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An Investigation of Accelerated Brightness
Reversion of Bleached Slash
Pine Kraft Pulp

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AN INVESTIGATION OF ACCELERATED BRIGHTNESS REVERSION
OF BLEACHED SLASH PINE KRAFT PULP

A thesis submitted by

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INTRODUCTION

Brightness is defined as the reflectivity of a sheet of pulp or paper for blue light measured under standardized conditions. It is well known that the brightness of bleached pulps is not permanent and that brightness reversion (fading, yellowing, color recession) is accelerated by exposure to light, heat, chemicals, and high humidities. Many statements concerning the causes of brightness reversion have been advanced largely on the basis of qualitative observations. However, this phenomenon has not been studied extensively, as have some of the other phases of pulp and paper technology.

Brightness reversion is relatively important commercially for several different but related reasons. Disputes naturally arise between the parties involved in the sale of a pulp if the brightness of that pulp decreases in transit. This is the only chemical or physical property of pulp which can change significantly under the conditions, and within the relatively short time interval involved during shipment. The yellowing or fading of pulp directly counteracts the results of the expensive bleaching operations. Since the bleaching cost per unit brightness increases rapidly as higher brightness values are attained, even a slight amount of yellowing of very bright pulps is disheartening to the producer. Perhaps the most important economic aspect of this subject lies in the relationship of color stability to the creation of new markets for bleached wood pulps. Only in recent years, as bleaching has been more thoroughly developed, have bleached wood pulps been able to compete successfully with rag or cotton pulps for end uses requiring a high degree of strength and color permanence.

Industrially, the bleaching of sulfite pulps has been practiced for about sixty years whereas the successful bleaching of kraft pulps has been developed only within the past thirty-five years. Prior to the realization of the advantages of multi-stage bleaching, it was thought that kraft pulps could never be bleached to a high degree of brightness without serious strength losses. Accordingly, the study of subsequent yellowing of bleached kraft pulps has been less extensive than that of sulfite pulps. Although many marked differences have been recognized between these two major chemical pulps, as yet the opinions concerning their relative color stability are contradictory. For example, one investigator (1) states that sulfite pulps are definitely more stable, while another (2) rates these pulps in reverse order.

The literature on brightness reversion was reviewed thoroughly in 1937 (3) and 1938 (4). Therefore, only the significant papers on this subject concerned primarily with bleached chemical pulps which have been published since that time will be reviewed. The papers published prior to 1938 and those which have appeared since that time are similar in the fact that in both series of articles the yellowing phenomenon has been attributed to nearly every constituent of pulp.

It is generally agreed that alpha-cellulose is the most stable component of bleached wood pulp. However, there is considerable disagreement concerning the major factors responsible for yellowing. Of the various constituents of bleached wood pulp, brightness reversion has been attributed to lignin (5, 6), hemicellulose (3, 6, 7), lignin-hemicellulose complex (8), pentosans (7), "bleach residues" (3, 4, 8, 9), natural resins (2, 3, 5), fats and waxes (5), degraded cellulose (6),

degraded lignin (5, 9), and iron salts (10). Sizing agents (3, 5) and fillers (5) may also contribute to the reversion of paper. The conditions maintained during bleaching have been considered to have a pronounced effect on brightness reversion by virtue of changes in the pulp components. The major factors considered of importance are over-oxidation of carbohydrates (2, 3, 6, 8), incomplete bleaching (6), sequence and conditions of all bleaching stages (11, 12), improper washing (8, 13), and the use of process water with a high iron content (5, 10).

The experimental evidence in support of these beliefs is meager. Although lignin has often been considered a prime factor in yellowing, there are no data to support this viewpoint. In one investigation it was found that the yellowing tendency of a pulp was directly proportional to its pentosan content, but this was not invariably the case (7). Data have previously been presented to demonstrate that the rate of reversion of bleached chemical pulps is directly proportional to the product of the copper number and carboxyl content of the pulp (2); however, the author of that hypothesis has recently stated that carboxyl content has no effect on yellowing and that carbohydrate aldehyde groups alone are responsible for the yellowing phenomenon (14). It seems quite probable that over-oxidation plays an important role in color reversion, but it is undoubtedly an over-simplification to state that yellowing is solely related to the degree of over-oxidation as measured by aldehyde content, carbohydrate content and degree of polymerization. No experimental data have been presented to support the point of view that fats, waxes, or iron salts are responsible for brightness reversion. It has definitely been shown that the natural

resins in bleached pulp contribute slightly to brightness reversion (2, 3); it has also been shown that added rosin sizing can contribute to the yellowing of papers prepared from bleached chemical pulps (3). Incomplete washing has been shown to have only a slight effect on color recession in contrast to the marked differences obtained by using different bleaching agents (13).

It seems improbable that brightness reversion can be directly related to the quantity of any of the pulp constituents which can be determined by conventional methods of analysis. Attempts to study the problem by this method have been unsuccessful for the most part. Other pathways for the resolution of this problem lie in direct chemical analysis of colored material formed, studies of the effects of additives on reversion and interpretation of the reasons for such effects, and the development of an understanding of the chemical and physical nature of the reaction products which are formed during bleaching. Although there is still disagreement among the various investigators concerning the role of lignin in brightness reversion, the complete lack of evidence that it has any effect suggests the probability that it is of less importance than the carbohydrate constituents of bleached chemical pulps. The facts that over-oxidation often correlates with yellowing and that bleaching agents with the mildest action on carbohydrate materials generally produce the most stable pulps is a strong indication that the oxidation of carbohydrates plays some part in this phenomenon. The actual reactions involved during yellowing are, of course, still unknown. The effect of additives on brightness reversion is easily determined, and it is an accepted fact that various paper fillers,

sizing agents, and additives may increase brightness reversion; however, it should be noted that most bleached pulps show a marked yellowing tendency even if additives are not used. It has been shown that the presence of calcium carbonate in very old rag-stock book papers markedly increased color stability (43).

Some data have been obtained concerning the physical chemistry of brightness reversion (3, 4, 15, 16), but these data have not been clearly interpreted. Both heat and ultraviolet light accelerate fading, but the effect of ultraviolet light is complicated by the fact that at higher wavelengths a bleaching reaction can occur (15, 16). Heat, however, in all cases accelerates reversion. This can be attributed to the fact that heat activates the yellowing reactions and/or increases the rate of diffusion of color or color forming materials through the capillary structure of the fiber (4). Others (9) also believe that diffusion is a controlling factor in reversion. It has been shown that the rate of aging is approximately doubled in a pure oxygen atmosphere, but surprisingly the rate is greater in a vacuum than in air! Allegedly this is due to changes in the physical structure of the fiber (3). The color stability of pulp can be increased by the combined action of heat and moisture without the removal of any constituents (4); this is unexplained. At a fixed temperature the reversion rate increases with increasing humidity (3, 4). Since the water to pulp ratio in the sheet is relatively low even at high humidities, it is apparent that the increased reversion is due to increasing quantities of water in the sheet at higher humidities. If, however, pulp were heated in slurry form, then by the law of mass action the slurry concentration should have little or no effect on yellowing

since water would be in great excess for the yellowing reactions which occur.

The fact is evident from the preceding that the problem of brightness reversion is still unsolved. It is impossible for one investigator to study all facets of this problem because of the diversity of variables. For this reason the present study has been limited to a single type bleached slash pine kraft pulp prepared by conventional methods. This choice was based on the rapid growth of the bleached kraft pulp industry in the South. It has been stated that these pulps show a greater yellowing tendency than sulfite pulps. This statement is, of course, difficult to evaluate properly without data representative of these pulps, and no attempt has been made in this study to determine the differences (if any) in the reversion characteristics of these two major bleached chemical wood pulps.

The slash pine wood species chosen for study is representative of the Southern pines (slash, loblolly, longleaf, and shortleaf). Usually mixtures of these wood species are used for the production of both unbleached and bleached pulp. Only a single unbleached kraft pulp was prepared.

Until recently nearly all of the bleached kraft pulp in this country has been produced by a conventional five-stage system utilizing an acid chlorination, a sodium hydroxide extraction, an alkaline calcium hypochlorite bleach, another caustic extraction, and another calcium hypochlorite bleach in that order. Today chlorites, chlorine dioxide, and peroxides are being used to supplement or replace calcium hypochlorite for bleaching since they give pulps of higher original brightness, greater strength, and greater color stability. However,

the bleaching effect obtained with these agents is more expensive than that obtained by the customary calcium hypochlorite, and in this study primary consideration has been given the conventional five-stage bleach.

The first phase of this study was the development of reproducible bleaching techniques. This was done for two purposes: (1) to permit an accurate evaluation of the effect of the various bleaching variables on brightness reversion and (2) to provide a bleached pulp for study whose history was known. The use of a commercial bleached pulp would not have successfully met either of these requirements. The interpretation of the effect of bleaching variables on brightness reversion is, of course, hampered by our limited understanding at the present time of bleaching reactions. Much fundamental work remains to be done in this field.

Only brightness reversion accelerated by heat was studied in this work. The correlation between such yellowing and that occurring on natural aging has been poor (4), but since heat is used in processing pulps and papers, in drying, sterilization, and various conversion methods, such a study is well justified.

An attempt has been made to determine the causes of reversion in bleached kraft pulp, and to evolve a better understanding of this phenomenon. One approach to this problem has been the isolation of a brown-colored component of aged pulp and the subsequent determination of its characteristics in an effort to ascertain the constituent of the pulp responsible for yellowing and the mechanism by which it darkens. A vast amount of work has been done on other unknown brown or yellow materials (melanoidins or humins), but as yet these materials have not

been clearly defined (17). However, it is believed that only when such work has been completed will the problem of brightness reversion be solved. Another general approach has been the study of the yellowing of isolated pulp components. Such an approach is naturally hampered by the difficulty in obtaining a "pure" unaltered pulp constituent.

The content of this study can be described by five general headings:

1. The effect of bleaching variables on brightness reversion,
2. The yellowing characteristics of the various fiber length fractions of bleached pulp,
3. The effect of additives on reversion,
4. A study of the yellowing of hemicelluloses, and
5. A study of a water-soluble dark-brown material formed during the accelerated aging of bleached pulp.

PRESENTATION OF THE PROBLEM

The purpose of this investigation was to obtain a better understanding of the brightness reversion which occurs when bleached kraft pulp is heated. The principle considerations have been to determine the conditions of bleaching, or pulp treatment, which promote or retard brightness reversion and also to learn which component, or components, of bleached chemical wood pulp are primarily responsible for this yellowing phenomenon.

Presumably this loss of brightness is due to chemical decomposition of one or more of the minor components of pulp with concurrent color formation. Previous attempts to correlate the extent of yellowing with any of the chemical constituents of pulp have been unsuccessful. It is important to realize that only a small, and not necessarily constant, fraction of any of the typical components, such as hemicellulose, lignin, pentosans, or extractives, of pulp may, by virtue of its instability, be responsible for yellowing. In such a case, obviously, direct quantitative analyses of the individual components would not be expected to correlate with reversion.

A portion of the color formed during the yellowing of chemical pulps is known to be water soluble. Since most pulp constituents are virtually water insoluble, water extraction provides a means of isolating at least a portion of the colored component in a relatively concentrated form. The direct analysis of this colored extract coupled with physical and chemical comparisons with the color which could be formed from relatively pure individual pulp constituents seemed to offer a sound approach to this problem and was therefore undertaken.

The initial phase of the program was the development of reproducible bleaching techniques to produce 80 to 85% G.E. brightness pulps since it was postulated that such relatively completely bleached pulps would exhibit a consistent reversion rate and that then the effect of deliberate variations in the bleaching procedures on brightness reversion could be measured. Such data were expected to demonstrate the optimum bleaching conditions for the production of stable pulps, and also it was expected that the known actions of the bleaching agents and their relationship to reversion could then be interpreted.

From the alleged difference in chemical composition and the apparent difference in the physical nature of short and long pulp fibers it seemed probable that studies of the reversion rates of pulp fractions based on fiber length would offer some insight into the actual factors involved in pulp yellowing.

Conjectures have been made concerning the role of ash and the metallic contaminants of pulp in yellowing, but the actual effect of such constituents on yellowing has never been demonstrated. Therefore, it was planned to study this problem both by the removal or complexing of ash constituents and also by their deliberate addition.

The studies which were undertaken are to a limited extent complete in themselves, but constitute only a portion of the work necessary to provide a complete understanding of the yellowing of bleached kraft pulps.

STANDARD METHODS AND MATERIALS

UNBLEACHED PULP

All experimental work was conducted with a single lot of unbleached slash pine kraft pulp which was prepared in a laboratory digester under conditions similar to those used in commercial practice. This pulp was shown to be truly representative by the comparison of its bleachability with two commercial kraft pulps and also by the analytical determination of its permanganate number and lignin content.

BLEACHING CHEMICALS

Only c.p. chemicals were used in all bleaches to prevent the introduction of iron or other contaminants. Calcium hypochlorite solution was prepared from chlorine water and calcium hydroxide immediately before using; any undissolved calcium hydroxide was removed by filtration. The total available chlorine concentrations of all bleach liquors were determined by Institute Method 112. Filtered tap water was used for the high-consistency bleaches, but distilled water was used for all low-consistency bleaches.

BLEACHING

HIGH-CONSISTENCY

In order to prepare 750 to 1500 grams of bleached pulp, the bleaching stages were conducted under the conditions shown in Table I which are similar to those used commercially. These conditions became the standard after experimental work demonstrated that they would result in an 80 to 85% G.E. brightness pulp.

TABLE I
CONDITIONS FOR HIGH-CONSISTENCY BLEACHING

Treatment	Chemical Added (Pulp Basis), %	Consist- ency, %	Temper- ature, °C.	Time, min.	pH
Chlorination (C)	6.00	3.0	23 \pm 2	60	--
Caustic extraction (E)	2.50	10.0	60 \pm 5	60	--
Calcium hypochlorite (H)	1.50 ¹	5.0	40 \pm 0.5	240	9.5-8.5
Caustic extraction (E)	0.75	10.0	50 \pm 5	120	--
Calcium hypochlorite (H)	0.50 ¹	5.0	40 \pm 0.5	240	9.5-8.5

¹Expressed as chlorine

The chlorination was carried out in a rubber-lined vessel fitted with a draft tube and a stainless steel propeller for agitation. Chlorine was added in the form of freshly prepared chlorine water, the concentration of which was determined by titration. At the conclusion of the chlorination the pulp was washed on a cloth drain box until the washings were neutral and free of chlorine.

The caustic extraction was conducted in a Pfaudler glass-lined mixer heated by water circulating through a jacket. The pulp and caustic solution were mixed thoroughly at the beginning of the extraction stage and were stirred frequently. This stage was concluded by washing the pulp on a cloth drain box until the washings were essentially colorless and at the same pH as the wash water. The tap water used for high-consistency bleaching had a pH value of about 9.

Earthenware crocks heated in a constant temperature bath were used for the hypochlorite stage. The pulp slurry was stirred manually.

The pH was checked frequently with a Beckman glass electrode pH meter and was maintained at 9.5-8.5 by the addition of small amounts of sodium hydroxide solution. At the conclusion of the hypochlorite stage the pulp was washed for about 45 minutes on a cloth drain box with a water flow rate of 5 to 10 gal. per min. It was then soaked overnight at 1% consistency, and the bleaching sequence was continued on the next day.

The second caustic extraction stage was carried out in the same manner as the first extraction, and the second hypochlorite stage was also similar to the first. After the CEHEH pulp had been soaked at 1% consistency overnight, it was again washed thoroughly, filtered on a Buchner funnel, and stored at 25 to 35% consistency in polyethylene bags at 9°C.

LOW-CONSISTENCY

For the preparation of 10 to 20 grams of pulp the bleaching stages were conducted at 1% consistency. This low consistency was necessary for the efficient handling and agitation of these small quantities of pulp. The conditions maintained are shown in Table II.

The percentage sodium hydroxide used in the caustic extraction stages of the low-consistency bleaches was increased over that for the high-consistency bleaches in order to give the same concentration of caustic in solution in both cases. No adjustment was made for the concentration of calcium hypochlorite in the low-consistency bleaches and this resulted in slightly lower chlorine consumption.

TABLE II
CONDITIONS FOR LOW-CONSISTENCY BLEACHING

Treatment	Chemical Added (Pulp Basis), %	Consist- ency, %	Temper- ature, °C.	Time, min.	pH
Chlorination (C)	6.50	1.00	23 ± 2	60	--
Caustic extraction (E)	25.0	1.00	55 ± 0.5	60	9.5-8.5
Calcium hypochlorite (H)	1.50^1	1.00	40 ± 0.5	240	--
Caustic extraction (E)	7.85	1.00	50 ± 0.5	30	9.5-8.5
Calcium hypochlorite (H)	0.50^1	1.00	40 ± 0.5	240	--

¹Expressed as chlorine

All stages were conducted in two-liter brown-glass stock bottles. Continuous agitation was maintained for thorough mixing but at a slow rate to prevent "beating" of the fibers. The reaction bottles were immersed in a constant temperature bath for temperature control.

At the conclusion of each reaction stage the pulp was filtered on a 10 cm., medium porosity, sintered-glass Buchner funnel and was washed thoroughly with distilled water. During the hypochlorite stages the pH was maintained at 9.5 to 8.5 by the addition of small amounts of sodium hydroxide solution. After a thorough washing following the second hypochlorite stage, the pulp was soaked in water overnight at 1% consistency; it was then again washed thoroughly, diluted to 0.1% consistency, and made into brightness handsheets.

SHEET FORMATION

Brightness sheets were prepared according to Institute Method 412 with the following modifications: The pulp slurry was filtered on three sheets of 15-cm. filter paper instead of one to prevent the brightness sheet from conforming to the holes in the Buchner funnel. After pressing five minutes at 50 p.s.i., the three sheets of 15-cm. filter paper were replaced with one sheet of 18.5 cm. filter paper, and the sheets were again pressed at 50 p.s.i. for one minute. After air drying for three to four hours, each sheet was cut into four-two inch squares and a 1/4-in. hole was punched on one side so that each square could be suspended from a glass rod. The squares were then evenly spaced along the rod and placed approximately in the center of the aging oven.

ACCELERATED AGING

For the accelerated aging of the brightness sheets a CENCO electric oven was used which was cylindrical, 15 in. in diameter by 12 in. deep. The oven temperature cycled over a 2°C. range at 100°C. and completed a cycle in approximately five minutes.

Air was passed through a preheater composed of 6-mm. glass tubing wound with nichrome wire and asbestos insulation before it entered the oven. By adjusting a voltage regulator the air could be preheated to any desired temperature. This prohibited moisture condensation during aging runs made at various relative humidities. To obtain a relative humidity of approximately 0%, the air was first passed through a tube filled with anhydrous calcium chloride.

Unless otherwise specified, all accelerated aging was carried out at 100°C. and essentially 0% relative humidity for two hours.

REFLECTANCE MEASUREMENTS

All brightness measurements were made by means of a General Electric reflection meter which was in agreement with the master instrument located at The Institute of Paper Chemistry. A pad of 16 squares was used for each brightness value, and one reading was made for each sheet. The procedure differed from TAPPI Standard T 452 m-48 only in the number of readings made.

DETERMINATION OF REVERSION RATE

The numerical value of the extent of brightness reversion is expressed as $\Delta k/s \times 10^4$. The relationship between reflectivity and k/s developed by Kubelka and Munk has been presented by Steele (18). This relationship is:

$$k/s = (1 - R_{\infty})^2 / 2R_{\infty}$$

k = the absorption coefficient of the sheet

s = the scattering coefficient of the sheet

R_{∞} = the reflectivity of the pad of paper expressed
decimally against magnesium carbonate considered
as 0.98.

The number s is considered to be nearly constant throughout the course of aging (3), so that the change in k/s , $\Delta k/s$, expressed the change in the light absorption capacity of the sheet.

In their studies of the brightness reversion of sulfite pulps, Tongren (3) and McIntyre (4) expressed the rate of reversion as the slope of the graph of k/s versus the square root of the aging time

since this relationship was nearly linear. In this dissertation the measure of discoloration is not expressed in this manner since the relationship was found to be nonlinear for the aging conditions used. The standard reversion is expressed as the increase in k/s , $\Delta k/s$, for an aging time of two hours at 100°C . and 0% relative humidity.

