the acid-soluble color is different in hue from the other liquor fractions, it is impossible to make direct quantitative comparisons by using $\underline{k}$ at one wavelength. However, it does afford a means of differentiating this color. A very sharp difference can be seen between the acid-soluble color found in the black liquors and that formed by cooking purified thiolignin in white liquor. This is shown in Figure 20. Again factors have been used to make the comparison clearer. This figure shows that the acid-soluble color formed by heating thiolignin in alkali has a log $\underline{k}$-wavelength curve nearly parallel to that of the original lignin. Within the limits of accuracy of the methods used, no difference is apparent. However, the very steep curves of the acid-soluble color from black liquors show that this color is quite different.

Figure 20 shows that cooking isolated lignin produced acid-soluble color similar in hue to the lignin color. This same lignin was present in the 2 1/2-hour black liquor. In the course of the cook it was held at cooking temperature for three hours. Yet this cooking, in the presence of pulp and dissolved organic material, did not produce any new acid-soluble color, but rather decreased the amount slightly. This can be seen by comparing the acid-soluble curves in Figure 20 for the 2 1/2- and the 5 1/2-hour liquors, and is further evidence that it is unwise to apply the results of cooks of isolated materials to black liquors. It also indicates that the acid-soluble color found in black liquors is not degraded lignin.

FIGURE 20
SPECTRAL ABSORPTION OF SPECIAL PREPARATIONS
FROM KRAFT BLACK LIQUORS



It has been mentioned that quantitative color comparisons of different fractions could not be made by using k at one wavelength because of the differences in the slopes of the log k-wavelength curves. However, such a comparison at 500 mmu will give a general idea of the relative importance of the color in the various fractions. These values from Table XXIV are plotted against cooking time in Figure 21. Since each fraction maintained the same hue throughout the cook, the rate of color formation as shown by the slope of these curves is accurate.

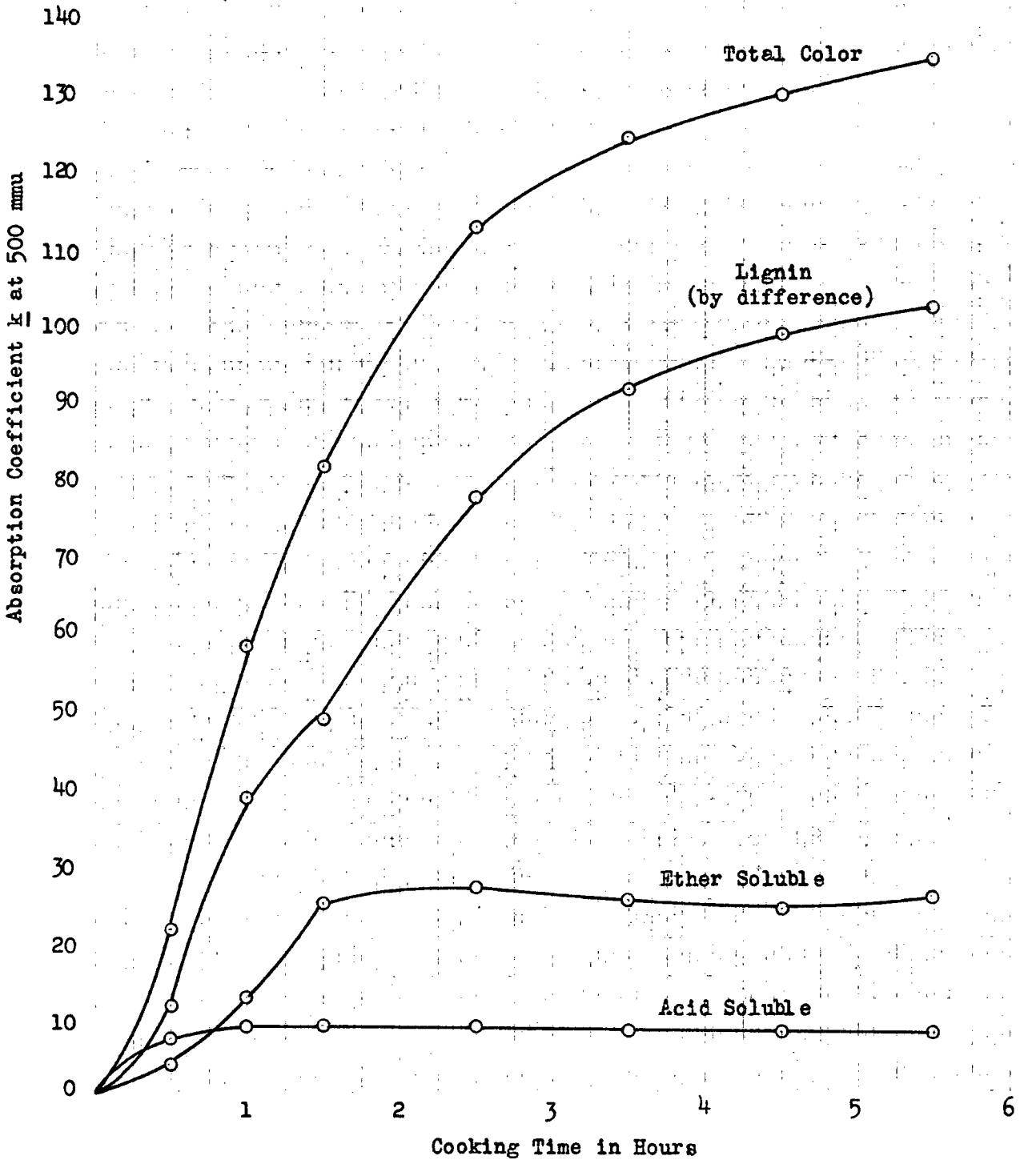
Acid-soluble color develops during the first hour of the cook before maximum temperature is reached and then remains nearly constant--a further indication that this color is formed from easily dissolved wood constituents, and not by the degrading action of the hot alkaline cook on the lignin. The ether-soluble part of this color is not plotted but Table XXIV shows that about two-thirds of the total acid-soluble color can be extracted with ether. This extract has the same steep log k-wavelength curve as the total acid-soluble color.

5. Correlation of Optical and Chemical Analyses

The previous section has shown that the acid-insoluble-ether-soluble color and the lignin color have parallel log k-wavelength curves and, hence, may be compared quantitatively by the use of absorption coefficients at one wavelength. It has also indicated that, if the absorption coefficients of the several fractions are added, they come very close to the absorption coefficients determined

FIGURE 21

COLOR DUE TO VARIOUS LIQUOR FRACTIONS IN KRAFT BLACK LIQUOR



for the whole liquor at wavelengths near 500 mmu. Therefore, k at 500 mmu can be used as a measure of color in these fractions for comparison with the gravimetric determinations.