EXPERIMENTAL RESULTS AND DISCUSSION

PREPARATION OF UNBLEACHED PULP

In order to have a uniform pulp supply of known history, a single lot of approximately fifty pounds of an unbleached kraft pulp was prepared in the following manner:

Four four-foot slash pine logs of 10-in. diameter were obtained from the Savannah, Georgia area. These logs were barked with a hand draw-knife and were then reduced to half-inch chips with a Carthage semicommercial chipper. Fine material was removed by screening the chips on a 0.25-in. wire screen; knots, slivers, and oversize chips were removed by hand. The moisture content was 43.0%.

One hundred and five pounds (ovendry basis) of these chips were pulped in an A. O. Smith stainless steel-lined tumbling digester under the conditions, and with the results, given in table III.

The pulping conditions, yield, and analytical constants all show the product to be a typical, bleachable grade of slash pine kraft pulp, hence suitable for this study. The screened, unbleached pulp was stored at 30 to 35% consistency in polyethylene bags in a room held at about 9°C.

REPRODUCIBILITY OF BRIGHTNESS AND REVERSION RATE DATA

The reproducibility of brightness and reversion rate data was determined to ascertain the number of replicate bleaches and brightness readings necessary to obtain reliable data.

TABLE III

PULPING DATA

Charge	47.5 kg.
Liquor/wood ratio	4.5 ml./g.
Active alkali [NaOH + Na ₂ S (as Na ₂ O)]	20%
Sulfidity [Na ₂ S/NaOH + Na ₂ S all as Na ₂ O]	20%
Maximum temperature (false pressure relieved at 100°C.)	170°C.
Time to maximum temperature	2 hr.
Time at maximum temperature	2 hr.
Pressure at blow-down	80 p.s.i.
Screenings	0.18%
Yield	<u>ca.</u> 50%
Permanganate number (Institute Method 410)	17.1%
Lignin content (Institute Method 428)	4.2%
Original brightness, G.E.	22.3%

In each instance of obtaining a brightness value, readings were obtained for each of 16 brightness tabs cut from four brightness handsheets prepared from a single pulp. A typical group of readings is tabulated herewith:

TABLE IV

% G.E. BRIGHTNESS, PULP 130

84.7	84.7	85.6	85.1
85.1	84.9	85.4	84.4
85.4	84.8	85.2	84.9
85.7	85.8	85.7	85.5

Average 85.2

The brightness readings obtained throughout this study were, in general, as precise, or more precise than this series. By application of Student's "t" distribution (19), it was shown that the 80% confidence interval for these readings was $85.2^{+.09}$ and the 95% confidence interval was $85.2^{+.18}$.

No attempt was made initially to ascertain or improve the reproducibility of the brightness or reversion data for pulps bleached at high consistency, since comparisons were not to be made for different pulps prepared in this manner. It was found at the conclusion of the work, however, that the reproducibility of data for the high-consistency bleaches was in general better than that for the low-consistency bleaches. Some attention was given to the effect of bleaching variables on original brightness and brightness reversion in the low-consistency bleaches, and therefore the reproducibility of this type data was determined before proceeding with studies of bleaching variables.

A series of nine low-consistency bleaches was made with three bleaches run per day on three consecutive days. A summary of these bleaches is given in Table V.

TABLE V

REPRODUCIBILITY OF LABORATORY BLEACHING

Pulp number	Group A			Group B			Group C			Average 155-157	
	149	150	151	Average 149-151	152	153	154	Average 152-154	155		156
Chlorine consumed, %											
Chlorination	4.72	4.75	4.82	4.76	4.84	4.87	4.83	4.85	4.84	4.69	4.75
1st Hypo-chlorite	1.23	1.19	1.18	1.20	1.18	1.18	1.18	1.18	1.16	1.17	1.18
2nd Hypo-chlorite	.26	.25	.26	.26	.28	.28	.28	.28	.26	.27	.27
Total	6.21	6.20	6.26	6.22	6.30	6.23	6.29	6.27	6.26	6.13	6.20
Original Brightness, % G.E.	80.2	80.2	80.1	80.2	80.6	81.2	81.5	81.1	82.1	82.3	81.7
$\Delta k/s \times 10^4$	303	300	307	303	257	264	243	254	250	271	272

For bleaches made simultaneously the original brightness values agree within several tenths of a point and there is a spread of less than 8% of the $\Delta k/s \times 10^4$ value. However, the average reversion values for bleaches conducted on different days had a maximum spread of 18%; consequently, for all work in which bleaching or processing variables were studied, duplicate bleaches were made for each condition, and the various bleaches in a given set were made simultaneously.

ACCELERATED AGING

EFFECT OF TEMPERATURE AND HUMIDITY

It has been stated that an increase of either temperature or relative humidity increases the rate of brightness reversion, that the relationship between the reversion rate ($\Delta k/s$) and humidity is approximately linear between 25 and 90% R.H., and that the logarithm of $\Delta k/s$ bears a linear relationship to the aging temperature (4). For these reasons it has been suggested (4) that accelerated aging should be conducted at 95°C. and 55% R.H. to obtain the best possible correlation with natural yellowing.

In this work the effects of temperature and humidity on the reversion rates of bleached kraft pulps were determined in order: (1) to detect similarities or dissimilarities in the comparative yellowing rates of bleached kraft pulps and bleached sulfite pulps, and (2) to ascertain the possible advantages of determining accelerated reversion at any particular relative humidity.

The equipment used for this study has been described previously (3). The various relative humidities were obtained by adjustment of

the saturator temperature. The saturator temperature (T_2) needed for a given % R.H. was calculated by multiplying the saturated vapor pressure (p_1) at the aging temperature (T_1) used by the % R.H. to obtain a new saturated vapor pressure (p_2). The temperature (T_2) corresponding to this saturated vapor pressure (p_2) was then determined from steam tables. The saturator temperature was controlled within $\pm 0.1^\circ\text{C}$.

Five bleached pulps were used—three laboratory prepared kraft pulps, a commercial Mitscherlich spruce pulp, and a commercial sulfite mixed hemlock and spruce pulp with original brightness values of 81.6, 84.3, 84.5, 80.5, and 87.0, respectively.

The kraft pulps were prepared by common chlorination, first caustic extraction-, and first hypochlorite stages of 750 grams of pulp. The pulp was then divided into three equal portions and second caustic extractions of 0, 1, and 4 hours were conducted before the final hypochlorite stage. The data for these bleaches (170-A, 170-B, 170-C) are given in the Appendix.

Handsheets prepared from these five pulps were aged simultaneously for two hour periods at 100°C . and relative humidities from 0 to 68%. The reversion data for these pulps are presented in Table VI and in graphical form in Figure 1.

If the data for bleached slash pine kraft pulps 170-B and 170-C are recalculated as percentages of the reversion rate of pulp 170-A, assuming it to be 100% for all humidity intervals, it can be seen from Table VII that these percentages are constant throughout the humidity range studied.

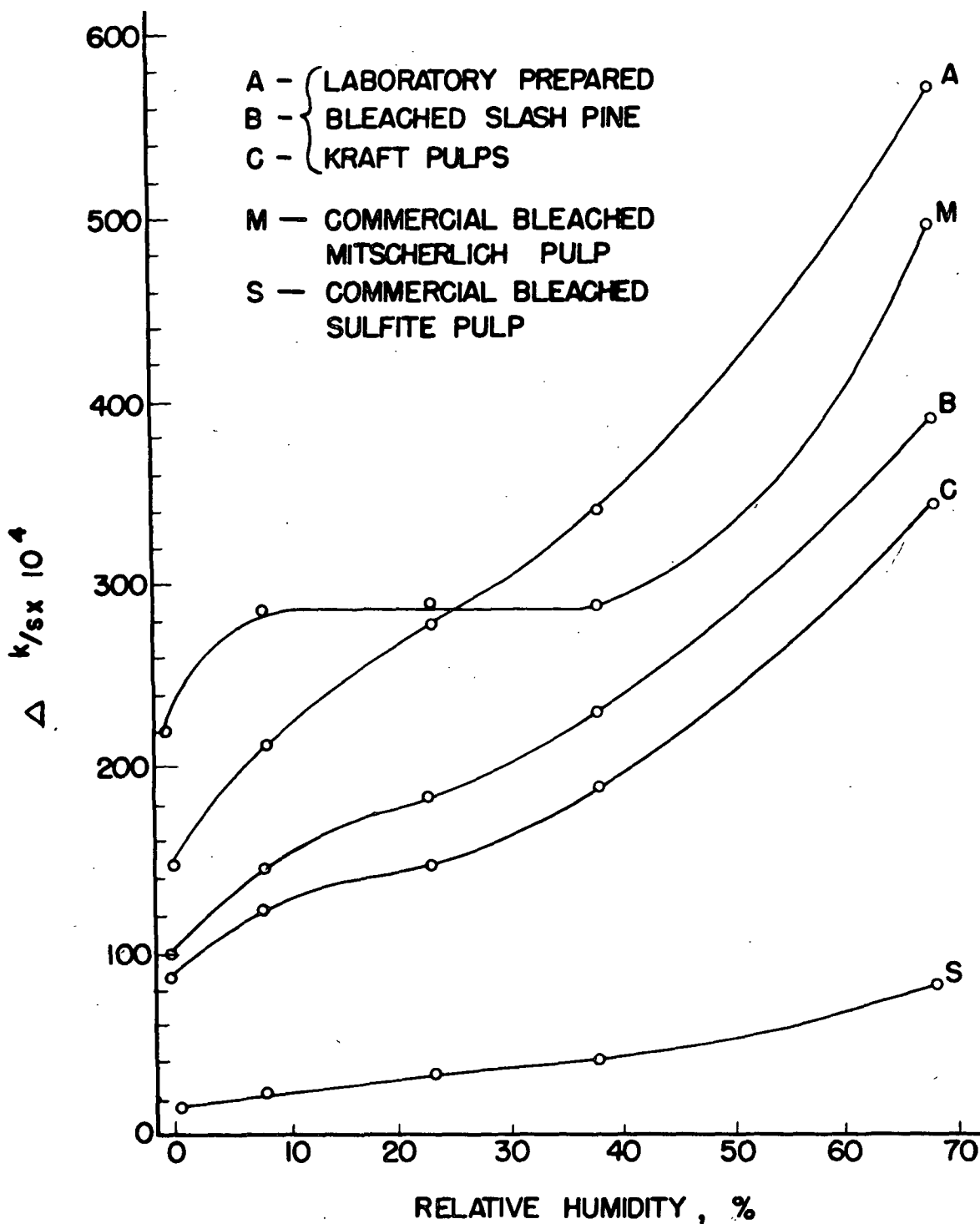


Figure 1

Pulps Aged at 100°C. for 2 Hours at Various Relative Humidities

TABLE VI

EFFECT OF HUMIDITY ON REVERSION

$\Delta k/s \times 10^4$ Values

R.H., %	170-A	170-B	170-C	Mitscherlich	Sulfite
0	149	97	83	217	13
8.5	212	146	122	286	23
22.6	275	183	147	290	34
37.3	339	229	190	286	40
68.2	568	388	342	494	78

TABLE VII

RATIOS OF REVERSION RATES OF THREE KRAFT PULPS

R.H., %	170-A	170-B	170-C
0	100%	67%	59%
8.5	100	69	58
22.6	100	67	54
37.3	100	68	56
68.2	100	<u>68</u>	<u>60</u>
	Average	68 \pm 1	57 \pm 2

This fact is significant since it shows that there can be no possibility of better correlation with natural aging on aging at any particular relative humidity since the pulps are rated in an identical manner throughout the range. However, accelerated aging at essentially 0% R.H. is advantageous from the standpoint of easy humidity control,

while high humidity aging conditions would be advantageous in the reduced length of time required to obtain a given $\Delta k/s$ value.

The marked difference in the shape of the curves for the Mitscherlich and kraft pulps presents an obvious difficulty in rating the stability of different type pulps; at humidities on either side of the intersection of these curves, these pulps would be rated in reverse order.

METHOD OF EXPRESSING REVERSION RATE

Previous investigators (2, 4) have expressed the reversion rates of the pulps which they studied as the slope of the curve k/s versus the square root of time, since it was observed (3) that this graph is approximately linear.

Graphs were prepared in this manner for the reversion data of slash pine kraft pulps aged at 100°C. and 0% relative humidity and were found to be nonlinear. Since Tongren (3) observed this relationship with sulfite pulps, the possibility existed that sulfite and sulfate pulps differ in this respect and therefore aging curves were obtained for a laboratory slash pine kraft pulp, a commercial sulfite pulp, and a commercial Mitscherlich.

For the particular aging conditions used none of the curves of k/s versus the square root of aging time in Figure 2 are linear. There would be an advantage in expressing the reversion rate as $\Delta k/s$ divided by $\Delta \sqrt{\text{aging time}}$ only if this relationship were strictly linear since in such a case any deviations of the points from a straight line would point

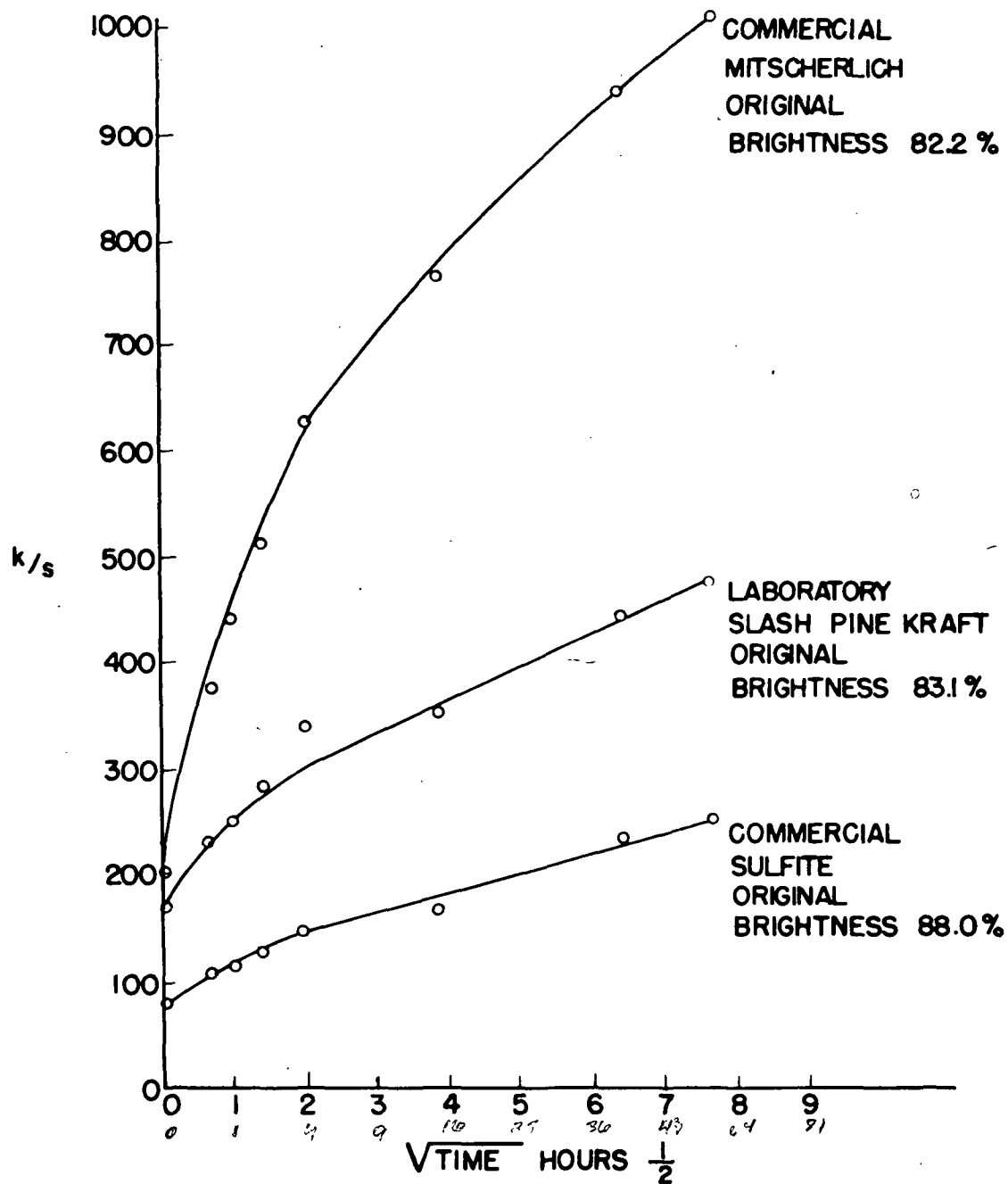


Figure 2

k/s Versus $\sqrt{\text{Time}}$ Aged at 100°C.--0% R.H.

to experimental error. For this reason, in this dissertation yellowing is expressed not as the reversion rate but rather as the extent of reversion; as standard procedure the $\Delta k/s$ values reported in this study are the increases in k/s which occurred when the brightness sheets were heated for two hours at 100°C. and essentially 0% R.H.

EXTENDED AGING AND REVERSION

For some of the sulfite pulp samples which he studied, McIntyre (4) found that the k/s versus square root of aging time relationship was nonlinear after about nine hours. This raises the important question of the progress of yellowing on extended aging. That is, does yellowing diminish or cease after a certain low brightness value is reached. This would be the case if the quantity of color precursors were limited and of sufficient amount to cause only incomplete yellowing.

In order to determine the effect of extended aging on yellowing, a set of brightness sheets prepared from Pulp 170-A was autoclaved at 120°C. and 100% R.H. for a total time of 155 hours. The brightness values obtained on aging are shown in Table VIII.

Aging was stopped after 155 hours since yellowing was continuing even as the original brightness, 22.3%, of the unbleached kraft pulp was approached. Thus, it is apparent that for such a system of accelerated aging the quantity of color precursors present cannot be considered as limited. It may well be that even highly stable pulp components, such as alpha-cellulose, yellow as this drastic treatment is continued since it is known that cotton becomes brown as it is steamed (44).

TABLE VIII

EXTENT OF YELLOWING ON PROLONGED HEATING

Time, hr.	Brightness, % G.E.	k/s x 10 ⁴
0	84.5	142
1	65.3	922
4	58.7	1453
5	50.6	2411
62-1/4	44.8	3401
155	31.2	7586

BLEACHING VARIABLES AND RATE OF REVERSION

WASHING

The washing operation at the conclusion of the five bleaching stages removes both inorganic and organic materials. These "bleach residues" allegedly consist of ash, low molecular weight carbohydrates, carbohydrate degradation products, and lignin degradation products, all of which have been considered as causes of subsequent yellowing after the bleaching operation; therefore, washing studies were conducted both to understand the relationship of washing to yellowing and also to aid in the development of a reproducible laboratory bleaching technique. Only distilled water washing has been considered; soaking and washing with acidic solutions has not.

Some criterion of the thoroughness or degree of washing was needed and in this study the relative amounts of carbohydrates present in the wash liquors were determined by colorimetry. Some of the various agents

which have been used for such a determination are phenol, orcinol, resorcinol, phloroglucinol, alpha-naphthol, picric acid, and anthrone (20, 21). In this instance orcinol was chosen.

It was necessary to completely remove all pulp fibers from the filtrate since they could cause large errors in the determination. Twenty-five milliliters of cold 90% sulfuric acid and 2 ml. of orcinol solution (0.200% orcinol in absolute ethanol) were slowly added to 10 ml. of chilled filtrate in a 100-ml. test tube. The mixture was agitated by pouring back and forth into another test tube, and it was then heated for twenty minutes in a boiling water bath. It was found that color formation due to the presence of carbohydrates was complete after this interval. The solution was then cooled and the 425 to 430-m μ minimum transmittance value was then determined with the General Electric recording spectrophotometer using a blank of distilled water treated in this same manner. It was shown that the color formed obeyed Beer's Law at the concentrations used. This test procedure gave a transmittance value of 66.4% or an optical density of 0.177 for 0.01% solution of glucose.

All washing studies were begun immediately after the conclusion of the second hypochlorite bleaching stage since in this manner the effect of diffusion could be detected. The pulps were stored at 9°C. between filtrations to inhibit bacterial attack. The bleached pulps used were Nos. 146, 147, and 148. Only data for the filtrates were obtained for pulp 146, but both brightness and reversion data also were obtained for pulps 147 and 148. The bleaching data for these pulps are tabulated in the Appendix.

Immediately after completion of bleach 146, the pulp was filtered to give filtrate 1 and was then successively soaked five minutes at 1% consistency and 40°C. before filtering to give filtrates 2, 3, 4, and 5. For the next six days the 1% slurry was stored at 9°C. and filtered once each day to give filtrates 6 through 11. Distilled water was added after each filtration. On the sixth day of soaking the pulp was again washed with 40°C. water at 1% consistency for six additional times to give filtrates 12 through 17. The transmittance data for the carbohydrate tests on these filtrates are shown in Table IX.

TABLE IX

SOLUBLE CARBOHYDRATE REMOVAL DURING WASHING

Days After Bleach	Filtrate No.	Trans- mittance, %	Log 1/T	Days After Bleach	Filtrate No.	Trans- mittance, %	Log 1/T
0	1	62.4	.205	5	10	75.5	.121
0	2	76.5	.116	6	11	89.4	.048
0	3	81.7	.087	6	12	92.0	.035
0	4	81.7	.087	6	13	93.2	.029
0	5	80.7	.092	6	14	93.2	.029
1	6	46.0	.336	6	15	91.5	.038
2	7	56.0	.251	6	16	94.4	.025
3	8	64.8	.187	6	17	94.4	.025
4	9	69.3	.158				

These data show that an equilibrium was reached in washing liquor concentration after about three washes both immediately after the bleach and also after six days soaking. Although the concentration of material in the washings (directly proportional to $\log 1/T$) diminishes rapidly on continued soaking, it does not reach zero and materials are still dissolving out after the six-day period.

On the basis of the data for Pulp 146, Pulps 147 and 148 were given three successive washes on each of several days. Immediately after bleaching, washing was done at 1% consistency and 40°C. and on succeeding days at 1% consistency and room temperature. The colorimetric orcinol test was applied to only the first of the three filtrates obtained each day. Brightness and reversion data were also obtained and are given in Table X and presented graphically in Figure 3.

TABLE X

EFFECT OF WASHING ON BRIGHTNESS AND REVERSION

Time, days	Brightness, % G.E.		Standard $\Delta k/s \times 10^4$		Colorimetric Orcinol Test, $\log 1/T$ at 425-430 mmu	
	Pulp 147	Pulp 148	Pulp 147	Pulp 148	Pulp 147	Pulp 148
0 ¹	80.7	80.8	182	246	.135	.111
1	82.1	79.1	177	245	.169	.211
4	81.0	79.0	186	218	.038	.054
7	81.4	79.4	155	208	.031	.032
11	81.0	79.1	161	208	.028	.016

¹Initial filtrate

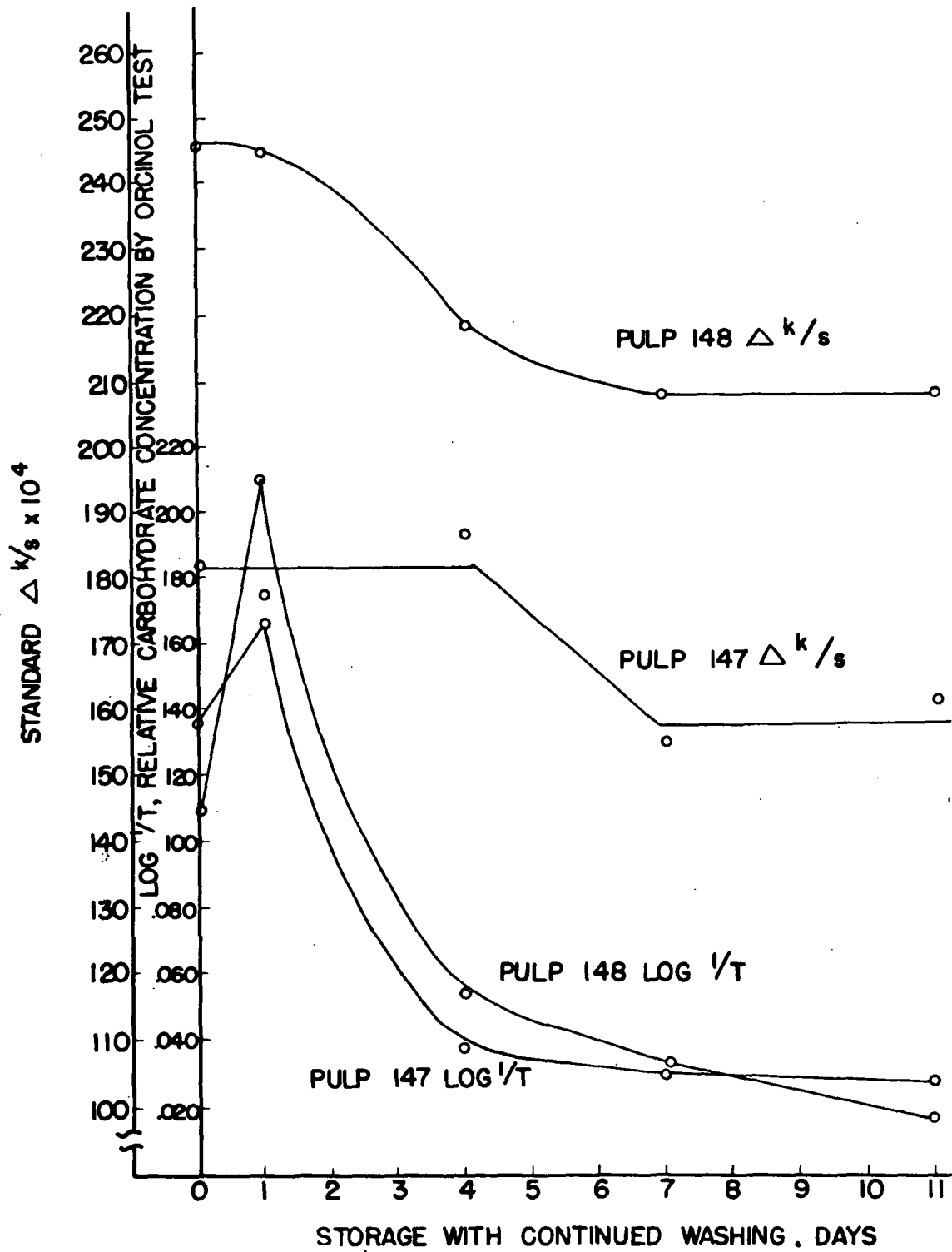


Figure 3

Carbohydrate Concentrations of Filtrates From Washings
and Effect of Washing on Reversion Rate

These data show that there is a definite lowering and stabilizing of the reversion tendency after thorough washing of bleached pulp. The diffusion of constituents from within the fiber is relatively slow and therefore several days are necessary for complete pulp washing. Although this indicates that $\Delta k/s$ depends on the degree of washing, from the standpoint of comparing bleaches reproducible data can be obtained if the brightness sheets are formed soon after the pulp is bleached. The procedure adopted was to wash the pulp thoroughly after the second hypochlorite stage, allow it to soak overnight, and again wash it thoroughly the following morning prior to the preparation of brightness handsheets.

HYPOCHLORITE STAGE pH

The equilibrium mixture of chlorine, hypochlorous acid, and the hypochlorite ion is known to be affected markedly by pH. At low pH chlorine predominates, at neutrality hypochlorous acid predominates, and at high pH the hypochlorite ion is the major component. Obviously then the bleaching reactions involved at different pH values are not identical. It has been observed that during hypochlorite bleaching of cotton cellulose, carbohydrate oxidation increases as neutrality is approached (22). In a study of the bleaching of sulfite pulp it has been shown (2) that reversion also increases if hypochlorite bleaching is done under neutral rather than alkaline conditions. The present study was conducted to determine the degree of color stability attainable by highly alkaline hypochlorite bleaching.

Two series of bleaches, 131, 133, 134, 136, and 137 through 145 were carried out to study this effect. The pH was varied in both hypochlorite stages of the individual bleaches of the first series but only in the second hypochlorite stages for the latter series.

Chlorine consumptions for bleaches 131, 133, 134, and 136 are given in the Appendix but other pertinent data are tabulated in Table XI. The initial pH values recorded are the pH readings taken five minutes after the addition of the calcium hypochlorite solution since the pH changes rapidly during this period. No buffering agent or additional base was added to the slurries during the course of the bleach. Brightness sheets were aged for one hour at 100°C., 0% R.H.

TABLE XI

EFFECT OF pH OF HYPOCHLORITE STAGE ON REVERSION

	Bleach No.			
	133	134	131	136
1st Hypochlorite				
Initial pH	9.5	9.1	8.1	6.7
Final pH	8.1	7.2	6.8	5.3
Arithmetic average pH	8.9	8.2	7.4	6.0
2nd Hypochlorite				
Initial pH	9.8	9.4	8.2	6.3
Final pH	8.9	8.5	7.7	5.8
Arithmetic average pH	9.3	8.9	7.9	6.0
Average pH both H stages	9.1	8.5	7.7	6.0
Original brightness, % G.E.	80.6	81.2	81.9	80.2
$\Delta k/s \times 10^4$	134	144	147	175

A definite increase in reversion rate occurred as the pulp was bleached at lower pH values.

For duplication of this effect the pH was varied in the second hypochlorite stages of bleaches 137 through 145. Inadvertently, the consistency of the chlorination stage was 1.67% instead of 1%, resulting in high chlorine consumption (6.2%) for this stage and low chlorine consumption (0.28%) for the first hypochlorite stage. The bleaching data are given in the Appendix and the pH and reversion data are tabulated in Table XII.

TABLE XII

EFFECT OF pH OF HYPOCHLORITE STAGE ON REVERSION

	Bleach No.								
	137	138	139	140	141	142	143	144	145
2nd Hypochlorite									
Initial pH	10.6	10.0	9.5	8.9	8.5	8.0	7.5	7.0	6.5
Final pH	10.5	9.6	8.6	8.3	8.0	7.6	7.1	6.6	6.0
Arithmetic av.	10.5	9.8	9.0	8.6	8.2	7.8	7.3	6.8	6.2
Original bright- ness, % G.E.	82.3	82.6	82.6	83.3	83.2	83.7	83.2	82.9	82.6
Standard Δk/s x 10 ⁴	143	153	150	156	160	164	163	174	185

It can be seen that the reversion rate increases if the pH of the second hypochlorite stage or of both hypochlorite stages is decreased toward neutrality. The reduction in $\Delta k/s$, obtained by bleaching at pH 10 instead of pH 6, is about 20%; therefore, it is apparent that although yellowing can be minimized by bleaching at high pH it cannot

be prevented. It is probable that carbohydrate oxidation is to some degree responsible for the yellowing of pulp. It is interesting to note that for both series of bleaches the maximum brightnesses were obtained for hypochlorite stage pH of 8 to 7.

CONSISTENCY

Experimental bleaches were conducted at low consistency (1%) and high consistency (3 to 10%) for the preparation of 10 to 20 grams and 750 to 1500 grams of pulp, respectively. (See Standard Methods.) There were two major differences other than consistency for these bleaches: (1) The total chlorine consumption was higher in the high-consistency bleaches. (2) The duration of the second caustic extraction stage was two hours for the high-consistency bleaches, but only one-half hour for low-consistency bleaches. The lower chlorine consumption at low consistency was due to the effect of concentration while the extraction time was intentionally reduced since it was thought that at the relatively high dilution the extraction would proceed more rapidly.

Standard $\Delta k/s \times 10^4$ values were about 270 for the low-consistency bleaches while only 130 for the high-consistency bleaches. In order to determine the cause for this, the effect of consistency was first eliminated by preparing triplicate low-consistency bleaches 166, 167, and 168 which differed from the standard low-consistency bleaches in the fact that the chlorine consumptions and all other variables except consistency were held as closely as possible to the conditions for high-consistency bleach 165. The data for these four bleaches are given in Table XIII.

TABLE XIII

EFFECT OF BLEACHING CONSISTENCY ON REVERSION

	High consistency	Low Consistency		
Bleach No. - -	165	166	167	168
Chlorine consumed, %				
Chlorination	5.35	5.39	5.36	5.42
1st Hypochlorite	1.38	1.35	1.42	1.43
2nd Hypochlorite	.29	.17	.20	.21
Total	7.02	6.91	6.98	7.06
Original brightness, % G.E.	84.0	82.8	83.8	82.6
Standard $\Delta k/s \times 10^4$	127	141	128	157

The consistency of these bleaches evidently has no effect on reversion. This is of course applicable only to the range studied. The consistency of the hypochlorite stages was 1% for Bleaches 166 to 168 and 5% for Bleach 165. It has recently been shown that a very pronounced increase in reversion occurs as the consistency of the hypochlorite stage for sulfite pulps is increased from 3 to 12% (23). Although this investigator did not report the degree of process control maintained at the various consistencies, it is probable that localized overbleaching and underbleaching, uneven pH, and poor temperature distribution at the higher consistency were the causes of the lower stability.

SECOND CAUSTIC EXTRACTION STAGE

The effect of the duration of the second caustic extraction was determined since it has been shown (9) that diffusion of materials

from within the fiber during this stage is relatively slow. Low-consistency bleach 169 was carried out using 100 grams which was divided after the first hypochlorite stage into two equal portions for individual bleaching. Duplicate bleaches were made for 0, 1/2, 1, and 2 hours of caustic extraction with a single bleach for the 3-hour extraction. The data for these bleaches are given in Table XIV and are presented graphically in Figure 4.

TABLE XIV

VARIATIONS IN DURATION OF SECOND CAUSTIC EXTRACTION

Bleach No.	Duration of 2nd Caustic Extraction, Hr.	Chlorine Con- sumed, 2nd Hypochlorite, %	Original Brightness, % G.E.	Standard $\Delta k/s \times 10^4$
			Av.	Av.
169-1	0	0.24	77.0	243
169-2	0	0.23	76.9	236
		0.23	76.9	239
169-3	1/2	0.23	78.5	246
169-4	1/2	0.23	78.1	201
		0.23	78.3	223
169-5	1	0.24	78.5	210
169-6	1	0.24	78.7	207
		0.24	78.6	208
169-7	2	0.24	78.7	165
169-8	2	0.23	79.0	182
		0.23	78.9	173
169-9	3	0.24	79.0	165
		0.24	79.0	165

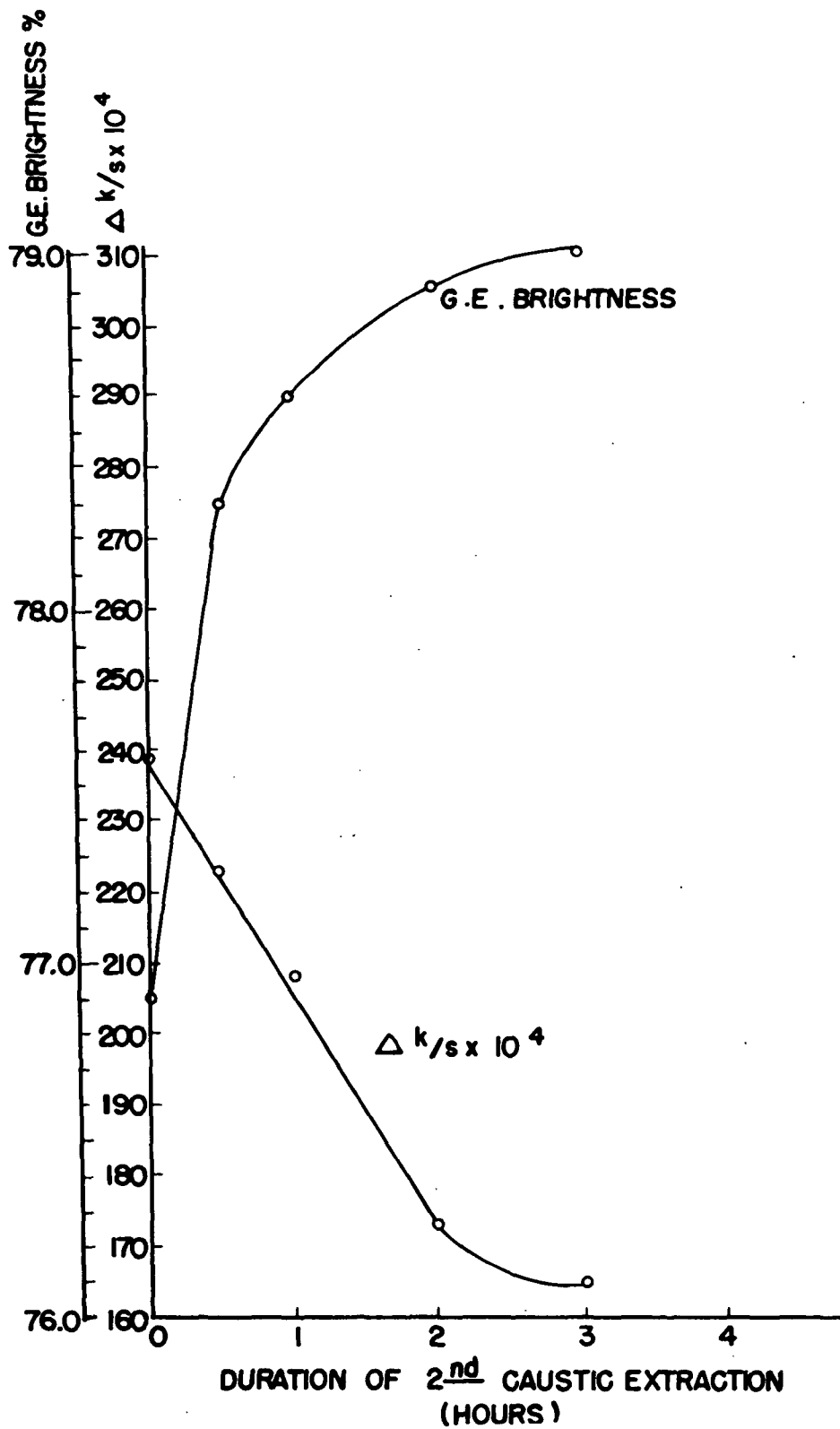


Figure 4

Effect of Caustic Extraction on Brightness and Reversion

The extended caustic extraction reduces the rate of reversion by about 30% and increases the brightness by 2%. Evidently the materials removed by this extraction do not consume a noticeable amount of oxidant since there was no variation in the second stage hypochlorite consumption. The brightness gain and increased color stability obtained demonstrate the value of an extended caustic extraction for commercial kraft bleaching. For experimental purposes variations in this stage afford an easy method for the preparation of pulps with similar chemical characteristics but different color stabilities and different original brightnesses.

HIGHLY PURIFIED PULPS

The preceding paragraphs have been concerned only with CEHEH bleaching. During the course of preparing hemicellulose, Pulp 165 was chlorited by a modification of Jayme's method described by Wise (24) and extracted overnight at room temperature (exposed to air) with 10% potassium hydroxide. According to Kaverzneva (25) the chloriting treatment should convert the aldehyde groups formed during hypochlorite bleaching to carboxyl groups. Since such a treatment is known to increase color stability it was of interest to determine the effect of producing more aldehyde groups by subsequent drastic hypochlorite bleaching of the chlorited and the chlorited potassium hydroxide extracted pulps.

The hypochlorite bleaches were conducted at 1.0% consistency, 40°C., four hours, pH 7.0 to 6.5 with 1.00% chlorine added. The results are given in Table XV.

TABLE XV

BRIGHTNESS AND REVERSION OF CEHEH PULP
ON ADDITIONAL PURIFICATION

	Chlorine Con- sumed 3rd Hypochlorite, %	Original Brightness, Standard % G.E. $\Delta k/s \times 10^4$	
Pulp 165	---	84.0	127
Pulp 165 - chlorited	---	88.0	64
Pulp 165 - chlorited - hypochlorite	0.36	89.3	76
Pulp 165 - chlorited - KOH extracted	---	88.9	25
Pulp 165 - chlorited - KOH extracted - hypochlorite 0.33	0.33	91.7	33

The additional hypochlorite bleach raised the G.E. brightness by 1 and 3% respectively, for the chlorited and the chlorited potassium hydroxide extracted pulps, but the $\Delta k/s$ values were increased only slightly. These data indicate that the color precursor is either altered or removed by the acidified chlorite treatment and that subsequent hypochlorite bleaching has little effect on reversion even though under the conditions used considerable carbohydrate oxidation should occur (22).

FIBER LENGTH FRACTIONATION STUDIES

From the preceding sections it is apparent that bleaching variations have a pronounced influence on brightness reversion. One method of eliminating these variables is to study fibers which have been

subjected to identical bleaching conditions such as fractions based on fiber length. It has been shown that the short fibers of hard bleached sulfite pulp yellow to a greater extent than the long fibers; this difference was attributed to overoxidation of the fines during bleaching (2). Others (26) found the short fibers of bleached kraft pulp to have greater color stability than the long fibers. It should be possible by the study and interpretation of such data to draw some conclusions regarding yellowing since the fines and long fibers differ not only in physical characteristics but also in chemical analysis. Generally, the shorter fibers contain less alpha-cellulose, and more resins, fats, ash, and lignin than the long fibers (27). Since all of these components except alpha-cellulose supposedly contribute to yellowing, the long fibers should be more stable than the fines.