As mentioned before, the color caused by the lignin can be estimated in two ways. In the first, the absorption coefficient of purified thiolignin at one gram per liter is multiplied by the grams per liter of lignin determined. This would give the correct result only if the color of lignin did not change during the cook. As an alternative, the absorption coefficients of acid-soluble and of ether-soluble color are subtracted from the total color. This has been shown to give good results for the 2 1/2-hour liquor. In Table XXVI, for comparative purposes, the results of both of these calculations are shown. Those found by difference represent the lignin color actually present; those found by calculation serve as a reference to indicate how much the color of the lignin has been changed by cooking.

Examination of these figures shows that, during the actual cook, the depth of color of the lignin does not change much, although at the end of the cook it begins to darken a little. This is illustrated by Figure 22, in which the absorption coefficient of color resulting from the lignin is plotted against the lignin content for the periodic liquor samples. The dotted line is based on the absorption coefficient of purified thiolignin and, therefore, represents the "calculated" values in Table XXVI. Following this line closely is the curve for the values determined experimentally by difference. The agreement is good until the end of the cook, when the

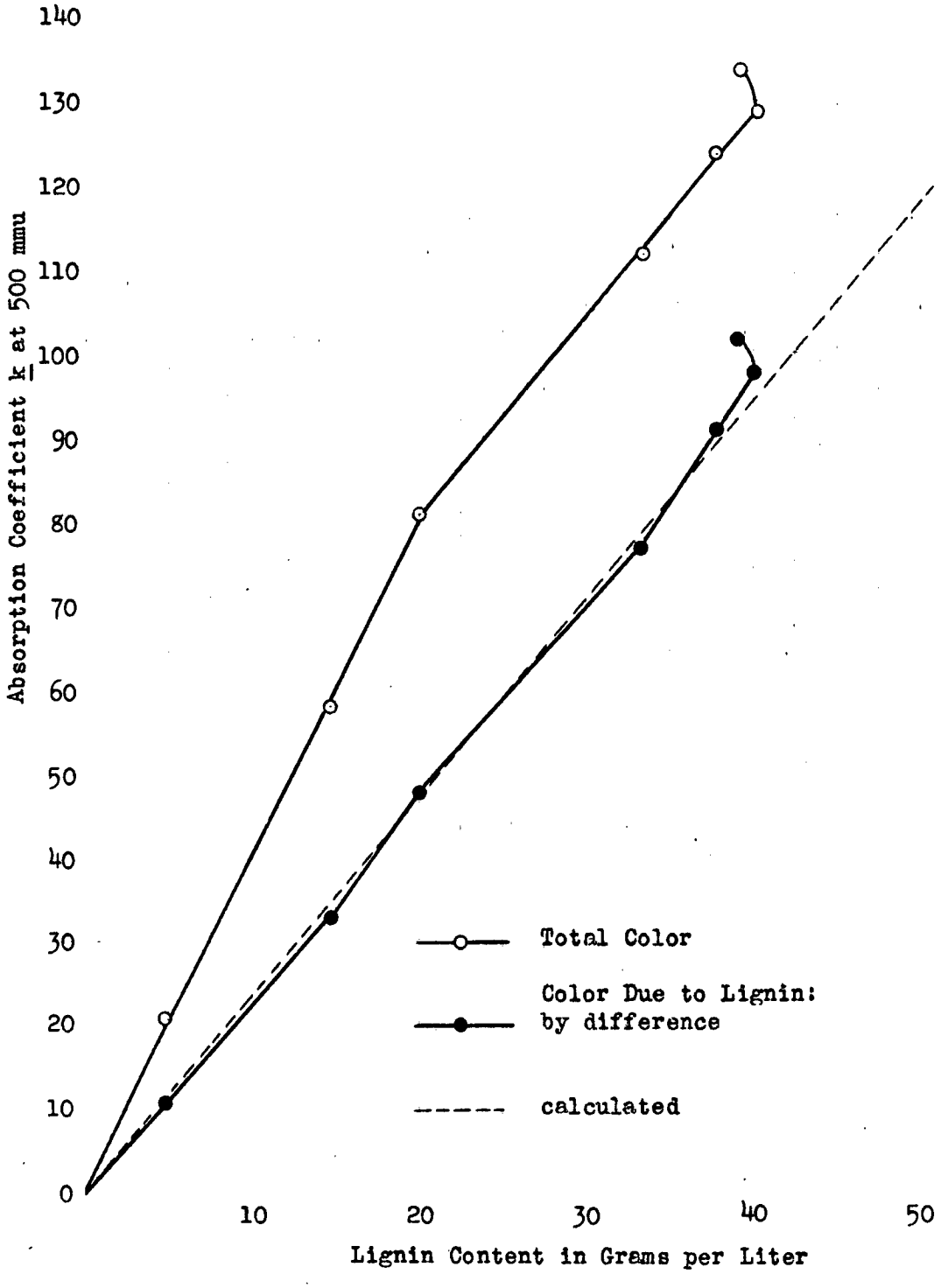
TABLE XXVI

COLOR OF LIGNIN AND ETHER-SOLUBLE MATERIAL IN KRAFT BLACK LIQUORS

Cooking hr.	Lignin: Grams per liter	Lignin: k at 500 mmu, By calculation	Lignin: k at 500 mmu, By difference	Lignin: k at 500 mmu, for 1 g./l.	Ether Soluble: Grams per liter	Ether Soluble: k at 500 mmu, Direct Determination	Ether Soluble: k at 500 mmu, for 1 g./l.
Original Liquors							
1/2	4.9	11.5	11	2.24	1.72	3.3	1.92
1	14.9	36	38	2.55	4.76	12.0	2.52
1 1/2	20.0	47	48	2.40	8.75	24.6	2.81
2 1/2	33.4	78	77	2.32	10.4	26.5	2.54
3 1/2	37.8	89	91	2.42	10.9	24.8	2.28
4 1/2	40.2	94	98	2.44	9.9	23.6	2.38
5 1/2	39.2	92	102	2.60	12.1	25.0	2.06
Reheated Liquors							
1/2	1.06	2.5	2	1.89	4.14	10.8	2.60
1 1/2	13.6	32	63	4.66	8.1	32.6	4.03
3 1/2	32.1	75	123	3.83	11.6	29.4	2.54
5 1/2	35.0	82	186	5.32	13.6	21.2	1.56
Purified lignin solution:							
Original	-----	----	---	2.35	-----	----	----
Reheated	-----	----	---	5.70	-----	----	2.07

FIGURE 22

COLOR AS A FUNCTION OF LIGNIN CONTENT
IN KRAFT BLACK LIQUOR



lignin begins to darken. However, this effect is not nearly as great as in the soda cook (Figure 15).