The Bauer-McNett classifier was used to separate the long and short fibers for both unbleached and bleached pulps. The fractionation of unbleached slash pine kraft pulp obtained with this apparatus when operated according to Institute Method 415 is given in Table XVI.

TABLE XVI

BAUER-MCNETT FIBER CLASSIFICATION
OF UNBLEACHED KRAFT PULP

	% of Total
Retained on 28-mesh screen	86.3
Retained on 48-mesh screen	6.6
Retained on 150-mesh screen	3.1
Through 150-mesh screen	4.0

In order to fractionate the pulp rapidly, the standard method was modified. Screens of 28, 200, 35, and 200 mesh were placed in the Bauer-McNett classifier in that order. Twenty grams of pulp were added to both the 28 and 35-mesh compartments and the fractionator was run 10 minutes at a flow rate of 3 gal./min. filtered water before draining. The pulp retained by the two coarse screens was combined, and that retained by the two fine screens was combined. The resulting separation gave about 90% long fibers and 4.5% fines. The data are given in Table XVII.

TABLE XVII

MODIFIED BAUER-MCNETT FIBER CLASSIFICATION

	% of Total
Retained on 28-mesh screen	45.0
Retained on 200-mesh screen	2.7
Retained on 35-mesh screen	45.7
Retained on 200-mesh screen	1.8
Lost to sewer	4.8

No chemical analyses were made on these two fractions, but it is probable that the differences, if any, were slight since the fines seem to be for the most part broken or cut long fibers. This can be seen in Figures 5 and 6, photographs of the fines and the unfractionated fibers. The fiber length distribution by Graff's method (28) is given in Table XVIII for the unfractionated pulp, the long fibers, and the



Figure 5

Unfractionated Unbleached Slash Pine Kraft Pulp

Compare with Figure 6.



Figure 6

Fractionated Unbleached Slash Pine Kraft Pulp
(Through 35 mesh, retained on 200 mesh screen)

These fibers differ from those of Figure 5
only in the fact that they are broken and cut.

finer. It can be seen that a marked difference in length exists between the two fractions and that there is little overlapping.

TABLE XVIII

LENGTH DISTRIBUTION OF FRACTIONATED FIBERS

Length Interval, mm.	Unfractionated Fibers, (Weight, %)	Long Fibers, (Weight, %)	Short Fibers, (Weight, %)
> 4	23.4	37.5	--
3.0-3.9	31.6	28.0	--
2.0-2.9	24.3	23.3	2.9 ¹
1.0-1.9	16.4	10.4	32.2
< 1.0	4.3	.8	64.9

¹Length interval > 2.0 mm.

Average Fiber Length, mm.

Unfractionated	2.42
Long fibers	2.98
Short fibers	0.72

Bleached pulps 120 and 130 were fractionated before the preparation of brightness handsheets. The bleaching data for these pulps are given in the Appendix. Pulp 120 was fractionated by Institute Method 415 with 28, 48, and 150-mesh screens, and pulp 130 was fractionated with 28, 200, 35, and 200-mesh screens in series. The data for the fractions from these two pulps are given in Table XIX.

TABLE XIX

REVERSION AND BRIGHTNESS OF FIBER LENGTH FRACTIONS

Pulp	Original Brightness, % G.E.	Δ k/s x 10 ⁴	
28 fraction of 120	84.3	116	Aged 4 hr. at 100°C. 0% R.H.
48 fraction of 120	84.0	82	
150 fraction of 120	81.9	91	
Long fraction of 130	85.2	114	Aged 1 hr. at 100°C. 0% R.H.
Fine fraction of 130	83.5	79	
Unfractionated	84.6	115	

It can be seen that the ratio of the reversion rate of the fines to that of the longer fibers is from 0.65 to 0.70. One explanation for this difference could be that the action of the bleaching agents used is different on the two fractions; since the bleaching system is heterogeneous it may be that the oxidizing power of the bleach is not divided proportionately between these two fractions. In order to study this, the unbleached pulp fractions were bleached separately. Duplicate bleaches were made on each fraction; the data for the individual bleaches are given in the Appendix. The averages of these are given in Table XX.

These data show that the fines consume slightly more chlorine during the chlorination stage, but approximately the same percentage chlorine in the first and second hypochlorite stages. It can be seen that the differences in color stability noted in the reversion of fines

stability than long fibers since fines comprising 5% of the pulp passed the 200-mesh screen and were lost to the sewer. It may well be that a portion of the fines which truly differ in both morphological and chemical nature may yellow more extensively than the long fibers. Even if this is the case, however, the removal of fines to increase the color stability of a pulp would be of doubtful value since it is apparent that some of the fines are definitely more color stable than the unfractionated pulp. Cutting or breaking the fibers before the bleaching operation would seem to be advantageous since a higher proportion of these more stable fines would be produced in this manner. This could possibly be done either by decreasing the chip size and thus increasing the number of cut fibers, or by "beating" the pulp before bleaching.

THE EFFECT OF ADDITIVES ON REVERSION

INTRODUCTION

The study of reversion by the introduction of materials into the sheet has for the most part been aimed at the commercial application of certain compounds to increase color stability. The ammonium salt of dicyanamide has been suggested to stabilize the pH of the sheet and thereby reduce yellowing (29). Ammonium oxalate has been claimed to reduce reversion by destroying the catalytic effect of iron in the sheet (30). In a study of groundwood fading the inhibiting effects of 130 compounds were tested without success (31). The detrimental effect of additives is also of interest, particularly if the additive

used normally occurs in bleached pulp such as calcium salts, iron, and resins.

The additives investigated in this study were iron, Versene, and sodium bisulfite— the first for possible detrimental effect and the latter two for possible beneficial effects.

IRON

Iron has often been considered to promote brightness reversion by catalyzing oxidation. In order to study the relationship of this constituent to reversion, a series of pulps of varying iron content were prepared.

An attempt was made to prepare an iron-free control sample of bleached pulp by a dilute hydrochloric acid wash. This method has been reported to remove all ash except silica from samples of unbleached kraft pulp (32). Pulp 165 was soaked 45 minutes in 0.1 N hydrochloric acid, washed thoroughly, soaked overnight in distilled water, and washed several times again before forming brightness handsheets. Pulp 180 was given the same general washing sequence; two samples were soaked in 0.1 N hydrochloric acid for one hour and 11-1/2 hours, respectively. The iron contents of both pulps 165 and 180 were approximately halved while the total ash was reduced only slightly for the former pulp but markedly for the latter. It can be seen in Table XXI that in no instance did ash removal increase color stability. The brightness increase obtained by soaking Pulp 180 in hydrochloric acid was completely offset by the subsequent increase in the reversion rate; at the conclusion of the standard two-hour aging interval the

control and acid-washed sheets had brightness values of 80.9, 81.1, and 80.9, respectively.

TABLE XXI

ASH REMOVAL WITH DILUTE HYDROCHLORIC ACID

Pulp Designation	Treatment	Ash, %	Fe, p.p.m.	Original Brightness, % G.E.	Standard Δ k/s x 10 ⁴
165	None (control)	.17	27	83.7	130
165	Soaked 45 min. in 0.1 N HCl	.14	16	83.5	128
180	None (control)	.15	15	85.4	101
180	Soaked 1 hr. in 0.1 N HCl	¹ —	¹ —	86.6	116
180	Soaked 1 1/2 hr. in 0.1 N HCl	.04	7	86.4	119

¹Analyses lost

The pulp samples of varying iron content were prepared in accordance with the findings (33) that iron is more strongly adsorbed under neutral or alkaline conditions and that more iron is adsorbed as the iron concentration of the soaking water is increased. Eight-gram samples of pulp 170-C were soaked one-half hour in two liters of distilled water containing known quantities of ferric ammonium sulfate at pH 7. The pulps were then washed, made into brightness sheets, and

aged under standard conditions. The amount of iron present in the ash of the aged sheets was determined by the colorimetric thiocyanate method (34). The data for these pulps are presented in Table XXII.

TABLE XXII

EFFECT OF HIGH IRON CONTENT ON PULP REVERSION

Sample No.	Fe ⁺⁺⁺ in Soaking Water, p.p.m.	Fe ⁺⁺⁺ in Pulp, p.p.m.	Original Brightness, % G.E.	Standard Δ k/s x 10 ⁴
1	0	20	84.1	135
2	.05	22	84.0	127
3	.15 ¹	17	84.1	135
4	.80	39	82.2	151
5	1.50	81	79.3	175
6	3.00	127	74.1	200

¹Mill process water for the production of bleached pulp usually contains < .15 p.p.m. Fe.

These data are also presented graphically in Figure 7. The added iron lowered the original brightness of the pulp to an extent proportional to the quantity of iron present. The increase in k/s before aging due to the iron added was approximately .0023 units for each part per million iron added. Not only did the iron lower the original brightness, but it also increased the subsequent accelerated reversion rate. It can be seen that the reversion rate is increased by about 50% as the iron content is increased from 20 to 127 p.p.m. This increase may be due to both catalytic acceleration of the

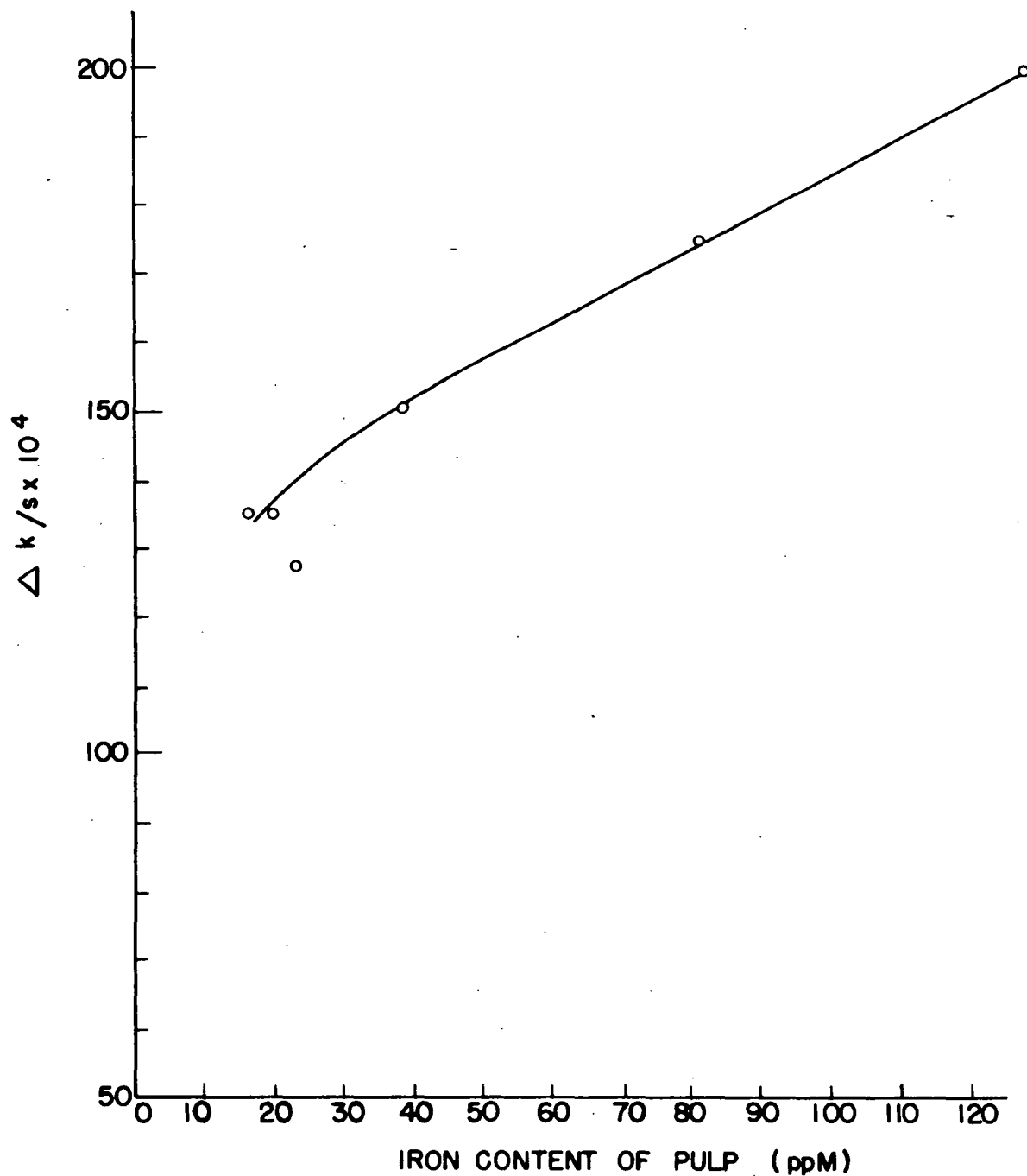


Figure 7

Iron Content vs. $k/s \times 10^4$ Aged 2 Hours 100°C.--0% R.H.

reversion reactions and to color intensification by the formation of iron salts or complexes of the organic colored materials which originated either with or without iron catalysis. Color formation and intensification is observed when iron salts, such as ferric chloride, are added to many phenols and similar compounds.

VERSENE

An attempt was made to remove the ash constituents, including iron, of bleached pulp by treatment with Versene, the sodium salt of ethylenediamine tetraacetic acid. This compound forms complexes with metallic ions, thereby rendering them inactive; it will dissolve water-insoluble salts, e.g., calcium oxalate, by exchanging its sodium ions for the metallic ions of the insoluble salt. Thus, this compound could be effective in lowering the yellowing rate of pulp by removing or complexing ash constituents which could possibly catalyze reversion and also contribute to the alkalinity of the sheet.

Eight-gram samples of Pulp 165 were soaked overnight at 0.2% consistency with 0.82 grams Versene Fe-3 added. This particular agent was chosen since it is claimed to be somewhat specific in the chelation of iron. The quantity used was equivalent to 51 mg. calcium carbonate or a pulp ash content of about 0.6%. All pulps except No. 4, were washed thoroughly the following day before preparing brightness handsheets and aging. The data are given in Table XXIII.

An unexpected result can be noted in Table XXIII. The application of Versene increased the brightness of all three pulps to which it was

applied by 1.2%. The pulp sample (No. 5) soaked in dilute caustic at pH 10.8 was a control for the samples (No. 3 and 4) soaked in Versene solution at this pH. Sample 4 was not washed after the overnight soak. It can be seen that the residual alkaline Versene solution in the sheet increased reversion considerably. No significant increase in brightness stability was obtained by this Versene treatment. The data presented also indicate the inadequacy of this treatment for either ash, or in particular iron, removal. It is probable that the detergent qualities of the Versene were responsible for the brightness increase.

TABLE XXIII

THE BRIGHTENING OF PULP WITH VERSENE

Sample No.	Additive	pH	Ash, %	Fe, p.p.m.	Original Brightness, % G.E.	Standard Δ k/s x 10 ⁴
1	None (control)	7.0	.17	27	83.7	130
2	Ve Fe-3	7.0	.15	15	85.0	116
3	Ve Fe-3	10.8	.14	23	84.9	116
4	Ve Fe-3	10.8	.17	23	84.9	182
5	Dilute NaOH soln.	10.8	.16	25	83.7	127

SODIUM ACID SULFITE

The stabilizing effect of sulfurous acid bleaching has often been considered to be due to the reduction of residual chlorine. When

brightness sheets were first formed from bleached pulp 164, a set was also made with added sodium acid sulfite to determine its effect on reversion.

Sodium acid sulfite (0.400 g.) was added to the four-liter slurry of eight grams of pulp and agitated 45 minutes at pH 4.8 before preparing the brightness sheets. It was calculated that the dried brightness sheet should retain about .01% sodium acid sulfite on the pulp basis; this calculation was based on the assumptions that the pulp did not specifically adsorb sodium acid sulfite, and that the pressed brightness sheet contained 50% moisture.

The sheets from the untreated and the acid sulfite-treated pulp had virtually identical original brightnesses of 85.1 and 85.2%, respectively. The pulps were aged separately under standard conditions to prevent the possibility of free sulfur dioxide affecting the untreated pulp. The treated pulp had a $\Delta k/s$ value of 118×10^{-4} , while that for the untreated pulp was 123×10^{-4} .

Thus, the sodium acid sulfite had no effect on either the original brightness or the reversion rate. The treatment which was given should have effectively reduced residual chlorine, and it is probable that the actual chemical bleaching action on the pulp by sulfur dioxide rather than strictly its reduction of residual chlorine is responsible for its ability to increase color stability. This, of course, does not disprove the definite effects noted by others (12) of last stage sulfurous-acid bleaching in both increasing brightness and lowering reversion.

THE COLORED WATER-SOLUBLE MATERIALS OF AGED PULP

INTRODUCTION

It has been noted previously by Braun and Rollinson (26) that a portion of the color formed during either natural or accelerated yellowing of bleached pulp (sulfate or sulfite) can be removed by water extraction. Since, in many commercial instances, the pulp or paper does not receive any washing after yellowing, this water-soluble color is as detrimental as that which cannot be removed. The purpose of this work was the characterization and study of the nature of this water-soluble colored material.

RATE OF FORMATION

Pulp 180 was prepared by the standard high-consistency techniques and 36 brightness sheets were made in the usual manner. One series of sheets was aged at 100°C. and 0% R.H., while another was autoclaved at 120°C. After aging, the brightness drop which occurred was determined and the sheets were then disintegrated for about one minute with a small Hamilton-Beach mixer. The pulps were soaked at 1% consistency and room temperature overnight. The following day each eight-gram pulp sample was washed with 800 ml. of distilled water at 20°C., followed with a wash with 800 ml. of distilled water at 80°C. Brightness sheets were then formed in the usual manner. From Table XXIV it can be seen that from 50 to 60% of the total color formed was removed by this washing.

TABLE XXIV

RATE OF FORMATION OF WATER-SOLUBLE COLOR

Time aged at 100°C., 0% R.H., hr.	Before Washing		After Washing		
	Bright- ness, % G.E.	$\Delta k/s \times 10^4$ on Aging	Bright- ness, % G.E.	$\Delta k/s \times 10^4$ on Aging and Washing	Reduc- tion in $\Delta k/s$, %
0	85.2	--	85.8	--	--
1	81.8	74	84.3	28	.62
2	81.0	94	84.0	34	.64
4	80.3	113	83.5	45	.60
7	79.2	144	83.0	56	.61
				Average	.62
Time aged at 120°C., 100% R.H., hr.					
0	85.2	--	85.8	--	--
1/2	67.1	678	74.3	327	.52
1	62.9	965	70.4	514	.47
2	59.3	1268	67.6	658	.48
4	56.1	1589	65.0	824	.48
				Average	.49

Some change may have occurred in s , the scattering coefficient, by the treatment, and if so, the amount of color removed by the washing would not be directly proportional to the change in $\Delta k/s$. However, it is probably safe to assume that only minor changes occurred in the s values.

It is apparent from these data that the reduction of $\Delta k/s$ after the washing treatment is fairly constant within, but somewhat different between, the two aging conditions. The samples aged at 120°C., 100% R.H. yellowed much more than those aged at 100°C., 0% R.H., and it may be that as extensive yellowing progresses a portion of the water-soluble colored material becomes insoluble either by condensation with itself or with the pulp. Also, it is possible that a higher proportion of water-insoluble colored material is formed when the samples are aged under conditions of high humidity. In any event, about one-half of the colored material formed when the pulp is subjected to either of these accelerated aging conditions can be removed from the pulp by water extraction.

The rate of formation of water-extractable colored material was also determined by transmittance measurements of the water extract of autoclaved pulp 165. This was done spectrophotometrically since the transmittance of these water extracts was found to obey Beer's Law ($\log 1/T \propto \text{concentration}$). Samples of 0.500 gram were autoclaved at 120°C. for various time intervals and were then agitated for 10 minutes with 100 ml. of hot water before filtering. The transmittance of each filtrate was determined at 400 m μ with the GERS. The data are given in Table XXV.

The formation of this water-extractable color parallels the total yellowing of bleached pulp; the rate decreases but does not cease as time progresses.