Kraft cooking does not degrade carbohydrates as much as soda cooking. This indicates that the same thing may be true of lignin, at least as far as color is concerned. However, when isolated liquor samples are heated, kraft lignin shows fully as much evidence of degradation as does soda lignin. The curve for total color has been included to show the relative importance of the lignin color.

Kraft lignin remains constant in color throughout most of the cook, yet is considerably darker than soda lignin (Table XXVII). Whatever the cause of the color difference (probably the introduction of sulfur into the lignin molecule), this indicates that the reaction must be almost complete by the time the lignin is dissolved.

Further examination of Table XXVI shows that, when isolated black liquors are heated, the lignin darkens much more than it does during an equivalent time in the digester. Also, if the other organic material is removed and the lignin alone is heated in white liquor, the increase in color is even greater. This is another manifestation of the degradation of lignin as shown by methoxyl content, solubility in ether, and solubility in acid. In each case the figures show that the pulp and other organic materials protect the lignin from degradation. Perhaps this is due to a buffer action.

Table XXVI also gives grams per liter and absorption coefficient at 500 mmu for the ether-soluble material extracted from

the lignin precipitate. During the cook, this material appears to have nearly the same absorption coefficient per gram as does the lignin itself. The values are not as consistent as those for lignin, perhaps because of analytical difficulties. With one exception, it was not darkened by reheating, although the total amount increased somewhat. That part of the purified thiolignin made soluble in ether by cooking was not highly colored when compared with the part which was still ether insoluble. The figures show that apparently this ether-soluble material is formed in small quantities from the ether-insoluble lignin during the cook and on heating isolated liquors. A comparatively large amount is formed early in the cook, perhaps because of lignin degradation before the other organic materials are in solution. This hypothesis is supported by the decrease in lignin and increase in the weight and color of the ether-soluble fraction when the 1/2-hour sample is reheated. It should also be noticed that the acid-soluble color does not increase (Table XXIV).

COMPARISON OF KRAFT AND SODA BLACK LIQUORS

Cooks L-2 (soda) and L-4 (kraft) were made on the same wood and under the same conditions, except that the alkali ratio was reduced for the kraft cook to give a pulp of approximately the same lignin content as the soda cook. Some of the absorption coefficients for liquors from these cooks have been reproduced in Table XXVII. The values showing the final liquor samples and the acid-soluble color in these samples are comparable only so far as the cooks are comparable. As far as lignin content of the pulps is concerned, this is quite good. The log $\underline{k}$-wavelength curves are given in Figures 23 and 24. These graphs show that the curves for kraft whole liquor and acid-soluble color are considerably steeper than those for soda. This makes it impossible to compare the colors quantitatively by using the absorption coefficients at one wavelength. However, it does show that the sodium sulfide in the kraft cook has an effect on the color. This is also shown by the behavior of kraft black liquor on dilution with sodium hydroxide solution (Table XVIII). The behavior indicates that at least a part of this reaction is reversible. Dilution of soda black liquors with kraft white liquor also illustrated this. When this was done, the log $\underline{k}$-wavelength curves for soda black liquor became somewhat steeper, but did not reach the values attained by the kraft liquors.

Table XXVII also shows the absorption coefficients for purified alkali lignin from soda liquor as compared with those for thiolignin from kraft liquor. Since these values are known on a gram per