TABLE XXV

RATE OF FORMATION OF WATER-SOLUBLE COLOR

Duration of autoclaving, min.	0	10	60	90	150
Transmittance at 400 mmu, %	99.3	98.1	97.7	97.4	97.1
Total color formed in 2-1/2 hr., %	25	65	80	90	100

PREPARATION

Since the total solids which were removed from the autoclaved pulp by water extraction constituted only about 0.4% of the total pulp weight, a relatively large quantity of pulp was used for the preparation of this extract. For the preparation of about three grams of total solids, 750 grams of bleached pulp was autoclaved for four hours and was then packed into a 3 by 48-in. glass column and eluted with 25 liters of 80-90°C. water over a two-hour period. This water solution was then concentrated under reduced pressure in a circulating evaporator at 35-45°C. to approximately one liter; evaporation proceeded at the rate of about 1-1/2 liters per hour. After concentration this solution was filtered through a well-washed celite bed to remove all pulp fibers. It was then sterilized for about 15 minutes at 120°C. to prevent bacterial attack and was stored in a corked bottle in a refrigerator. Fresh water extract was prepared as it was needed. These water extracts are designated as solutions with the number of the bleached pulp from which the water extract was prepared following the word solution - e.g., Solution 165.

CHARACTERIZATION

Methoxyl Content

A relatively high methoxyl content of a wood or pulp structural constituent indicates the presence of lignin or lignin degradation products since softwood lignin and softwood chlorolignin have methoxyl contents of about 15 and 5%, respectively, in contrast to the methoxyl content of the carbohydrate fractions of wood pulp which is usually less than 1%.

The methoxyl content of the total organic solids in Solution 164 was found to be 0.25% by Institute Method 18. These solids are not all colored, and it was found that a highly-colored portion of the material could easily be removed by carbon adsorption. However, it was not found possible to recover this adsorbed material. Therefore, the methoxyl content was determined on the decolorized solids and was 0.14%. Since 18% by weight of the solids was removed by the carbon, a material balance shows that the methoxyl content of the adsorbed colored material was 0.72%. The color absorption of the solution was reduced by 87% by this carbon decolorization. These low methoxyl contents indicate that ligneous materials are either absent or present in only very small quantities.

Polysaccharide Content

A positive Molisch test (35) was obtained on Solution 165 at total solids concentrations as low as .003%; this is considered a reliable test for the presence of carbohydrates. Since simple sugars

and oligosaccharides are known to be colorless, it was apparent that such components of the water extract did not contribute to the color. However, one approach to the separation and analysis of the colored component was to first determine the types and quantities of the other constituents present.

The reducing value of Solution 165 was determined by the Somogyi method (36). Three milliliter aliquots containing 6.3 mg. (0.21%) of organic material plus 60 mg. (2%) of sulfuric acid were hydrolyzed at 100°C. for 0, 1, 2, 3, 4, 5, 7, and 15 hours. After hydrolysis, the sulfuric acid was removed with barium hydroxide and the reducing power was determined as equivalent milligrams of glucose. The maximum reducing power, 1.55 mg. glucose was obtained with five hours hydrolysis and indicates a simple sugar content of $1.55/6.3$ or about 25%. The reducing power before hydrolysis was 0.45 mg. equivalent glucose; this indicated that the average D.P. of the polysaccharides present was $1.55/0.45$, or approximately 3.5. This is, of course, based on the assumption that all of the reducing power is due to simple sugars and oligosaccharides. This very low D.P. is in accord with the fact that these polysaccharides are water soluble.

As a check on the Somogyi determinations and also to establish which sugars are present in the water extract, a semi-quantitative chromatographic method was used. Fifty milliliters of Solution 165 containing 85 mg. organic material was hydrolyzed four hours at 2% sulfuric acid concentration. The hydrolyzate was neutralized with barium hydroxide solution and filtered before being concentrated under vacuum and dried in a vacuum desiccator. The dry residue was

dissolved in 0.625 ml. water and used for preparing spots on chromatograms adjacent to known quantities of sugar. A 0.005-ml. pipette calibrated in 0.001-ml. divisions was used for spotting both the known sugar solutions and the unknown solution. Spots of 0.01 ml. of the unknown solution were used in all cases, and the spots of the solution of known mixed sugars were varied from 0.001 to 0.01 ml. The concentrations and ratios of the known sugars were varied until the unknown sugar color was bracketed with more- and less-colored spots of known quantities of known sugar. When the final comparison was made, the quantities of sugars present on the chromatogram varied from 0.018 mg. for glucose to 0.14 mg. for xylose. The sensitivity of the comparison depends to some extent on the quantity of sugar present. Butanol:pyridine:water (10:3:3) developer was used to resolve all sugars except mannose and arabinose, and these sugars were resolved on separate chromatograms developed with ethyl acetate:acetic acid:water (9:2:2). The chromatograms were sprayed with aniline hydrogen phthalate solution and heated four minutes at 110°C. before visual comparison of the known and unknown quantities of sugars. The results are given in Table XXVI. This analysis gives a total of 20 mg. sugars in 85 mg. of total organic material, or 23%. This is in surprisingly good agreement with the 25% sugars calculated as glucose determined by the Somogyi method since the chromatographic quantitative determination is probably accurate to only $\pm 15\%$ of the total quantity of sugar present.

TABLE XXVI

SUGAR CONCENTRATION IN HYDROLYZATE

Sugar	Mg./ .001 ml.	Ratio
Glucose	.0014	1.0
Galactose	.0035	2.5
Arabinose	.0065	4.5
Mannose	.0070	5.0
Xylose	.0140	10.0

Lignin Content by Alkaline Nitrobenzene Oxidation

An effort was made to establish definitely the absence or presence of lignin degradation products in the water extracts since such materials, by the nature of their conjugated double bonds, could obviously contribute to a portion, or all, of the color of the water extracts. The presence of such products can be proved satisfactorily by the identification of typical oxidation products (vanillin, vanillic acid, and 6-chlorovanillin) after submitting the material to be examined to an alkaline nitrobenzene oxidation.

The micromethod of oxidation described by Stone and Blundell (37) was used. The paper chromatograms prepared were developed with butanol saturated with 2% aqueous ammonia (38), and were sprayed after drying with bis-diazotized benzidine reagent (38).

The various materials which were oxidized and the results obtained are given in Table XXVII.

TABLE XXVII

CHROMATOGRAPHIC IDENTIFICATION OF ALKALINE
NITROBENZENE OXIDATION PRODUCTS

Sample Oxidized (Weights are Dry Ash-Free Solids)	Alkaline Nitrobenzene Oxidation Products Ident- ified on Chromatograms
10 mg. Klason lignin from un- bleached kraft pulp	Vanillin
10 mg. Klason lignin from bleached pulp 165	Vanillin
10 mg. Spruce native lignin	Vanillin
5 mg. Spruce native lignin	Vanillin
2 mg. Spruce native lignin	Vanillin
70 mg. Solution 130 + 5 mg. spruce native lignin	Vanillin
70 mg. Solution 130 + 1 mg. spruce native lignin	Vanillin
Control (1 ml. 2 <u>N</u> NaOH + 0.06 ml. nitrobenzene	None
70 mg. Solution 130	None
250 mg. Solution 165	None
70 mg. Dialyzed Solution 165	None
70 mg. Carbon decolorized Soln. 165	None
50 mg. Dialyzed Solution 165	None

Vanillin was detected in every instance in which lignin was used, but was not found in the oxidation products of any of the water extracts. Although the smallest quantity of lignin used was one milligram, the method is probably sensitive to approximately 0.5 mg. lignin since a very well defined vanillin spot was obtained when one milligram of native lignin was oxidized. This indicates that lignin is probably absent from these water extracts, since in the largest sample taken (250 mg.) a lignin content of less than 0.2% should have been detectable.

Therefore it is quite probable that the color of the water extracts is due not to lignin but to carbohydrate-derived materials.

Solubility in 1,4-Dioxane

Ligneous materials can be separated from carbohydrates by the use of 1,4-dioxane since the former dissolve in this solvent while the latter do not. The method of effecting the separation is to add dioxane to a moist mixture of the two and then distill off the constant boiling mixture of dioxane and water. Repeated additions of fresh dioxane with subsequent distillation after each addition insures the removal of all water from the system.

The application of this separation method to Solution 165 indicated that 12% of the total solids was soluble in the dioxane. However, the material dissolved had the same methoxyl content, ash content, and specific color absorption as that which did not dissolve. Since the total solids used contained 29% ash, it is probable that this material dissolved in a salt-water-dioxane system rather than in pure dioxane.

For this reason the dioxane solubility was determined for the dialyzed organic solids of Solution 165. These solids amounted to 29% of the original organic material in the water extract and had an ash content of less than 1%. An 87-mg. sample was used and dried, purified dioxane was re-added four times. This material was found to be completely insoluble in dioxane; this is a strong indication that ligneous materials are not present in these water extracts.

Ultraviolet and Visible Light Absorption

Absorption in the ultraviolet light region (200-400 mmu) was determined with a Beckmann UV spectrophotometer, while visible light absorption (400-700 mmu) was determined with a General Electric Recording Spectrophotometer. Absorption curves were obtained for all of the various water extracts prepared (Solutions 130, 164, and 165) and were quite similar.

It was found that at concentrations varying from 0.1 to 1.0% total solids the transmittance of Solution 164 obeys Beer's Law at visible wavelengths. This holds, however, only if the solutions are compared at the same pH since the depth of color is intensified with increasing pH. This is shown graphically in Figure 8.

The absorption curve (200-790 mmu) for Solution 164 is given in Figure 9. It can be seen that there are inflexions at about 260 mmu and 300 mmu indicating a possible masked maximum at 280 mmu . Both lignin and furan compounds exhibit a maximum in absorbance at this wavelength. It is probable that this masked maximum is due to a furan since furfural was identified both by its ultraviolet absorption curve and by the acidic aniline test (39) in a distillate of Solution 170-C. This water extract was prepared from pulp 170-C which has been autoclaved for four hours at 120°C. in a sealed glass tube to prevent the loss of volatiles.

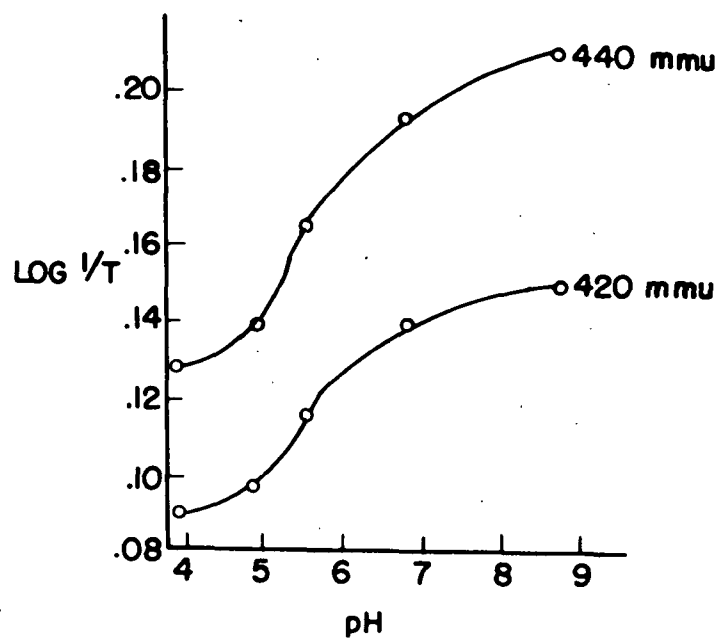


Figure 8

Effect of pH on Light Absorbance of Water Extract

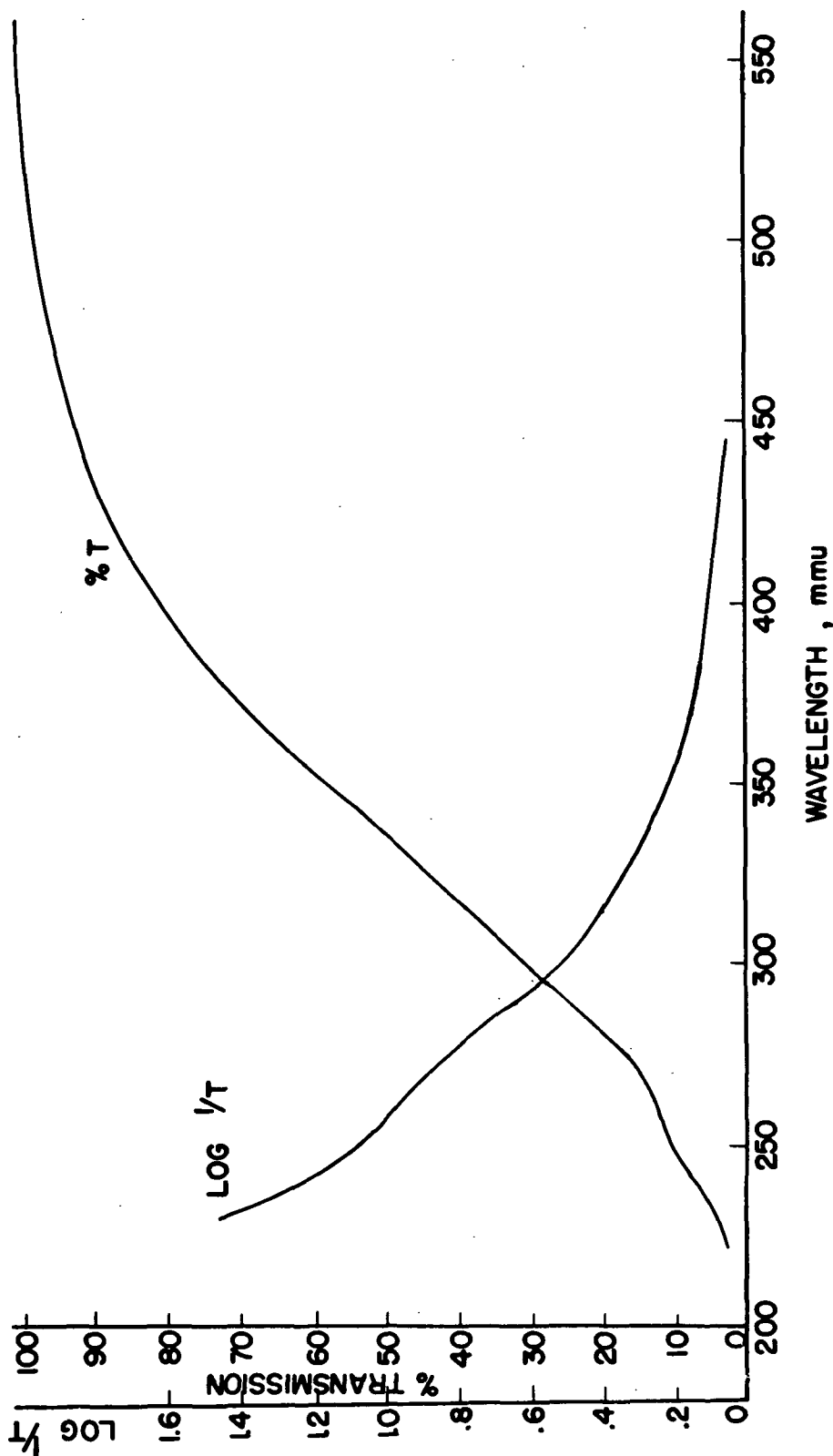


Figure 9

Light Absorbance of Solution 164

Ash Content

The water extracts obtained from the autoclaved pulp samples contained from 5 to 25% ash as determined by igniting at 600°C. for four hours. Qualitative spectrographic analysis of this ash by the Physics Department showed that the cations of the ash from Solution 165 were principally calcium and magnesium with traces of aluminum, manganese, chromium, copper, sodium, silicon, iron, zinc, nickel, tin, and boron. A similar spectrographic analysis with calcium and magnesium predominating was also obtained for the ash of bleached pulp 165.

Since iron salts often possess a yellow to brown color in solution, the possibility existed that a portion or all of the color in the water extracts was due to iron. For this reason the iron content of the ash (5% of the total solids) of Solution 165 was determined by the colorimetric thiocyanate method (34) and was found to be 2.4% of the ash. This corresponded to 0.2 p.p.m. iron concentration in the original Solution 165. Samples of Solution 165 were prepared with one-half the original total solids concentration or 0.89 mg./ml. and iron contents of 0.1, 0.3, 0.7, and 1.0 p.p.m. by the addition of ferric ammonium sulfate. Complete visible light (400-700 mμ) absorption curves were obtained with the GERS and were found to be identical for the four solutions. Another sample of Solution 165 (0.2 p.p.m. iron) was diluted with an equal amount of Versene Fe-3, an organic chelating agent, to give the same concentration total solids (0.89 mg./ml.) as was present in the other

samples. Again the light absorption curves were identical even though the chelating agent had complexed the iron sufficiently to prevent its detection by the colorimetric thiocyanate test (34); before the addition of this agent the iron present was easily detected by this test. Therefore, it can be seen that the small quantity of iron present in these water extracts does not noticeably contribute to their color.

SEPARATION INTO COMPONENTS

It was apparent that the colored water extracts under investigation were composed of more than one material, and an attempt was made to separate the highly colored constituent from those which were noncolored or only slightly colored. The various separation methods attempted were chromatography, fractional precipitation, calcium precipitation, carbon adsorption, and dialysis.

Chromatography has been used successfully for the separation of the components of many complex mixtures. For unknown mixtures, however, the choice of a suitable developer solvent is sometimes difficult. Initially, two developers which have been used frequently for the chromatographic separation of sugars, butanol:pyridine:water (10:3:3) and butanol:acetic acid:water (63:10:27) were used. The colored water extract was spotted and allowed to dry on a 7-1/2 by 24 in. strip of Whatman No. 1 paper. The colored material remained at the starting line with the butanol:pyridine:water, but diffused generally over the sheet with the butanol:acetic acid:water. In neither case was a separation effected. Various ratios of alcohol and water were tried

as developers, and it was found that the color of Solution 165 moved with an R_f of 0.7 using a developer of isopropanol:water:acetic acid (30:69.7:0.3). However, this material had the same specific light absorption as the original given in Figure 7; no separation occurred.

Fractional precipitation of these water extracts by the addition of alcohol was not studied thoroughly, but there were indications that at least a partial separation could be obtained in this manner since about 37% of the total solids were precipitated at ethanol concentrations above 70%.

The major portion of the color of the water extracts was precipitated on the addition of calcium hydroxide. This together with the fact that the color is mobile with acidic chromatographic developers, but immobile with a basic developer, indicates that the colored material is acidic. In substantiation of this fact, it was shown that 60% of the colored material was taken up by 1R4B, and anion exchange resin. However, probably due to physical adsorption, 19% of the color could also be removed from solution with 1R120, a cation exchange resin. Due to the subsequent necessity of removing calcium after calcium precipitation, and due to probability of physical adsorption on ion exchange resins, neither of these possible means of separation was explored further.

Activated carbon has been found applicable to the decolorization of a variety of materials. The adsorption of colored material usually follows the Freundlich isotherm, $x/m = kc^{1/n}$, where x is the amount of colored constituent moved by m grams of carbon, c is the amount of colored constituent left in the treated solution at equilibrium, and k

and $1/n$ are constants which for any given solution are characteristic of the carbon. After it was shown that the adsorption of the colored component of Solution 165 followed this relationship, it was possible to calculate the amount of carbon needed for a given degree of color removal. In this way excesses of carbon which could adsorb noncolored components were avoided. The experimental conditions for the decolorizations are given in Table XXVIII.

TABLE XXVIII

CARBON DECOLORIZATION CONDITIONS

Temperature	20-25°C.
Concentration	0.2%, organic 0.08% inorganic
Time	1/2 hour
pH	3.8, adjusted with acetic acid 5.5, adjusted with carbon dioxide
Darco G-60 carbon	varied from 2 to 20 times the weight of organic material present

It was found that the carbon could remove 87% of the color from Solution 165 while removing only 16% of the total organic material. When more complete decolorization is obtained, the ratio of colored material to organic material removed decreases. With 98% decolorization, 50% of the organic material of Solution 165 is removed. Light absorption curves for the original solution, the decolorized solution, and the adsorbed material calculated are given in Figure 10.

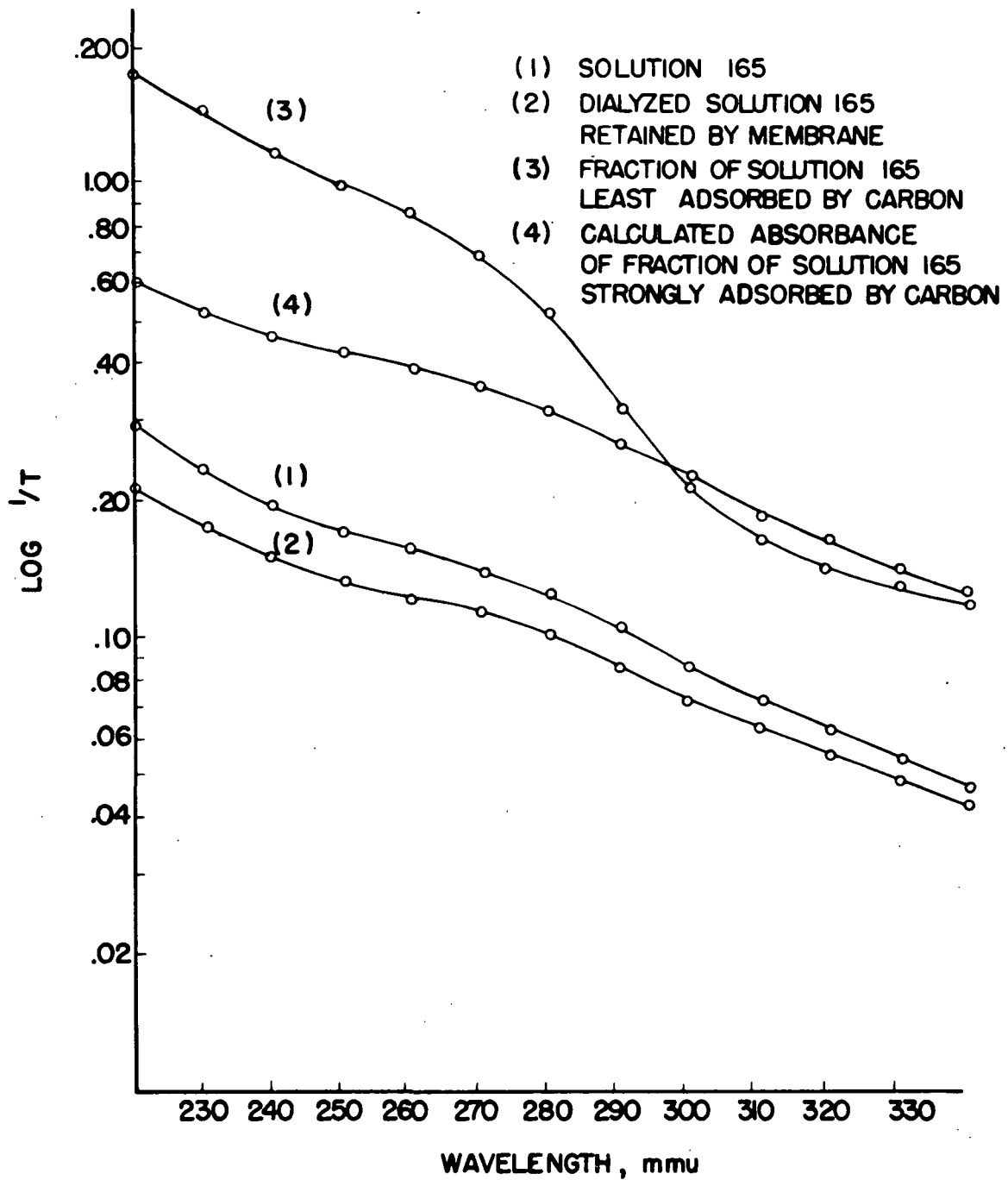


Figure 10

Light Absorbance of Solution 165 and Fractions

Recovery of the adsorbed color was attempted by mixing the carbon thoroughly with dilute aqueous solutions of sodium carbonate, sodium hydroxide, and ammonium hydroxide. All of these alkaline solutions peptized the carbon and made filtration impossible. However, most of the carbon could be removed by centrifuging, and the colloiddally dispersed carbon was then coagulated by acidification. Although some color was undoubtedly readsorbed, the amount was small in comparison to that present in the solution since the major portion of the carbon was removed by centrifuging. The recovery was estimated from transmittance data to be about 10% of the total color taken up by the carbon. This cannot be estimated accurately since the colors of the two solutions are different; the solution obtained by alkaline elution of the carbon absorbs light more strongly at lower wavelengths than Solution 165.

In an effort to separate the constituents of Solution 165 according to molecular size, 200 ml. containing 400 mg. (0.2%) total solids was dialyzed batchwise in "Visking" cellulose sausage casing against distilled water for a four-day period. The distilled water was changed twice daily. This work was duplicated. It was found that 29% of the organic material was retained by the membrane and the ash content was reduced from 17.4% to less than 1%. Both the material passed and that retained gave a positive Molisch carbohydrate test (35). The color absorption curves for these fractions is given in Figure 11. On this type of plot (loglog $1/T$ versus wavelength) the curves of identical colors are parallel. It can be seen that the material adsorbed by carbon and that retained by the dialysis membrane have similar colors.

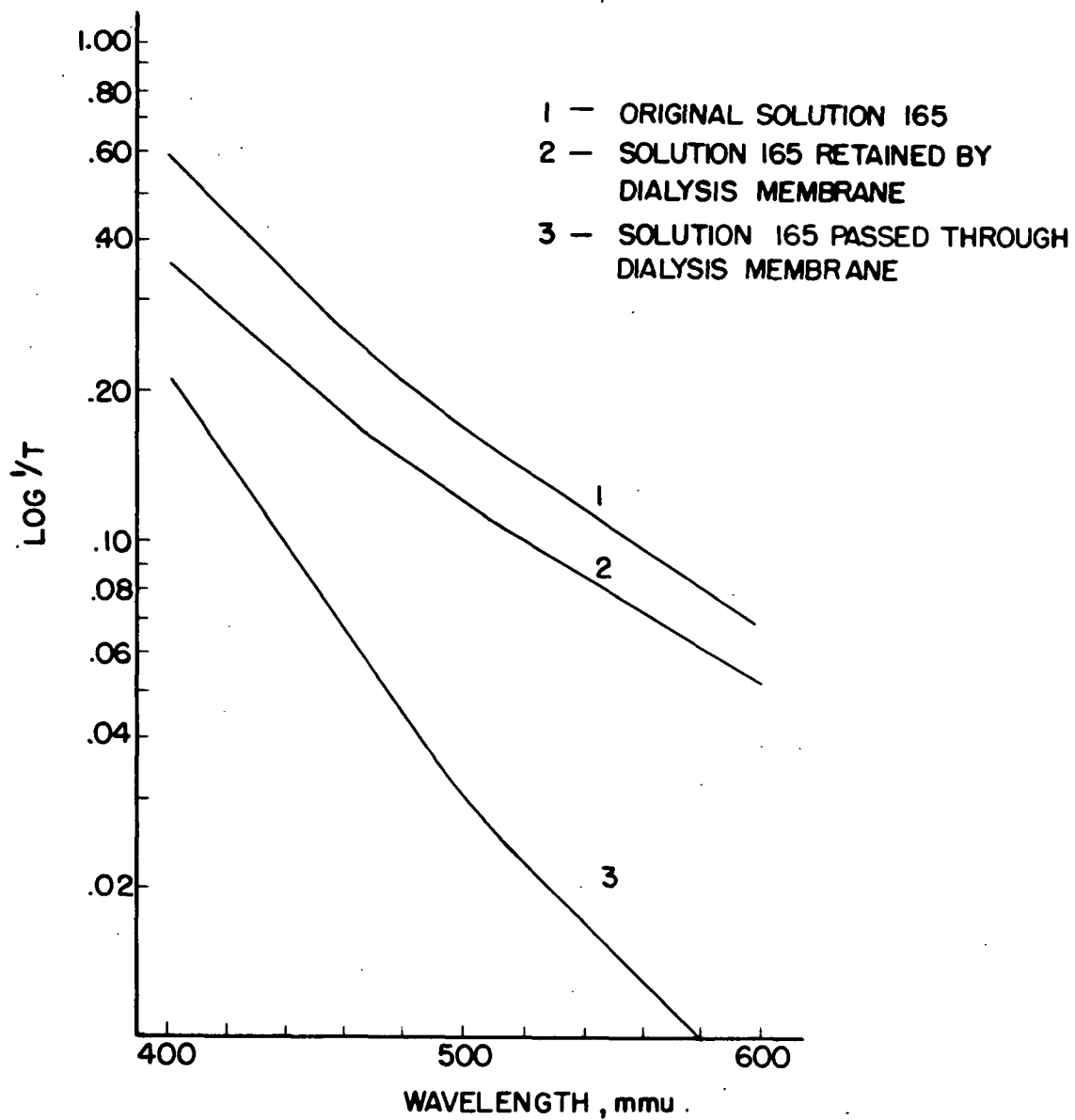


Figure 11

Light Absorbance of Solution 165 and Fractions

SUMMARY

It has been shown that the rate of formation of colored water-soluble material parallels the total discoloration of the pulp and that this material accounts for from 50 to 60% of the total yellow color formed during accelerated aging. Even though this substance is soluble, it is of considerable importance commercially since it would not normally be removed.

A complete analytical description of this colored material has not been obtained, but all of the evidence obtained supports the hypothesis that it is carbohydrate derived. About 23% of the water-soluble material consists of oligosaccharides which can be hydrolyzed to simple sugars typical of the hemicelluloses. Apparently ligneous materials are absent; this statement is based on the low methoxyl content, dioxane insolubility, and the absence of any of the typical lignin oxidation products when the material is subjected to an alkaline nitrobenzene oxidation. The masked maximum at 280 mμ in the ultra-violet absorbance curves for these water extracts is probably attributable to the presence of small amounts of furfural. Although iron is present in these water extractables, the data indicate that it does not noticeably contribute to their color either by its own color or by color intensification.

Although no direct evidence has been obtained concerning the water-insoluble colored materials formed during accelerated aging, it is postulated that this color is of the same general nature as the water-soluble color and owes its lack of solubility to either

its location in the fiber or to condensation with itself or with the cellulosic constituents of the fiber.

THE YELLOWING OF HEMICELLULOSES

The term hemicellulose will be used in this discussion to describe all polyoses present in bleached pulp except alpha-cellulose. It is realized, however, that pectic materials and low molecular weight glucans often are not included in this category.

If the yellowing of bleached pulp is due to carbohydrate materials, it is apparent that hemicelluloses must be responsible since alpha-cellulose is known to possess a high degree of color stability. This study was undertaken, therefore, to determine the type of color formed on heating hemicelluloses and the factors which influence their yellowing. Solutions of hemicelluloses were studied rather than the dry materials since in this manner the color formed could be determined for smaller quantities of material, pH could be readily controlled, and the effect of relative humidity on the dry material could be eliminated.

Several different preparations were used, and are listed with their sources in Table XXIX.

These hemicelluloses were heated both before and after bleaching. The bleaching conditions used were modeled after the conditions of commercial hypochlorite bleaching and are tabulated in Table XXX.

TABLE XXIX

SOURCES OF HEMICELLULOSES

Hemicellulose	Plant Source	Prepared By
Slash pine, Hemi A	Slash pine	L. E. Wise laboratory
Slash pine, bleached	Slash pine kraft pulp	S. M. Rollinson ¹
Xylan	Paper birch	A. P. Yundt
Mannan	Ivory nut	A. P. Yundt
Arabogalactan	Western larch	E. V. White
Pectic acid	Citrus	Commercial

¹Prepared by 10% KOH extraction of bleached Pulp 165 after chlor-
iting to remove any residual lignin

TABLE XXX

BLEACHING CONDITIONS

Temperature	40°C.
Consistency	1%
pH	7.0
Chlorine concn.	0.4 g./l.
Chlorine added (hemi- cellulose basis)	4.0%
Time	4 hr.

After bleaching slash pine Hemi A, the solution was acidified,
precipitated with ethanol, and the precipitate was successively washed
three times with absolute ethanol and twice with absolute ether. Ten

milligram samples of the unbleached and bleached Hemi A were dissolved in 3 ml. 0.1 N sodium carbonate solution and autoclaved for four hours at 120°C. Both solutions yellowed, but there was no apparent difference in the two. It was found, however, that if the unbleached hemicellulose was precipitated and purified after the alkaline autoclaving treatment, a considerable increase in color stability occurred. Evidently a color precursor was removed during either the alkaline autoclaving treatment or the alcoholic precipitation. These data are given in Table XXXI. It was further observed that this color stability was then decreased by a subsequent calcium hypochlorite bleach.

TABLE XXXI

400 mμ TRANSMITTANCE DATA FOR AUTOCLAVED SLASH PINE
HEMICELLULOSE "A" SOLUTIONS

Treatment	log 1/T Be- fore Auto- claving	log 1/T After Autoclaving	Difference
None	.127	.455	.328
Alkaline autoclaved, precipitated and purified	.132	.159	.027
Alkaline autoclaved, precipitated and purified, bleached, precipitated and purified	.054	.101	.047

During the acidified alcoholic precipitation of hemicelluloses after the bleaching treatment, the possibility exists that degraded material capable of a high degree of yellowing remains in solution.

For this reason several of the solutions of hemicelluloses were autoclaved after bleaching without prior precipitation. At the conclusion of the bleach, the excess chlorine was destroyed by the addition of acetone (haloform reaction) and sufficient sodium hydroxide to raise the pH to 11.9. The chlorine consumption was determined by thiosulfate-iodimetric titration of duplicate samples which were subsequently discarded; these chlorine consumptions are given in Table XXXII.

TABLE XXXII

CHLORINE CONSUMPTION

Hemicellulose	Chlorine Consumed, %
Slash pine	1.36
Pectic acid	1.72
Mannan	1.92
Xylan	2.86
Arabogalactan	3.24

Both the unbleached and bleached hemicelluloses were autoclaved at various pH levels for one-half hour at 120°C.; the hemicellulose concentration in all cases was 0.25%. The pH was adjusted by the use of a buffer system of dihydrogen potassium phosphate and sodium hydroxide or hydrochloric acid and did not change during the course of the autoclaving.

Due to cloudiness, it was impossible to obtain transmittance measurements for the xylan or slash pine hemicellulose solutions but these were observed visually.

The xylan samples showed practically no yellowing-- the least of all five materials. The slash pine hemicellulose samples closely paralleled the mannan and only in the case of these two materials did the bleached sample yellow to a greater extent than the unbleached. The $(\log 1/T)_{\text{pH } 10.7} - (\log 1/T)_{\text{pH } 6}$ values given in Table XXXIII indicate that the relative color stability of these hemicelluloses is in the order: xylan, pectic acid, mannan, slash pine, and araboglactan.

Complete visible and ultraviolet light absorbance curves were obtained at pH 10.7 for these colored solutions and are given in Figures 12, 13, and 14. On this type of plot (loglog 1/T versus wavelength) the curves of identical colors are parallel. One of the colored water extracts, Solution 165, discussed in the preceding sections, has been plotted on these graphs and in the visible region its color resembles that of pectic acid while in the ultraviolet range its absorbance is very similar to that of xylan. For a complex mixture such as Solution 165 analysis by light absorbance is obviously quite difficult, but it is apparent that its color may very well be due to a mixture of the yellow materials formed during the degradation of hemicelluloses.

The absence of the yellowing phenomenon when these hemicellulose solutions are neutral suggests that basicity or acidity is a requisite for color formation. Therefore, in the yellowing of pulp, ash might contribute to color formation due to its alkaline nature and oxidized

TABLE XXXIII

EFFECT OF pH ON COLOR FORMATION IN HEMICELLULOSE SOLUTIONS

	Log 1/T at 400 mmu				$[(\log 1/T)_{\text{pH } 10.7}] -$
Heated at	$\text{pH } 6^1$	$\text{pH } 7$	$\text{pH } 8^1$	$\text{pH } 10.7^1$	$[(\log 1/T)_{\text{pH } 6}]$
Xylan U ²	Too cloudy for measurements; no color before or after heating				
Xylan B ³					
Slash pine U	Too cloudy for measurements; yellowed when heated at pH 10.7; B sample had higher color intensity than U sample				
Slash Pine B					
Mannan U	Cloudy, no color	.022	.024	.067	.045
Mannan B	Cloudy, no color	.017	.024	.084	.067
Arabogalactan U	.055	.070	.087	.126	.071
Arabogalactan B	.023	.030	.045	.084	.061
Pectic acid U	.058	.059	.055	.090	.032
Pectic acid B	.025	.029	.042	.062	.037

¹All log 1/T data adjusted to pH 7 by a factor to correct for higher color intensity at higher pH values; multiplication factors were .71, .86, 1.00, and 1.05 for pH values of 10.7, 8, 7, and 6 respectively

²U - unbleached

³B - bleached

The original transmittance values of these solutions before heating was very nearly that recorded after heating at pH 6 or 7.