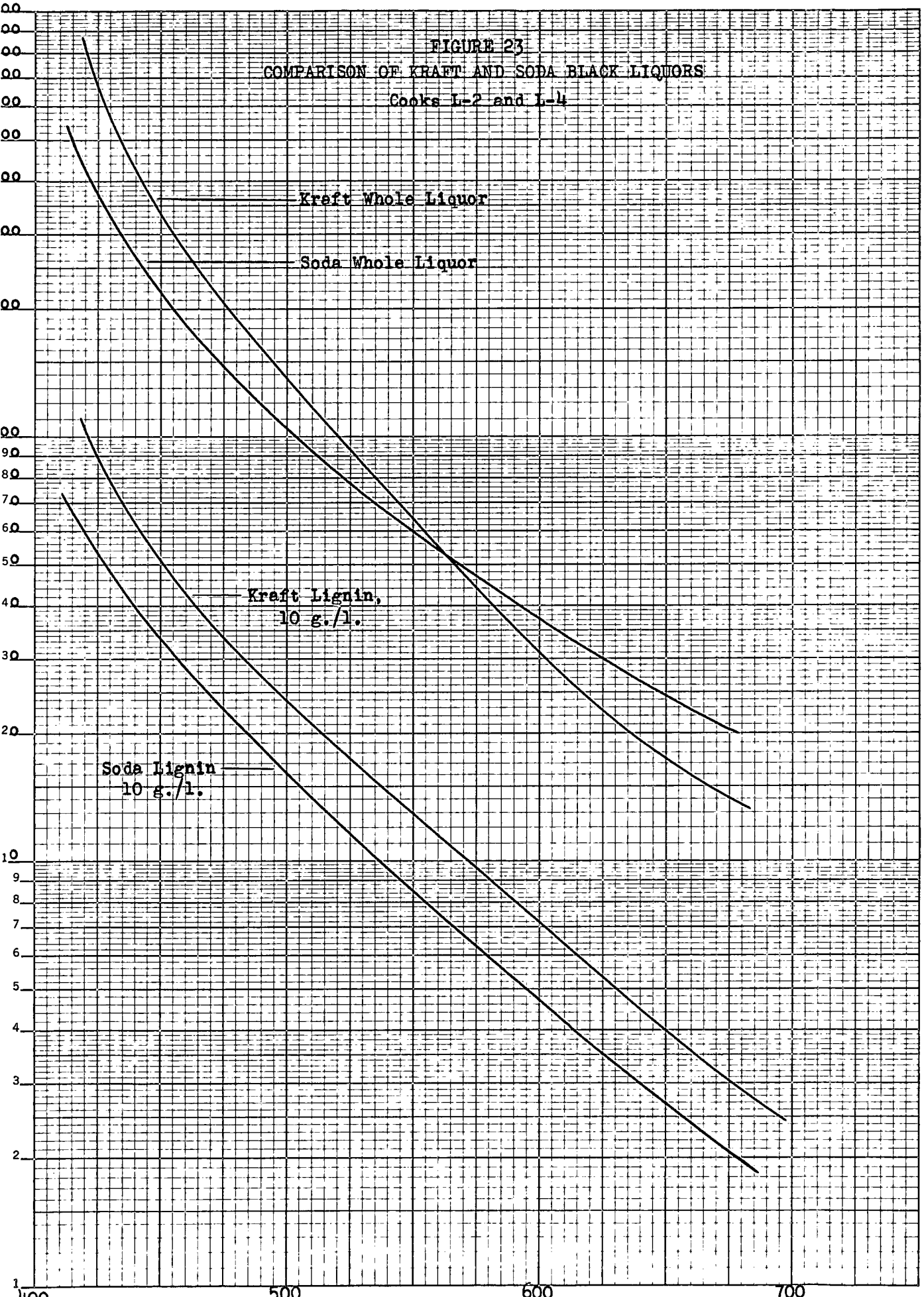
TABLE XXVII

COMPARISON OF KRAFT AND SODA BLACK LIQUOR COLOR

Cooks L-2 and L-4

Wavelength mmu	420	470	500	540	600	680
			Absorption coefficient k			
5 1/2-hr.						
Whole liquors:						
Soda	410	154	104	65	37	20.1
Kraft	780	226	134	74	32	13.6
Acid soluble:						
Soda	24.4	7.6	4.5	2.8	1.4	0.8
Kraft	53.2	13.4	7.2	3.4	1.4	0.36
Purified lignin, one g./l.						
Soda	5.88	2.45	1.61	0.95	0.47	0.195
Kraft	10.95	3.65	2.35	1.45	0.72	0.290

FIGURE 23
COMPARISON OF KRAFT AND SODA BLACK LIQUORS
Cooks L-2 and L-4



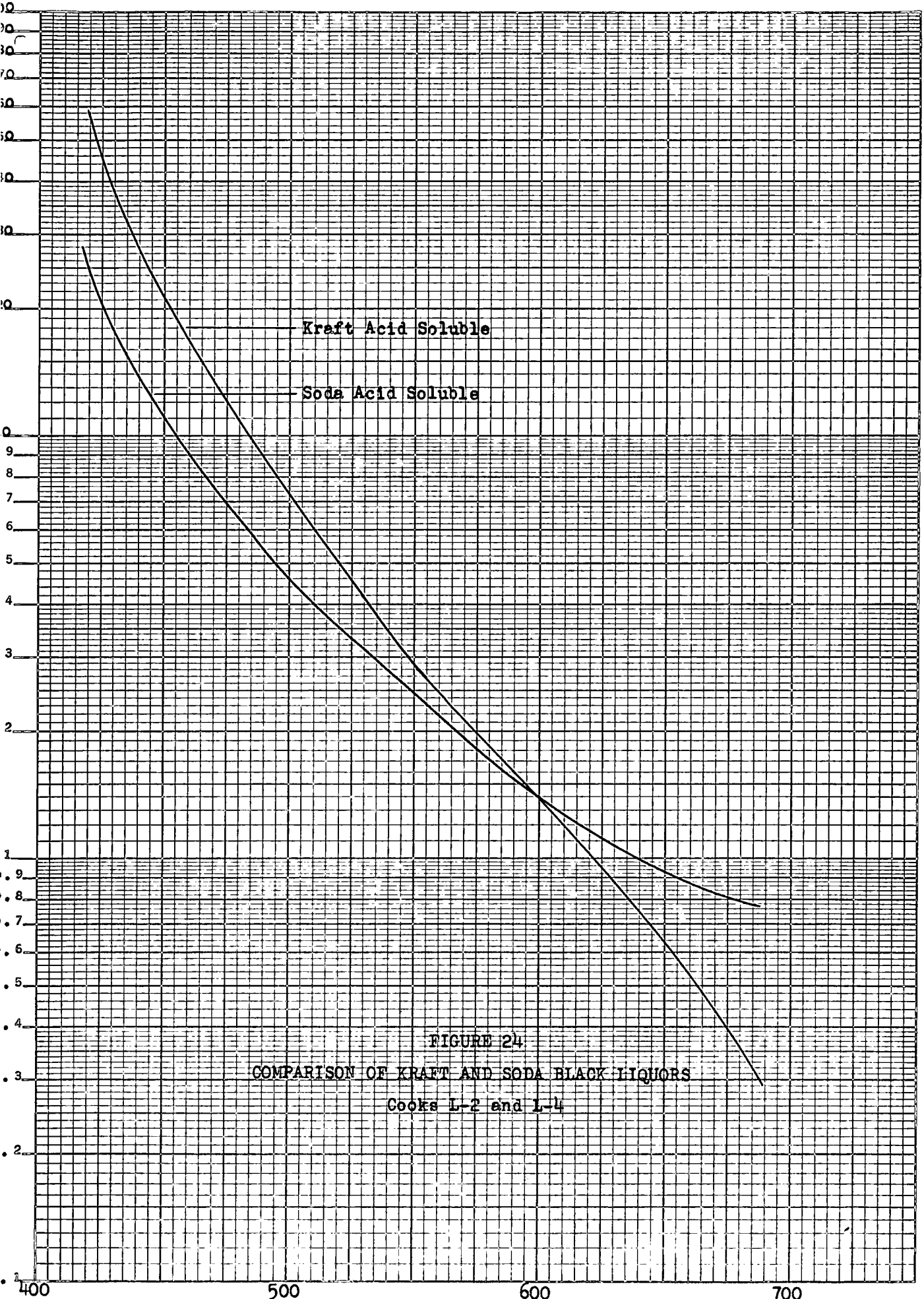


FIGURE 24

COMPARISON OF KRAFT AND SODA BLACK LIQUORS

Cooks L-2 and L-4

liter basis, they can be compared directly. The log k-wavelength curves are shown in Figure 23. In this case the curves are parallel and absorption coefficients can be used for a quantitative comparison. At 500 mmu, such a comparison shows that the soda lignin had only about 68 per cent as much color as the kraft lignin; therefore, the introduction of sulfur darkened the lignin but did not change the hue.

These values were obtained with the alkali lignin in sodium hydroxide solution and the kraft lignin in kraft white liquor solution. Apparently the difference in hue between kraft and soda liquor is not due to the lignin. Figure 24 shows that a large part of this difference is found in the acid-soluble fraction.