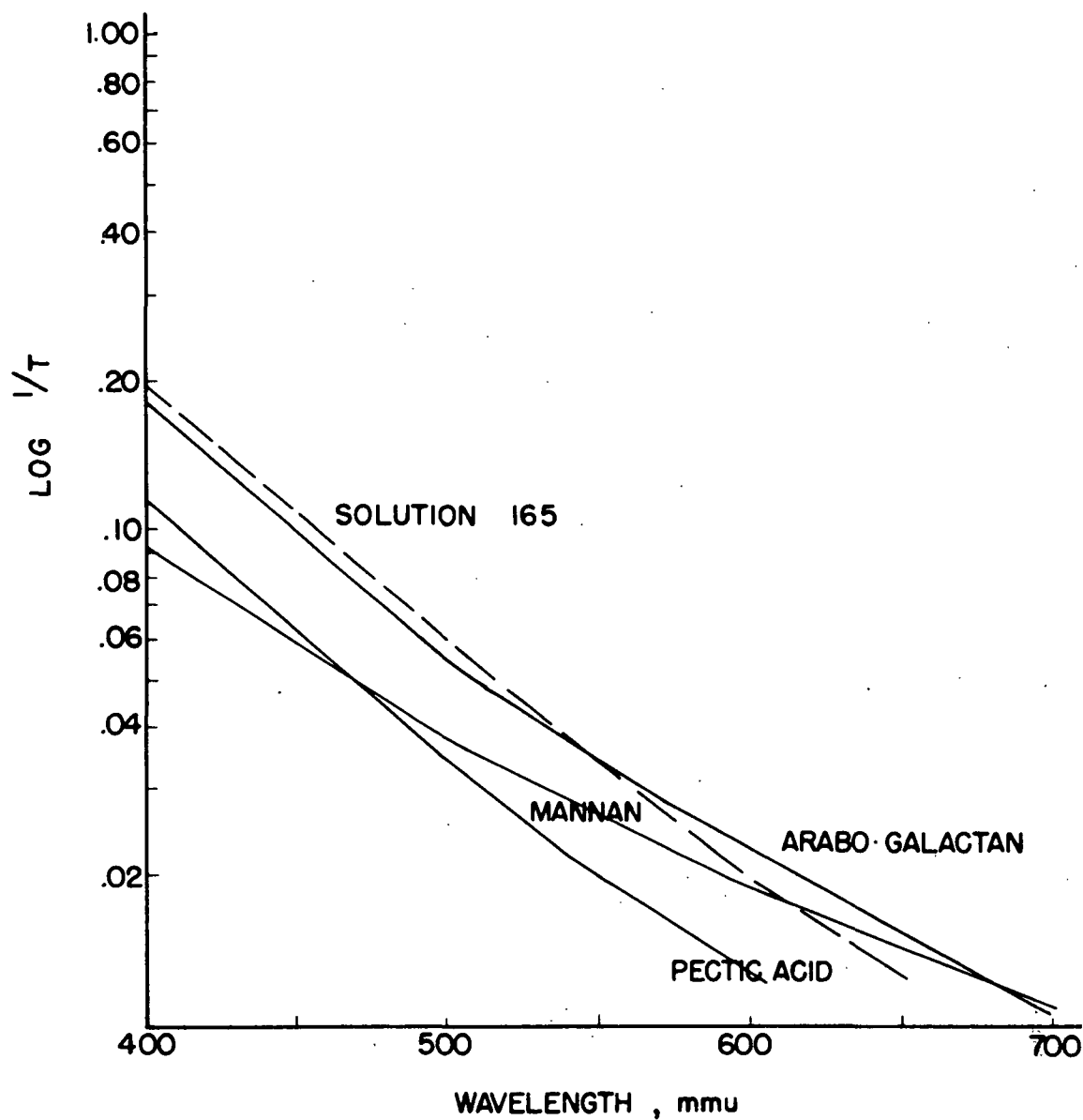


Figure 12

Light Absorbance of Hemicellulose Solutions

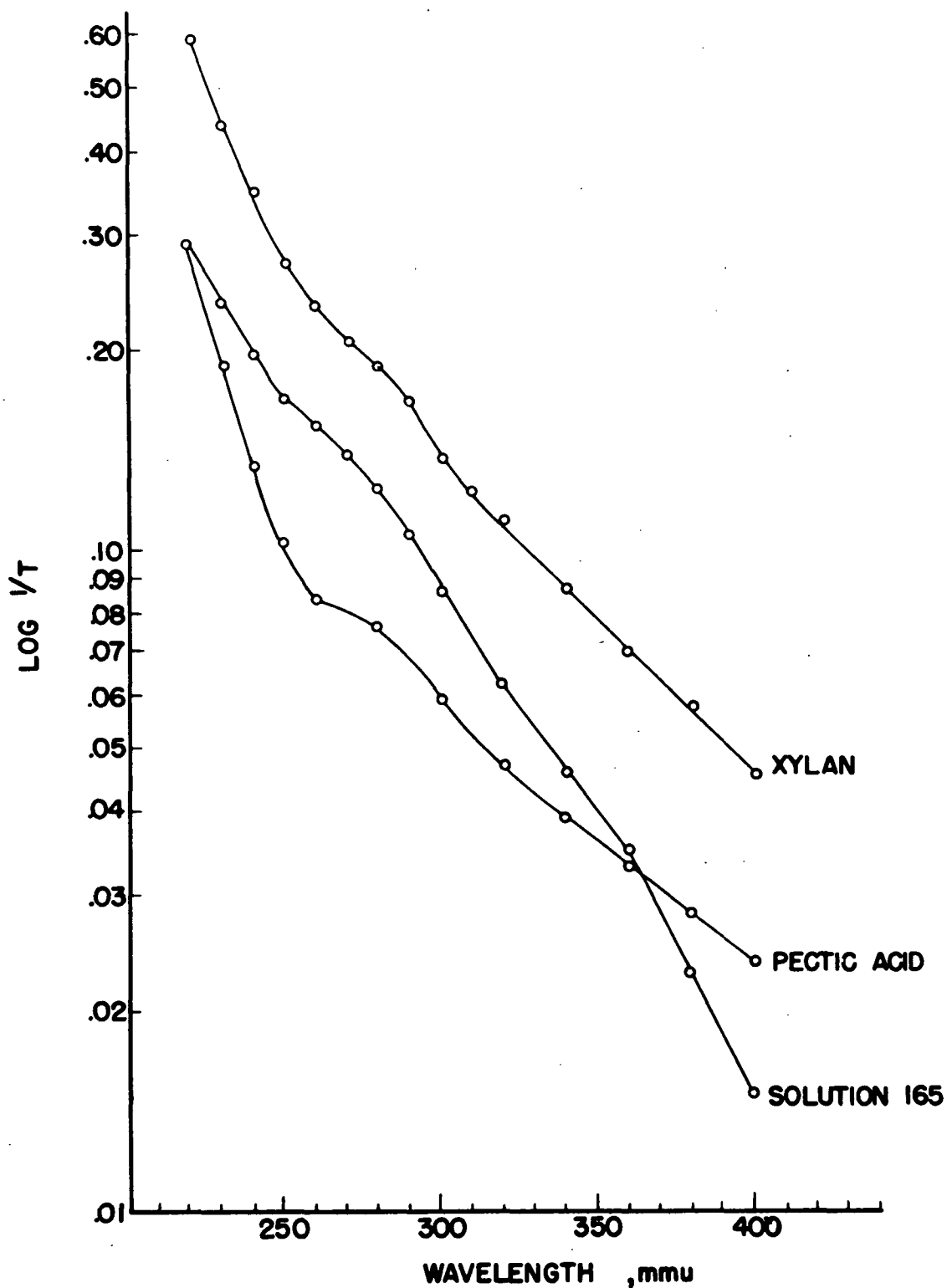


Figure 13

Ultraviolet Light Absorbance of Hemicellulose Solutions

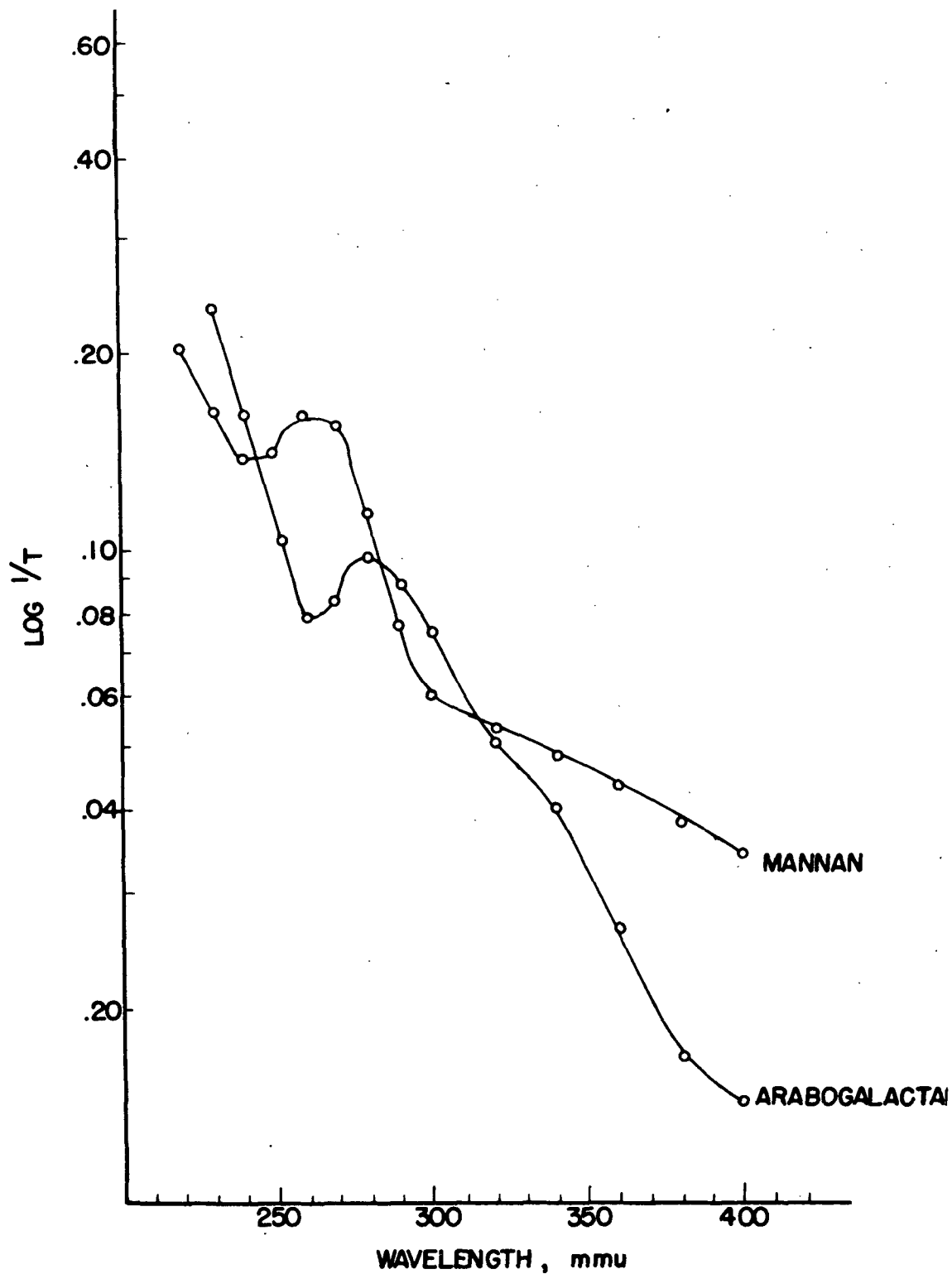


Figure 14

Ultraviolet Light Absorbance of Hemicellulose Solutions

carbohydrates with acidic groups might also be partially responsible since it is known that carbohydrates darken, or "caramelize" on acidic heating. Due to structural heterogeneity, both acidic and basic yellowing could possibly occur simultaneously within a single fiber!

SUGGESTIONS FOR FUTURE WORK

The wood species chosen for the production of any type of pulp is an obvious variable which may affect the properties of that pulp. As yet the effect of wood species on brightness reversion has not been determined. It would be desirable to study the effect of this variable for the purpose of both fundamental background and direct commercial application. If it is found that pulps with an identical history except for wood species possess varying degrees of color stability, it should be possible to determine the reasons for these differences. Also, the use of certain wood species for the production of bleached pulps of high stability would be indicated.

The differences existing between sulfate and sulfite pulps has been a subject of much research and conjecture (40-42). A careful comparative study of the reversion characteristics of these major types of chemical pulps would add both to our general knowledge of these pulps and would also demonstrate the limits of the color stability attainable with each.

Unfortunately, most of the theoretical bleaching studies which have been conducted have not been concerned with subsequent yellowing of the bleached pulp. A better knowledge of the degree and type of

carbohydrate oxidation together with reversion data for pulps prepared with various bleaching oxidants should be a valuable aid in the interpretation of this phenomenon. As an example, highly specific oxidants such as nitrogen dioxide should be used for chemical modification of the pulp to determine the effect of uronic acid content on reversion.

The exact structure of the water-soluble carbohydrate-derived colored material formed during the yellowing of pulp remains to be elucidated. Future work should be concerned with both the physical and chemical nature of this substance.

One very interesting subject for future investigation lies in the effect of relative humidity on the rate of reversion. The marked difference in the shape of the rate of reversion versus humidity curves for different type pulps undoubtedly is due to differences in the components responsible for yellowing. In previous work (4) the presence of a minimum in such a curve suggests the possibility that at least two different components are yellowing, one of which yellows more rapidly under dry conditions and one which yellows strongly in the presence of moisture. This work would, of course, be related to studies involving the effect of pulping and bleaching variables.

The need for further work in this field cannot be overemphasized. Only by extensive studies of the mechanisms of both bleaching and brightness reversion can this yellowing problem be solved.

SUMMARY

An investigation was made of the yellowing brought about by the heating of bleached kraft pulps. Pulps prepared from a single unbleached slash pine kraft pulp were used with a bleaching sequence consisting of chlorination, caustic extraction, calcium hypochlorite oxidation, caustic extraction, and calcium hypochlorite oxidation. The conditions maintained during these bleaches closely paralleled those used commercially.

The reproducibility of the bleaching techniques used was determined in order to establish the validity of all conclusions and comparisons. It was found that the original brightness values of pulps prepared simultaneously agree within 0.5% G.E. and that the standard $\Delta k/s$ values agree within 10% of the total numerical value.

After the precision of both brightness and reversion data was established, the effects of several bleaching variables on these properties were determined. The pH maintained during hypochlorite oxidation, the duration of the second caustic extraction, and the washing of newly bleached pulp were studied. Of these factors, a thorough caustic extraction has the greatest effect in reducing reversion. The process variables of caustic extraction and the pH of hypochlorite oxidation can easily be adjusted in industrial operations for the attainment of high color stability, but only by relatively long diffusion periods could commercial washing be changed to increase color stability.

A comparison was made of the reversion characteristics of long and short fibers of pulps fractionated both before and after bleaching.

The greater color stability which was found for the shorter fibers can be attributed to the more rapid diffusion of materials within the fibers during the course of the bleaching stages.

Iron, Versene, and sodium acid sulfite were individually added to the pulp before accelerated aging tests; the former was used for its possible detrimental effect and the latter two for their possible benefits in increased color stability. The presence of iron was shown to definitely increase brightness reversion, but no decrease of reversion was realized by the addition of either Versene or sodium acid sulfite. The addition of Versene did, however, increase the original brightness slightly.

The colored water-soluble materials which are formed during the accelerated aging of pulp were studied both by light absorbance methods and chemical analyses. The possible relationship between these colored bodies and the colored material formed during the heat degradation of low molecular weight carbohydrates was studied by experiments with isolated hemicelluloses.

The conclusions which have been obtained from the observations made during these studies are enumerated in the following pages.

CONCLUSIONS

The following conclusions can be presented concerning the brightness reversion obtained on heating bleached slash pine kraft pulp.

1. Reproducible brightness values and reproducible reversion rates can be obtained for bleached pulps prepared under standardized laboratory bleaching conditions, provided the bleaches are conducted simultaneously. Pulps within the 80 to 85% G.E. brightness range prepared simultaneously agree within 0.5% G.E. brightness and within 10% of the standard $\Delta k/s$ value.
2. Changes in the bleaching operations can cause marked changes in the yellowing tendency of the bleached pulp.
 - (a) Thorough washing can reduce reversion by 20%.
 - (b) Reversion is reduced by 20% by conducting the second hypochlorite stage at pH 10-11 instead of pH 6-7.
 - (c) Omission of the second caustic extraction stage in the standard five-stage bleach increases reversion by 50%.
3. The brightness alone of a given pulp cannot be used as an indication of its color stability.
4. The standard $\Delta k/s$ value of the fines, or short fibers, of bleached kraft pulp is approximately seven-tenths that of the long fibers. This difference exists whether the fibers are fractionated before or after bleaching.

5. The measurement of the relative reversion rates of pulps within a given type (e.g., slash pine kraft pulp bleached by a five-stage procedure) can be successfully carried out under widely varying humidity conditions at a fixed temperature.
6. The rate of brightness reversion of pulps aged at 100°C. and essentially 0% R.H. cannot be expressed as the slope of the curve of k/s versus the square root of the aging time since this curve is nonlinear.
7. Different pulps (e.g., bleached kraft and bleached Mitscherlich) differ in the changes in their brightness reversion effected by changes in relative humidity at a fixed aging temperature.
8. Although the yellowing rate ($\Delta k/s$ divided by time) of pulp effected by highly accelerated aging decreases rapidly with time, yellowing does not cease even on greatly extended aging.
9. Approximately one-half of the colored organic material formed during the accelerated aging of bleached pulp can be removed by water extraction. This water-soluble colored material has the following characteristics:
 - (a) It is insoluble in dioxane.
 - (b) The methoxyl content is about 0.2%.
 - (c) Neither vanillin, 6-chlorovanillin, nor vanillic acid are formed on alkaline nitrobenzene oxidation.
 - (d) Oligosaccharides of typical hemicellulosic nature constitute approximately one-fourth of the water solubles.

- (e) The light absorption curve of an aqueous solution of this material is a smooth curve from 700 to 200 m μ with increasing absorption at the lower wavelengths.
- (f) The colored component of this water-soluble material is of sufficiently high molecular weight to be retained on dialysis.
- (g) The major portion of this colored material is acidic.

From these characteristics it is concluded that this water-soluble color is nonligneous.

10. Isolated hemicelluloses do not yellow when heated in neutral solution, but they do yellow appreciably when heated in alkaline solution. The light absorption curves (200 to 700 m μ) differ considerably for the different hemicelluloses. The color of the water extracts of aged pulp resembles the visible (400 to 700 m μ) light absorption of pectic acid or arabogalactan solutions, while it resembles the ultraviolet (200 to 400 m μ) light absorption of xylan.
11. The presence of iron in the small quantities normally found in carefully bleached pulp (less than 20 ppm) apparently has little effect on brightness reversion. However, the reversion rate is increased by one-third as the pulp iron content is increased from 20 to 130 p.p.m.
12. The color stability of a pulp highly purified by acidified sodium chlorite bleaching and caustic extraction is decreased only slightly by a subsequent relatively drastic calcium hypochlorite bleach.

LITERATURE CITED

1. Hatch, R. S. Bleaching of alkaline-cooked pulps. In Ott's Cellulose and cellulose derivatives. p. 591-6. New York, Interscience Publishers Inc., 1943.

The bleaching of alkaline cooked pulps is discussed. It is stated that color reversion is one of the greatest drawbacks to bleached sulfate pulps but occurs to a much lesser extent than in sulfite pulps.

2. Giertz, H. W., Svensk Papperstidn. 48, no. 13:317-23(1945). (Translation)

The author's experimental work on the yellowing of bleached pulps is discussed. The color stabilities of eight paper samples were rated in the same order irrespective of aging temperature in the range 70 to 130°C. It was shown that extractable resin in sulfite papers is of secondary importance and presumably of even less importance in sulfate pulps due to the smaller quantities present. On the basis of experimental data Giertz believes yellowing is not due to lignin. He showed that a linear relationship exists between the product of copper number and carboxyl content, and the reversion rate. Oxidative attack resulting from the maintenance of a low pH during hypochlorite bleaching decreases color stability. Giertz found in one instance that the short pulp fibers, or fines, had a lower color stability than the long fibers of a bleached sulfite pulp.

3. Tongren, J. C. A reflectance method for determination of the rate of discoloration of papers and its application to the study of artificial aging of sulphite papers. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1937. 153 p.

A study was made of the accelerated discoloration of both unsized and rosin-sized sulfite papers. Rosin sizing was shown to effect a significant increase in the extent of yellowing. From the data obtained, Tongren concluded that the Kubelka and Munk number, k/s , is linearly related to the square root of aging time; therefore, the rate of discoloration was expressed as the slope of this curve. It was shown that the loglog of the aging rate was linearly related to the rosin content of sized pulp. Removal of the natural resins of pulp was shown to decrease the reversion rate slightly. Purification of sulfite pulp by caustic extraction greatly increases color stability. At 100°C., and above 25% relative humidity, increasing humidity was shown to increase the aging rate linearly.

4. McIntyre, J. W. The development of a quantitative technique for the evaluation of color stability of bleached pulps and the influence of natural aging and drying upon this evaluation. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1938. 125 p.

The accelerated rate of discoloration versus the humidity curve for a particular bleached Mitscherlich pulp was shown to have a minimum point at about 20% relative humidity. Several other pulps did not show this minimum rate; thus, relative humidity does not exert a proportional effect on the reversion rates of different types of pulp. It was postulated, but not proven, that accelerated aging would most nearly parallel natural aging if a normal amount of moisture was maintained in the sheet. Accordingly, 95°C. and 55.4% relative humidity were adopted as

standard aging conditions. Heat in the presence of excess moisture, a condition which exists during the machine drying of pulp and paper was found to increase color stability. Prolonged wet storage was shown to decrease the accelerated aging rate, while dry storage was without effect.

5. Mohrberg, W., Allgem. Papier-Rundschau no. 1:6-11(Jan 12, 1953): B.I.P.C. 23:591.

A discussion of several publications on the subject of brightness reversion and the author's views on this subject are presented. Mohrberg summarizes that for pulps of high color stability: (1) The pulp should be free of unbleached fiber. (2) The alpha-cellulose content should be greater than 90%. (3) The pH of a water extract of the pulp should be from 4.5 to 8.0. (4) The rosin content should be less than 0.5%. (5) Stable sizing agents should be used, and the use of alum should be avoided. (6) All process water should be free of heavy metals. (7) Fermentable materials should not be present in the pulp. (8) The fiber structure should not be destroyed by beating. (9) The pulp or paper should be protected during storage from light, heat, and humidity.

6. Swartz, J. N., Pulp & Paper Mag. Can. 47, no. 3:203-20(Convention Issue, 1946).

The theory of sulfate pulp bleaching and practical operating conditions are discussed extensively. The opinions of the author on color reversion are given but without experimental data. It

is stated that lignin degradation products are probably the basic cause of reversion, but for highly bleached pulps the presence of oxycellulose and hydrocellulose rather than lignin is responsible. Acidification is said to increase color stability; this is due to better diffusion of residues from within the fiber resulting from the change in the original swollen fiber structure.

7. Centola, G. Assoc. tech. ind. papetière Bull. 5, no. 3:111-15 (1951): B.I.P.C. 21:811.

Data are presented to show that the yellowing of a pulp is directly related to its pentosan content. Cotton linters, two grades of spruce sulfite pulp, spruce sulfate pulp, spruce semi-chemical pulp, and straw pulp were found to have pentosan contents of from 0.6 to 25% and brightness losses ranging from 5 to 22%.

8. Prelinger, H., Paper Trade J. 107, no. 1:121-6 (Sept. 15, 1938).

The author determined the oxygen consumed on heating the filtrates of bleached pulp slurries with acidified potassium iodate. Data are presented to show that this "oxygen number" is directly related to the rate of reversion of the pulp. Prelinger states that reversion is due both to bleach residues and to chemical and physical changes in the cellulose-lignin complex.

9. White, E. V., Swartz, J. N., Peniston, Q. P., Schwartz, H., McCarthy, J. L., and Hibbert, H., Paper Trade J. 113, no. 24:33-43 (Dec. 11, 1941).

Experimental data are given for the chlorination of wood pulps. The dissolution of chlorinated lignin into water or alkali is slow due to the necessity for diffusion. By analogy it is

thought that a similar diffusion of oxidized products is responsible for the brightness reversion of bleached pulps.