It is unfortunate that kraft and soda black liquors cannot be diluted with the same diluent. This makes comparisons less certain. However, since Beer's Law is followed fairly well, the results shown are close to those which would be obtained if the transmittances could be measured without dilution.

Comparative kraft and soda cooks were made on several species by the pulping class of The Institute of Paper Chemistry. Liquor samples were obtained from these cooks for optical analysis. The conditions used, yields, and permanganate numbers are given in Table XXVIII. In these cooks identical cooking conditions were used for kraft and soda and no attempt was made to cook to equivalent yields or bleachabilities.

Table XXIX gives the transmittance readings for 100 to 1 dilutions with white liquor for the final liquor samples from kraft

TABLE XXVIII

COMPARISON OF KRAFT AND SODA PROCESSES

Process	Cook number	Species	Screened yield %	Permanganate number
Soda	101	Aspen	50.3	13.7
	103	Spruce	45.0	34.8
	104	Jack pine	43.5	34.6
Kraft	201	Aspen	51.4	12.3
	203	Spruce	44.7	20.0
	204	Jack pine	43.3	23.7
	207*	Loblolly pine	43.3	29.5

Constant Conditions:

Digester--iron, circulating pump, outside heat interchanger
Active alkali ratio--24.0 per cent expressed as NaOH
Water ratio--6 g. total water per g. oven-dry wood
Maximum temperature--176° C.
Time to maximum--1.0 hr.
Time at maximum--3.0 hr.
Chip length--0.75 inch
Sulfidity--0 for soda cooks, 33.3 per cent for kraft cooks

* Cook 207 was made in a stainless steel digester, 1.5 hours to maximum temperature, 3.5 hours at maximum, maximum temperature 170° C. Cook 205 (used in investigating Beer's Law) was made under the same conditions with 7.75 to 1 water ratio.

TABLE XXIX

EFFECT OF SPECIES ON KRAFT BLACK LIQUOR COLOR

Whole liquors, 100 to 1 dilution with white liquors

Wavelength mmu	420	470	500	540	600	680
	Transmittance--per cent					
Wood						
Aspen (201)	4.3	33.9	51.2	67.7	82.9	91.8
Spruce (203)	2.2	31.7	50.0	67.6	83.0	92.4
Jack pine (204)	1.9	31.8	49.9	68.2	84.1	93.7
Loblolly pine (207)	3.2	32.2	50.5	67.5	82.5	91.6

cooks on four species. At any wavelength, the greatest spread of values is less than two per cent. Undoubtedly it is only by coincidence that such variables as lignin content of wood, degree of cooking, etc., should so counterbalance that these amazingly similar liquors should be obtained for these four woods of very different composition. However, it does show that the widely different extractives in spruce, jack pine, and loblolly pine are of only minor importance in liquor color. The transmittance values were quoted only to illustrate this point.

Absorption coefficients for whole liquors are given in Table XXX. The log k-wavelength curves for kraft and soda are compared in Figure 25. Those for jack pine have been plotted on a one-tenth scale to avoid interference. These curves show exactly the same thing as those in Figure 23. Examination of the absorption coefficients and the curves shows that, although jack pine contains more pitch and other extractives than spruce, this apparently does not have much effect on the liquor color. The soda and kraft liquor colors are quite different, however.

One other wood, black cherry, was pulped by the two processes. This wood gave extremely dark liquors with both kraft and soda liquors. Since this seemed to be an unusual case, not found in woods commonly used commercially, no further investigation was made.

The absorption coefficients shown in Table XXXI represent one further attempt to compare the liquors from the two processes. In

TABLE XXX

COMPARISON OF KRAFT AND SODA BLACK LIQUOR COLOR

Whole liquors diluted with white liquors

Wavelength mmu	420	470	500	540	600	680
	Absorption coefficient k					
Cook						
Spruce kraft (203)	770	234	140	78	37.0	16
Jack pine kraft (204)	800	240	140	77	35.0	13
Aspen soda (101)	366	165	108	66.4	34.6	18
Spruce soda (103)	426	156	106	66.0	35.2	16
Jack pine soda (104)	440	159	107	67.0	36.0	18

TABLE XXXI

COMPARISON OF KRAFT AND SODA BLACK LIQUOR FRACTIONS

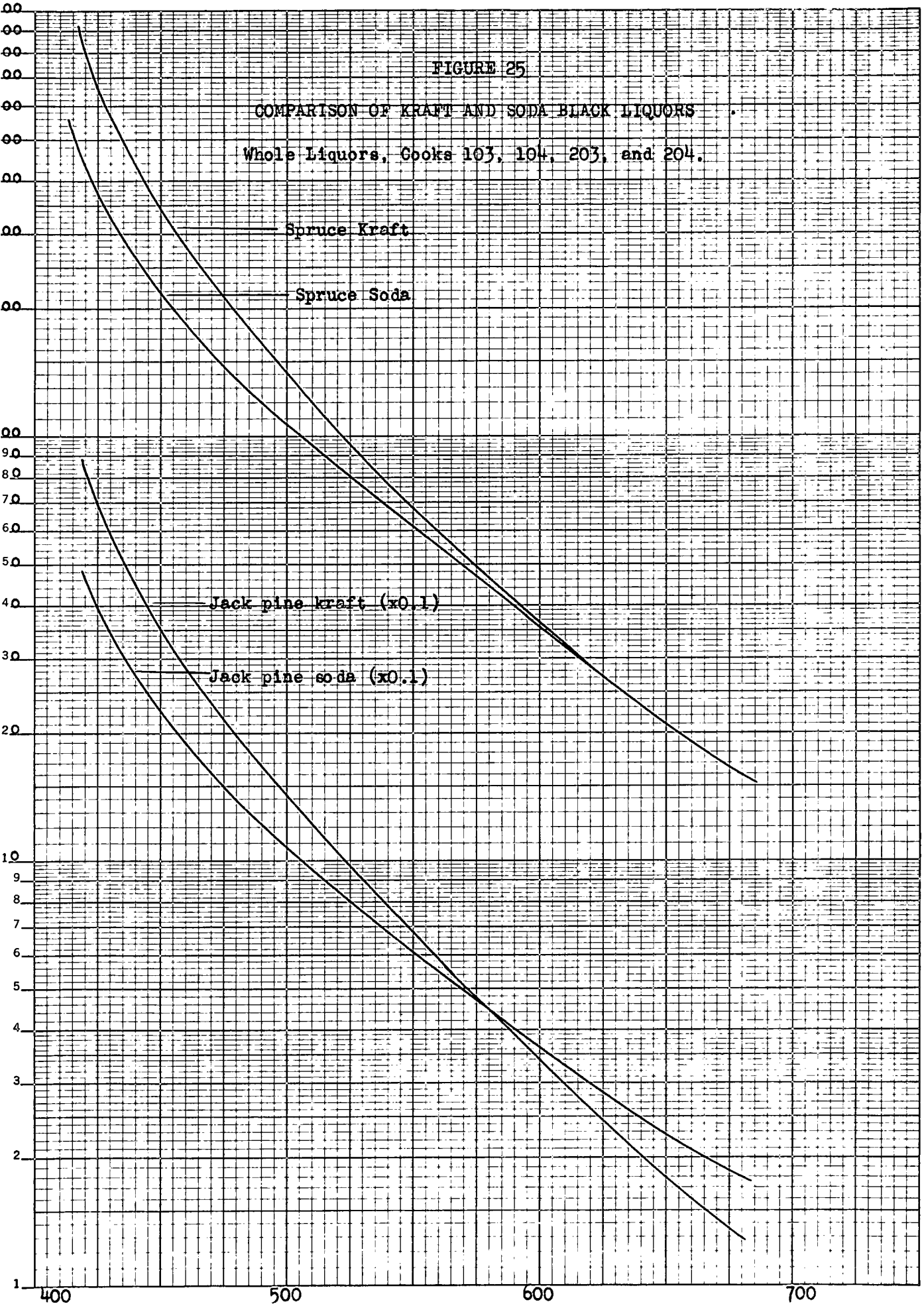
Both kraft and soda fractions diluted in soda white liquor

Wavelength mmu	420	470	500	540	600	680
			Absorption coefficient k			
Acid-soluble color:						
Spruce soda (103)	43.6	15.5	10.2	6.1	2.5	1.1
Jack pine soda (104)	48.4	18.4	12.3	7.5	3.2	0.8
Spruce kraft (203)	74	28.0	18.0	11.2	5.5	2.1
Jack pine kraft (204)	100	30.4	19.4	11.7	5.5	2.0
Ether-soluble color in acid insoluble:						
Spruce soda (103)	-----	24.4	14.4	7.3	3.0	1.2
Jack pine soda (104)	-----	24.4	14.8	7.0	2.8	1.0
Spruce kraft (203)	-----	26.6	15.2	7.8	3.4	1.2
Jack pine kraft (204)	-----	24.8	15.0	7.7	3.2	1.1

FIGURE 25

COMPARISON OF KRAFT AND SODA BLACK LIQUORS

Whole Liquors, Cooks 103, 104, 203, and 204.



this experiment the liquor fractions were separated as described under the analysis of kraft liquors. However, both the kraft and soda liquor fractions were made up with soda white liquor. Since this treatment undoubtedly distorts the absorption spectra of the kraft liquor fractions, the slope of the log k-wavelength curves is not significant. However, these values do furnish one further comparison of the liquors; the ether-soluble material from the lignin precipitate is nearly the same for kraft and soda and for both species; the acid-soluble color, however, shows a sharp difference between the two processes, and close similarity of the two woods in either process. This indicates that the wood constituents from which this acid-soluble color is formed are available in either spruce or jack pine. Since spruce has only a negligible amount, if any, of tannins, and phlobatannins, these materials evidently do not contribute much acid-soluble color in alkaline cooks of these commonly used woods.

PULP COLOR

The color of unbleached alkaline pulps can come from two sources. One is colored material which has never been dissolved by the cooking liquors. This is undoubtedly a very important factor, because a considerable amount of lignin remains in the pulp, and lignin is highly colored after an alkaline cook. This part of the pulp color would not be directly related to the color of the black liquor. The other possible source of pulp color is material which has been dissolved, but which contaminates the pulp because of adsorption, chemical reaction, or imperfect washing. Bard's experiments (14) indicate that this is also an important factor. Color from this source should be related to some of the colored constituents in the black liquor.

Pulp color can be compared with liquor color by comparing the log k-wavelength curves of the solutions with the log k/s wavelength curves of pulp handsheets, as explained by Bard. When this is done for Cooks L-2 and L-4, the difference in slope found for the acid-soluble fractions of the black liquors is the same as that found for the pulps. These cooks were made under nearly identical conditions, and the pulps cooked to almost the same lignin content. However, examination of pulps from the other comparative kraft and soda cooks shows that this relation is not general, at least, it does not hold when the pulps are cooked to different bleachabilities.

Several factors could be responsible for the lack of a direct relation between pulp color and liquor color. As mentioned

before, some of the color does not come from the liquor. Further, the color of a dry solid cannot always be predicted from the color of its solution. Other important variables are found in the drying conditions. This is illustrated by the widely different pulp colors obtained by drying a pulp which had been suspended in an alkaline, acid, and neutral medium.

It should be possible to relate at least a part of the color of alkaline pulps to some of the colored constituents in the black liquor. However, as can be seen by the above discussion, this is a rather involved problem which will require a detailed and careful study.

OPTICAL COOK CONTROL

Sulfite liquors change greatly in depth of color and in hue as the cook end point approaches (20), and this change is sometimes used in visual and photometric cook control. It has been shown (Figures 4, 5, 6, 7, 16, and 17) that such a change does not occur in alkaline liquors. Near the end of the cook the hue of the liquor does not change and the depth of color increases slowly.

The liquors are, of course, so dark that direct examination is useless. However, since the hue does not change, a single transmittance measurement at an effective wavelength between 450 and 500 mmu would give all the information of any value in comparing liquor samples. This could be made on a water dilution (about 100 to 1) by a simple photometric system.

Because of the use of black liquor as make-up and the normal variations in wood-liquor ratio, it would not be feasible to attempt to cook to a definite transmittance. The only practical criterion of the degree to which the digestion has progressed appears to be the rate of change of the liquor transmittance. Figures 6 and 16 indicate that the transmittance at 450 or 500 mmu drops rapidly early in the cook. However, during the last hour of these cooks (which are perhaps over-cooked) the transmittance decreases only one or two per cent. A system could be set up by which the cook was blown when, for example, transmittance dropped less than one per cent in 15 minutes. Unfortunately this method would be least sensitive near the end of the cook, and probably would not furnish a critical control method. As

an example, for Cook L-4 (Figure 16) it can be calculated that a one per cent change in the lignin content of the pulp would cause a change of only 0.52 per cent in the transmittance at 500 mmu. It must also be remembered that the lignin is darkening at this point in the cook; this would make the method even less sensitive. Since the color of the black liquor does not afford any better criterion, it appears that optical methods do not offer much promise for commercial control of alkaline cooks.

IV SUMMARY

The pulping action in alkaline cooking is very rapid in the early stages, even before maximum temperature is reached. Carbohydrate materials are removed most rapidly. Lignin is also removed quite rapidly, more so in kraft than in soda cooking. However, in both cases the removal of lignin continues when carbohydrates are no longer dissolving.

Liquor color increases in a smooth curve with time--rapidly at first and very slowly near the end of the cook. There is no significant change in hue during the cook.

Alkaline black liquors do not obey Beer's Law on dilution with water. They will follow Beer's Law closely if diluted with colorless kraft white liquors near the strength of the raw cooking liquors. The use of such diluents also insures that all transmittance measurements are made on solutions of the same pH, thus eliminating errors caused by indicator color changes. A thin-film absorption cell has been developed which can be used to check the conformity to Beer's Law over a wider range by determining the absorption curves of undiluted black liquors.

In both kraft and soda liquors the color due to lignin, acid-soluble material, and the ether-soluble part of the acid-insoluble fraction can be determined separately on the isolated fractions. When added together, the calculated color of these fractions

sums up to an absorption curve which is quite close over the entire visible range to the curve obtained for the original liquor. This shows that the color of the fractions is not seriously altered by the chemical treatment used in isolation, and that the color of such isolated fractions is representative of the color of these materials as they exist in the black liquor.

The absorption spectra of the various soda black liquor samples and liquor fractions are so similar that no differences exist in shape or slope of the log k-wavelength curves (k refers to absorption coefficient) which can be used in their differentiation. However, since this is true, absorption coefficients at one wavelength can be used to make quantitative comparisons of the amounts of color present.

This is not true of kraft liquors. The whole liquors have steeper log k-wavelength curves than the soda liquors. Most of this difference is caused by the acid-soluble fraction, since lignin and the ether-soluble material have curves similar in shape to the corresponding soda liquor fractions. This means that kraft acid-soluble color cannot be compared with other fractions on a quantitative basis, but can be differentiated from them.

The preceding observations as to similarity of curves are made with the knowledge that there are minor variations produced by the age of the sample, slight deviations from Beer's Law, and lack of instrumental sensitivity at very high and very low transmittance or wavelength. The differentiation of the kraft acid-soluble fraction

is based on a very marked difference which could not be caused by the factors mentioned above.

Lignin is degraded by prolonged cooking in alkaline liquor. This is shown by the darkening in color, the decrease in methoxyl content, and the decrease in the amount which can be precipitated by acids. In kraft cooking, no evidence of such degradation appeared during the first 4 1/2 hours. At this time the acid precipitate had its maximum weight, maximum methoxyl content of 14.40 per cent, and nearly the same absorption coefficient per gram per liter as the 2 1/2-hour lignin. After 5 1/2 hours the precipitate had a lower methoxyl content, lower total weight, and slightly higher absorption coefficient, thus showing the beginning of the degradation.

If liquor samples were removed from the digester and heated in the absence of pulp, much more degradation was evidenced by all three criteria, although no additional acid-soluble color was formed. This showed that the presence of pulp had a great effect on the reaction. Simerl (20) found a similar effect for sulfite liquors.

An even more rapid degradation of lignin occurred if purified thiolignin was dissolved in kraft white liquor and heated. In this case colored acid-soluble and ether-soluble fractions were formed, and the absorption coefficient was doubled. It is evident that such cooks of isolated constituents do not approximate the reactions which take place in a black liquor or in a cook on wood.

In soda cooks the lignin shows much the same reactions. However, the color begins to increase earlier in the cook, showing some

increase in absorption coefficient per gram after 3 1/2 hours and considerable increase by the end of the 5 1/2 hour cook. Soda lignin, however, is not demethylated as easily as kraft lignin. In fact, very little decrease is noted, and the purified alkali lignin increases in methoxyl content on heating in white liquor. All the other effects are very similar to those for kraft lignin.

Before any such signs of degradation or darkening in color appear, kraft lignin is considerably darker in alkaline solution than is soda lignin. Since kraft lignin is darker than soda lignin, yet maintains a constant absorption coefficient through most of the cook, the reaction which causes the color difference (probably the introduction of sulfur) must be nearly complete by the time the lignin is dissolved.

Possibly the darkening of the lignin near the end of the cook accounts for the darkening of overcooked alkaline pulps. This is very likely, since none of the other liquor constituents change in color near the end of the cook.

Carbohydrates which are still insoluble in acid do not contribute any appreciable color to either kraft or soda black liquor. These acid- and dioxane-insoluble materials contaminate the acid precipitates early in the cook, causing a low methoxyl content. Later in the cook the methoxyl content of these precipitates reaches nearly the value for purified lignin, showing that almost all of the carbohydrates have become acid soluble.

An extensive study of the ether-soluble material in the acid precipitate was made only for the kraft cook. This fraction should contain resins, fats, and other extractives as well as some ether-soluble lignin. Since the methoxyl contents are 11 to 12 per cent, it can be concluded that they contain considerable amount of lignin. Most of this material, as measured by weight or by color, appears early in the cook. Further cooking or heating of isolated liquors increases the amount slightly, although a considerable amount is produced by heating purified lignin in white liquor. The absorption coefficient per gram per liter did not increase with heating as it did for lignin. These facts indicate that the lignin in this ether-soluble fraction is different from the true thiolignin. Reheating of the 1/2-hour liquor shows that ether-soluble material can be formed from the lignin dissolved at low temperatures at the first of the cook. This may mean that such easily dissolved lignin is more easily degraded, or it may be caused by the greater strength of the liquor at this stage of the cook. The absorption coefficient per gram per liter and log k-wavelength curve of the ether-soluble material are quite close to those for lignin before degradation.

In the soda cooks a considerable amount of unstable colored material is formed in the early stages, reaching a maximum at 1 1/2 hours (when maximum temperature was reached). It is found in both the acid-soluble and acid-insoluble fractions. This color is mostly destroyed during the first hour at maximum temperature. It also disappears if the isolated liquors are heated, or if they are merely diluted and allowed to stand for three weeks. Since little of this

fugitive color is present at the end of the cook, it probably has little importance. No trace of such a color is found in kraft black liquors.

In addition to this unstable color, the acid-soluble fraction of soda liquor contains a very stable colored material which reaches a maximum amount in 1 1/2 hours and is changed very little thereafter, either by further cooking, aging of liquor samples, or reheating of isolated liquors. The acid-soluble color in kraft liquors is similar to this soda liquor fraction in rate of formation, but differs in shape of the log k-wavelength curve.

Some investigators have believed that the acid-soluble color in black liquor is related to the colored material in alkaline pulps. The colored material in the acid-soluble fraction of black liquor has been identified by various investigators as tannins, phlebatannins, tannin-base sulfur dyes, carbohydrate products, and degraded lignin. Schwartz, McCarthy, and Hibbert (19) have stated that the isolated colored material has a methoxyl content of 5.36 per cent and that it is formed by kraft cooking of either extracted or unextracted wood. To this the following new information can be added:

1. The acid-soluble color is formed early in the cook in both kraft and soda processes. It does not increase thereafter on continued digestion or on heating the isolated black liquors.

2. Although acid-soluble color can be formed by heating either isolated soda or kraft lignin in white liquor, such color is

optically different from the acid-soluble color formed in a digestion of wood. Apparently, such acid-soluble lignin color is not formed in a black liquor when other organic buffering materials are present. Since acid-soluble color is formed early in the cook and is not increased by further cooking, it seems unlikely that it could be due to degradation of lignin by the cooking process.

3. This fraction constitutes one of the major differences between kraft and soda liquor colors. In kraft cooks the color is darker and has a much steeper log k-wavelength curve than in soda cooks.

4. Spruce and jack pine produce nearly identical acid-soluble colors.

The acid-soluble color found in black liquors is not formed by the degrading action of the alkaline digestion on true alkali lignin or thiolignin. It also seems unlikely that tannins or similar extractives are responsible, because they are not present in appreciable quantities in spruce, and are certainly not the same in spruce as in jack pine. Probably there is no single source, and probably this colored material varies with the species of wood. However, the evidence suggests that the color could be caused by a humic substance, which perhaps is formed from sensitive carbohydrates. Whatever the material may be, it differs from true lignin in rate of solution in alkaline digestion, in solubility in acid, in methoxyl content, and in optical properties.

The acid-soluble color is relatively not an important part of the total liquor color. At the end of the soda cook, for example, it accounted for only about 5 per cent of the total color, whereas lignin accounted for 90 per cent. Ether-soluble material made up the remainder. In the kraft cook a quantitative comparison can be only an arbitrary comparison at one wavelength, due to the difference in shape of the log k-wavelength curves. At 500 mmu such a comparison would show five to six per cent of the color in the acid-soluble fraction, 76 per cent produced by lignin, and 18 or 19 per cent in the ether-soluble fraction, the last containing some of the lignin.

Comparative cooks on different species showed that kraft liquors from cooks on aspen, spruce, jack pine, and loblolly pine have very nearly identical transmittance curves. Soda cooks also gave similar liquors for various species. However, there was a sharp difference between the kraft and soda liquor colors.

The absorption spectra of the acid-soluble fractions from spruce kraft and jack pine kraft were quite similar. Again the soda liquors from these woods gave nearly identical acid-soluble fractions, which differed from the kraft acid-soluble color from the same woods.

Black liquors change only slightly in depth of color and not at all in hue during the critical period near the end of the cook. For this reason, optical methods do not seem very promising for commercial cook control.

V CONCLUSIONS

1. The color of alkaline liquor during the course of a cook increases in a smooth curve with time, rapidly at first, very slowly near the end of the cook. There is no significant change in hue during the cook.

2. Alkaline black liquors do not obey Beer's Law on dilution with water, but do so if diluted with colorless white liquors near the strength of the raw cooking liquors.

3. Alkaline black liquors can be separated into several fractions. The absorption coefficients of these fractions sum up to nearly the absorption spectrum determined on the whole liquors. Therefore, the color of the separated fraction can be considered to represent the color of the material as it exists in black liquor.

4. All soda black liquor fractions have nearly parallel log $\underline{k}$-wavelength curves. Therefore, the colors can be compared quantitatively but not differentiated.

5. Kraft black liquors have steeper log $\underline{k}$-wavelength curves than soda liquors. This difference is due to the acid soluble fraction, which has a very steep curve. Therefore, the color in this fraction can be differentiated from other color but not quantitatively compared.

6. Lignin is degraded by prolonged cooking in alkaline liquor. This is evidenced by darkening in color, decrease in methoxyl

content, and decrease in the amount which can be precipitated by acids.

7. Lignin is not degraded during the first part of the alkaline cook. This is indicated by the methoxyl content and the direct proportionality of lignin content of the black liquors and the absorption coefficient of the acid-insoluble fraction. Some signs of degradation begin to appear after three hours of soda cooking, and after five hours of kraft cooking. Degradation is much greater when liquors are heated in the absence of pulp, and is still more severe when purified lignin is heated in white liquor.

8. Since no other black liquor constituents change in color near the end of the cook, the darkening of overcooked alkaline pulps may be associated with the darkening of the dissolved lignin.

9. Carbohydrates which are insoluble in acid do not contribute any measurable color to either kraft or soda black liquors.

10. The ether-soluble part of the acid precipitate contains some lignin as well as resins and other extractives. This material dissolves early in the cook and is increased slightly by further digestion or by heating isolated liquors. Its absorption coefficient per gram does not increase on heating. Apparently part of this material is formed from ether-insoluble lignin by heating, especially when the free alkali is high.

11. In soda cooks an unstable colored material is formed early in the cook. This color is destroyed by further digestion,

by heating the liquor, or by aging. Such color is not formed in kraft cooks.

12. Acid-soluble color in kraft or soda cooking of spruce and jack pine is apparently not formed from tannins or by degradation of lignin. It could be due to the humification of sensitive carbohydrates.

13. One of the major differences between kraft and soda black liquors is the color of the acid-soluble fraction. Kraft acid-soluble color is darker and had a steeper log k-wavelength curve.

14. Another difference between kraft and soda liquors is the color of the lignin. Before any degradation occurs, kraft lignin is darker in alkaline solution than soda lignin. Both kraft and soda lignin have a constant absorption coefficient on a gram per liter basis during the first part of the cook.

15. Lignin is the most important colored constituent in alkaline black liquors, accounting for 75 to 90 per cent of the color. The acid-soluble color accounts for only about five per cent. The remainder is in the ether-soluble fraction, which also contains some lignin.

16. The total color is very similar for kraft liquors from aspen, spruce, jack pine, and loblolly pine. Soda liquors from different species are similar to one another, but not to the kraft liquors.

17. Optical methods do not seem very promising for commercial cook control.

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