10. Beeman, L. A., and Reichert, J. S. Peroxides in pulp bleaching processes. In The bleaching of pulp. TAPPI Monograph no. 10. p. 233, 253, 260. New York, Technical Association of the Pulp and Paper Industry, 1953.

It is stated that the presence of dissolved iron in bleach liquors results in brightness reversion for all pulps. Peroxide-bleached pulps are alleged to possess greater color stability than hypochlorite-bleached pulps.

11. Casciani, F., and Storin, G. K., Tappi 33, no. 12:588-94 (Dec., 1950).

Groups of kraft pulps prepared with different bleaching sequences were tested for strength, viscosity, brightness and brightness reversion. The first three stages of all pulps were chlorination (C), caustic extraction (E), and hypochlorite (H). The sequence which resulted in the pulp of lowest color stability was CEHEH, and that which gave the most stable pulp was CEH-chlorine dioxide-alkaline peroxide. Chlorine consumption for the CEHEH bleached pulp was 4.6, 1.2, and 0.5% respectively, for the chlorination, first hypochlorite stage, and second hypochlorite stage; this pulp had an initial brightness of 84.1% G.E. and lost 5.1 points when heated one hour at 100°C. The CEH-chlorine dioxide-alkaline peroxide bleached pulp had an initial brightness of 83.2% G.E. and lost 3.0 points when heated at the same conditions.

12. Oleskevich, V., Pulp & Paper Mag. Can. 48, no. 3:123-6 (Convention Issue, 1947).

Data obtained during mill trials are presented to demonstrate that acidification of pulp to pH 5.5 immediately after bleaching increases color stability.

13. Klingstedt, G., Finnish Paper Timber J. 31, no. 7A:38-44(1949); B.I.P.C. 19:817.

The author presents experimental data to show that washing of a pulp after bleaching reduces reversion only slightly. It is stated that the mechanism of the yellowing of pulp on exposure to ultraviolet light is probably the same as that which occurs during heating.

14. Giertz, H. W. Personal communication, 1954.

Giertz stated that the aldehyde groups formed during the oxidation of carbohydrates are primarily responsible for the yellowing phenomenon. He believes that future investigations of brightness reversion should be concerned with the relationship of sheet density to color stability.

15. Launer, H. F., and Wilson, W. K., J. Research Natl. Bur. Standards 30, no. 1:55-74(Jan., 1943); J. Am. Chem. Soc. 71:958-62(March, 1949).

Although the reflectivity, or brightness, of bleached chemical pulps decreases on exposure to far ultraviolet light, it was demonstrated that a bleaching action occurs for irradiation of 330 to 440 mμ. It was postulated that this bleaching action is due to the formation of ozone. The subsequent color

stability of irradiated papers is less than that of unexposed papers. The decreasing order of photochemical stability of several different pulps was found to be: new rag, sulfite, old rag, soda and sulfite mixed, and newsprint.

16. Nolan, P. A., Van den Akker, J. A., and Wink, W. A., Paper Trade J. 121, no. 11:33-7(Sept. 13, 1945).

Data are presented for the yellowing of groundwood papers on exposure to light. It was shown that atmospheric oxygen, high temperatures, and high humidities all accelerate the rate of yellowing. It was stated that absorption of light by lignin is responsible for initiating at least a portion of the yellowing reactions. The data indicate that at least two photochemical reactions occur; a bleaching action is produced by radiation of wavelengths greater than 385 m μ , and yellowing is produced by radiation of wavelengths less than 385 m μ .

17. Hodge, J. E., J. Agr. Food Chem. 1, no. 15:928-40(Oct. 14, 1953).

A comprehensive review of the literature concerned with "browning" is given. The following reactions are discussed: sugar amine condensation, Amadori rearrangement, sugar dehydration, sugar fragmentation, amino acid degradation, aldol condensation, and aldehyde-amine polymerization.

18. Steele, F. A., Paper Trade J. 100, no. 12:37-42(March 21, 1935).

The relationships for reflectivity, the scattering coefficient, and the absorption coefficient originally developed by Kubelka and Munk are discussed.

19. Hoel, P. G. Introduction to mathematical statistics. p. 140-7. New York, John Wiley and Sons, Inc., 1947.

Student's t distribution is discussed, and the utilization of this distribution to obtain confidence intervals for a mean is described.

20. Snell, F. D., and Snell, C. T. Colorimetric methods of analysis Vol. II. p. 449-505. New York, D. Van Nostrand Co., Inc., 1937.

Procedures and discussions are given for colorimetric analyses of sugars and polysaccharides.

21. Dreywood, R., Ind. Eng. Chem., Anal. Ed. 18:499(1946).

A qualitative carbohydrate test is described.

22. Clibbens, D. A., and Ridge, B. P., J. Text. Inst. 18:T133-67 (1927).

The authors investigated the hypochlorite bleaching of cotton in the pH range 5 to 10 and showed that the greatest oxycellulose formation occurs at neutrality.

23. Aalto, E. O., Paperi ja Puu 36, no. 3:71-6(1954). (English abstract)

The brightness reversion of sulfite pulp bleached by chlorination, caustic extraction, and a hypochlorite stage was investigated. Yellowing was accelerated by a 24-hour treatment at 110°C. The following conclusions regarding yellowing were made: (1) Discoloration decreases as higher percentages of chlorine are consumed in the chlorination stage. (2) Discoloration decreases as higher caustic concentrations are used in the extraction stage. (3) For increased color stability

the hypochlorite stage should be conducted at low temperatures and at pH values above 7. (4) Sulfurous acid acidification and washing both decrease reversion. (5) Ether extraction reduces reversion. (6) An increase in sheet density results in an increase in reversion. (7) Bleaching at high consistencies results in decreased color stability. The author hypothesized that very short split fibers and fibers damaged during bleaching are primary causes of brightness reversion.

24. Wise, L. E., Murphy, M., and D'Addieco, A. A., Paper Trade J. 122, no. 2:35-43(Jan. 10, 1946).

The techniques used for the preparation of chlorite holo cellulose are given and the method is critically discussed.

25. Kaverzneva, E. D. [U.S.S.R.] Commun. 13th Intern. Congr. Pure and Appl. Chem. Stockholm, 1953:305-27; 328-51(1953); B.I.P.C. 24:268-269.

The author's work and that of others concerned with cellulose oxidation is discussed. It is stated that, with alkaline hypochlorite, cellulose is oxidized by the formation of primarily uronic and non-uronic carboxyl groups. In contrast, oxycelluloses resulting from hydrogen peroxide oxidation contain aldehyde groups on the second and third carbon positions.

26. Braun, R., and Rollinson, S. Unpublished work, 1952.

This work was concerned with brightness reversion of five stage-bleached kraft pulp. It included studies on the effect of sodium peroxide super bleaching on the yellowing of different fiber length fractions, and on the colored, water-soluble material formed during the natural aging of pulp.

27. Perila, O., and Roschier, H., Paper and Timber (Finland) 33, no. 9:269-72(Sept., 1951); B.I.P.C. 21:173.

An unbleached and a bleached sulfite spruce pulp and an unbleached sulfite aspen pulp were fractionated into four fiber-length intervals each with a Clark's Classifier. The average fiber length of the various fractions ranged from 0.2 to 0.9 mm. for the aspen pulp and from 0.3 to 2.6 mm. for the spruce pulp. Typical pulp analyses were made on all fractions. The authors concluded that for all three pulps the parenchyma cells contain less alpha-cellulose and more resins, fats, ash, wax, and lignin than the other fibers; these parenchyma cells also have a higher copper number and a lower average D.P. The parenchyma cells of the bleached spruce pulp were of considerably lower brightness than the tracheids.

28. Graff, J. H. Pulp and paper microscopy. p. 6-8. Appleton, Wis., The Institute of Paper Chemistry, 1942.

A method for the determination of the fiber length distribution of pulp is described. A minimum of 200 individual fibers are measured and are then classified within a series of length intervals. The weight percentages of fibers within the given length intervals and the average fiber length can then be calculated.

29. Landes, C. G., and Pollard, J. D., U.S. patent 2,492,821(Dec. 27, 1949). Studeny, J., and Pollard, J. D., U.S. patent 2,539,558 (Jan. 30, 1951).

These patents cover the use of dicyanimides and dicyandiamide to maintain the pH of paper close to neutrality during

aging and thus increase permanence. The data presented show an increase in the retention of fold durability after aging but no detectable increase in color stability.

30. Langwell, W. H., Tech. Bull. Tech. Sect., Brit. Paper and Board Makers' Assoc. 29, no. 1:21-8; no. 2:52-7(1952); 30, no. 6: 170-5(1953).

The impermanence of both the strength and the brightness of pulp is attributed to the formation of sulfuric acid from atmospheric sulfur dioxide within the sheet. Since this oxidation is catalyzed by metallic ions, a series of metal complexing agents were added to the sheets to inhibit or prevent catalysis. The sheets were then aged in a sulfur dioxide-air atmosphere, and after a specified time the sulfate content was determined. Several different compounds were found to inhibit sulfuric acid formation.

31. Reineck, E. A., and Lewis, H. F., Paper Trade J. 121, no. 20: 27-30(Nov. 15, 1945).

An unsuccessful attempt was made to find an anti-oxidant or inhibitor to stabilize groundwood against fading; 130 organic compounds were tested.

32. McLean, D. A., Ind. Eng. Chem. 32:209-13(Feb., 1940).

A study was made of the ash constituents of unbleached kraft pulp and their extraction by dilute hydrochloric acid and distilled water. It was shown that exchange reactions of pulp account for the major portion of the ash content. It was found possible to remove all ash except silica by washing the pulp with hydrochloric acid and water.

33. Keller, E. L., and Simmonds, F. A., Paper Trade J. 115, no. 14: 98-104 (Oct. 1, 1942); Mimeo No. R1405 Forest Products Laboratory.

Wood chips were found to contain approximately 6 to 7 p.p.m. iron while unbleached pulp contains 30 to 200 p.p.m. iron. It was stated that the digestion process is the principal source of contamination. The iron content of loblolly pine kraft pulp produced in a stainless steel digester was 77 ppm but was 200 p.p.m. for pulp produced in a steel digester. It was shown that pulps irreversibly adsorb iron from aqueous solutions; the amount adsorbed increases with increasing iron concentration and with increasing alkalinity. Both chlorination and hypochlorite bleaching tend to decrease pulp iron content.

34. Kolthoff, I. M., and Sandell, E. D. Textbook of quantitative inorganic analysis. 3rd ed. p. 635-7. New York, The Macmillan Company, 1952.

The procedure for the quantitative colorimetric determination of iron by thiocyanate is given; this procedure is based on the formation of a ferric-thiocyanate complex. The effect of thiocyanate concentration, the influence of acidity on color, and interfering cations and anions are discussed.

35. Pigman, W. W., and Goepf, R. M., Jr. Chemistry of the carbohydrates. p. 134-5. New York, Academic Press, Inc., 1948.

The color reactions of carbohydrates are discussed.

36. Somogyi, M., J. Biol. Chem. 160:62-4 (1945).

An alkaline copper reagent is used for the determination of the reducing power of carbohydrates; the reduced copper is then determined iodimetrically.

37. Stone, J. E., and Blundell, M. J., Anal. Chem. 23, no. 5:771-4(May, 1951).

A micromethod for the alkaline nitrobenzene oxidation of lignified materials is described. The entire procedure is given including construction of the 2-ml. stainless steel bombs which were used, typical charge and operating conditions, and the chromatographic separation and quantitative determination of vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde..

38. Jayne, J. E. Study of the alkaline nitrobenzene oxidation products of chlorite lignin. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1953. p. 79-85.

The qualitative separation of the alkaline nitrobenzene oxidation products of chlorite lignin by paper partition chromatography is discussed.

39. Dunlop, A. P., and Peters, F. N. The furans. p. 308-9, 385-99. New York, Reinhold Publishing Corp., 1953.

A comprehensive review of the literature on 2-furaldehyde is given.

40. Jayme, G., and Köppen, A. von, Das Papier 4, no. 19/20:373-8; no. 21/22:415-20; no. 23/24:455-62(Oct., Nov., Dec., 1950); B.I.P.C. 21:394.

The results of a study of the chemical and physical differences of sulfate and sulfite pulps are discussed. The more difficult bleachability of sulfate pulps is attributed both to the chemical differences in thiolignin and lignosulfonic acids and also to the difference in the accessibility of the lignins to the bleaching agents; evidence is presented to show that

the lignin of sulfate pulps is distributed throughout the fiber while that of sulfite pulps is concentrated primarily on the outer surface of the fiber.

41. Giertz, H. W., *Svensk Papperstidn.* 56, no. 23:893-9(Dec. 15, 1953); *B.I.P.C.* 24:473.

Giertz believes that all of the differences between sulfite and kraft pulps can be explained by, and are probably due to, the formation of new carbohydrate bonds, such as ether linkages during alkaline pulping. This hypothesis was first presented by McKinney.

42. Brecht, W., and Michaelis, R., *Papier-Fabr.* 38, no. 30:173-80, no. 31/32:181-6(1940); *B.I.P.C.* 11:206.

The strength permanence of sheets made from both sulfite and sulfate pulps was determined after heating 24 hours at 120°C. The sulfate pulps were more permanent than the sulfite pulps, and the authors hypothesized that this was due to the greater hygroscopicity of the former. The pulps were fractionated according to fiber length, but no differences in heat stability were observed for fractions within a given pulp. The only method observed to increase the heat stability of a sulfite pulp was to pressure cook it in alkali.

43. Hanson, F., *Paper Ind.* 20, no. 11:1157-63(Feb., 1939).

Marked differences were observed in the extent of natural yellowing which had occurred in the individual sheets of a book published in 1576, and an investigation was made to determine the

reasons for these differences. Fiber analysis showed both the brown and white sheets to be composed of a mixture of linen and cotton. After an analytical study it was concluded that the presence of calcium carbonate, by virtue of its buffering properties, was responsible for the color stability noted in some of the sheets. The calcium carbonate content was about 2% for the brightest sheets and about 0.4% for the most discolored sheets.

44. Herzog, R. Chemische technologie der baumwolle. p. 11-12. Berlin, Springer, 1928. (Translation)

A discussion is given of the brown color formation which occurs when cotton is heated with steam. It is stated that this process has been used to give American cottons the appearance of Egyptian Mako-cottons.

APPENDIX

EXPERIMENTAL BLEACHES

The chlorine consumptions, original brightnesses, and $\Delta k/s \times 10^4$ values for a two-hour treatment at 100°C., 0% R.H. have been given for all experimental bleaches in Table XXXV.

The experiments and purposes for which these bleached pulps were prepared are given in Table XXXIV.

TABLE XXXIV

LOW CONSISTENCY BLEACHES

Bleached Pulp Designation	Experimental Use
101 through 103 112 through 115 149 through 157	The reproducibility of both original brightness and $\Delta k/s$ values
115 through 119 137 through 145	The effect of hypochlorite stage pH on reversion
146 through 148	The effect of washing on reversion
158 through 163	The bleaching of fractionated pulp
166 through 168	The effect of bleaching stage consistency on reversion
169-OL through 169-3LR	The effect of duration of second caustic extraction on reversion
120 and 130	Prepared for fiber length fractionation experiments
164 and 165	Prepared for water extraction after autoclaving treatment
170-A through 170-C	Used for $\Delta k/s$ versus temperature and humidity aging curves
180	Used for the determination of the rate of water-soluble color formation

TABLE XXXV

DATA FOR ALL EXPERIMENTAL BLEACHES

Bleach Design- nation	Chlorin- ation	Chlorine Consumed, % (Expressed as Cl ₂)		Total	Orig- inal Bright- ness, % G.E.	Standard Δk/s x 10 ⁴	Points Bright- ness Drop During Standard Aging
		First Hypo- chlorite	Second Hypo- chlorite				
101	4.68	1.27	.38	6.33	78.6	231	6.1
102	4.89	1.37	.43	6.69	78.2	209	5.6
103	4.95	1.38	.46	6.79	75.8	269	6.0
112	4.69	1.02	.25	5.96	79.9	187	5.5
113	4.75	1.06	.24	6.05	80.5	202	6.1
114	4.70	.94	.24	5.88	80.9	170	5.4
115	5.00	1.25	.39	6.64	81.7	281	8.4
116	5.00	1.22	.25	6.47	81.2	255	7.6
117	5.00	1.16	.23	6.39	80.1	261	7.3
118	5.00	1.14	.24	6.38	78.7	253	6.6
119	5.00	1.21	.26	6.47	81.0	237	7.1
120	5.74	1.23	.27	7.24	84.2	96	4.0
130	5.51	1.37	.28	7.16	84.6	168	6.5
131	5.50	1.22	.27	6.99	81.9	218	7.0
132	5.50	1.19	.28	6.97	79.9	244	6.8
133	5.50	1.24	.26	7.00	80.6	195	6.0
134	5.50	1.26	.26	7.02	81.2	212	6.5
136	5.50	1.21	.23	6.94	80.2	256	7.2
137	6.21	.28	.21	6.70	82.3	143	5.0

TABLE XXXV (Continued)

DATA FOR ALL EXPERIMENTAL BLEACHES

Bleach Designation	Chlorination	Chlorine Consumed, % (Expressed as Cl ₂)		Total	Original Brightness, % G.E.	Standard $\Delta k/s \times 10^4$	Points Brightness Drop During Standard Aging
		First Hypo- chlorite	Second Hypo- chlorite				
138	6.21	.28	.21	6.70	82.6	153	5.2
139	6.21	.28	.22	6.71	82.6	150	5.3
140	6.21	.28	.23	6.72	83.3	156	5.7
141	6.21	.28	.24	6.73	83.2	160	5.8
142	6.21	.28	.25	6.74	83.7	164	6.1
143	6.21	.28	.25	6.74	83.2	163	5.9
144	6.21	.28	.24	6.73	82.9	174	6.1
145	6.21	.28	.22	6.71	82.6	185	6.3
147	5.57	1.16	.31	7.04	80.7	155 to 186	4.9 to 5.7
148	6.00	1.26	.24	7.50	80.8	208 to 245	6.3 to 6.9
149	4.72	1.23	.26	6.21	80.2	303	8.4
150	4.75	1.19	.25	6.19	80.2	300	8.5
151	4.82	1.18	.26	6.26	80.1	307	8.7
152	4.84	1.18	.28	6.30	80.6	257	7.4
153	4.87	1.18	.28	6.33	81.2	264	7.8
154	4.83	1.18	.28	6.29	81.5	243	7.4
155	4.84	1.16	.26	6.23	82.1	250	7.8
156	4.69	1.17	.27	6.13	82.3	271	8.4
157	4.75	1.18	.27	6.20	81.7	272	8.1
158	5.62	1.12	.30	7.04	83.5	151	5.6

TABLE XXXV (Continued)

DATA FOR ALL EXPERIMENTAL BLEACHES

Bleach Design- ation	Chlorin- ation	Chlorine Consumed, % (Expressed as Cl ₂)		Total	Orig- inal Bright- ness, % G.E.	Standard $\Delta k/s \times 10^4$	Points Bright- ness Drop During Standard Aging
		First Hypo- chlorite	Second Hypo- chlorite				
159	5.50	1.19	.33	7.02	82.3	147	5.1
160	5.24	1.20	.32	6.76	81.5	226	7.0
161	5.38	1.20	.32	6.90	81.8	191	6.2
162	5.37	1.17	.32	6.86	82.0	211	6.8
163	5.47	1.18	.31	6.96	81.9	190	6.2
164	5.98	1.41	.35	7.74	85.1	123	5.2
165	5.35	1.38	.29	7.02	84.1	127	5.1
166	5.39	1.35	.17	6.91	82.8	141	5.1
167	5.36	1.42	.20	6.98	83.8	128	5.0
168	5.42	1.43	.21	7.06	82.6	157	5.5
169-OL	5.17	1.15	.24	6.56	77.0	243	5.9
169-OR	5.17	1.15	.23	6.55	76.9	236	5.7
169- $\frac{1}{2}$ L	5.17	1.15	.23	6.55	78.5	246	6.4
169- $\frac{1}{2}$ R	5.17	1.15	.23	6.55	78.1	201	5.3
169-1L	5.17	1.15	.24	6.56	78.5	210	5.6
169-1R	5.17	1.15	.24	6.56	78.7	207	5.6
169-2L	5.17	1.15	.24	6.56	78.7	165	4.6
169-2R	5.17	1.15	.23	6.55	79.0	182	5.1
169-3LR	5.17	1.15	.24	6.56	79.0	165	4.7

TABLE XXXV (Continued)
DATA FOR ALL EXPERIMENTAL BLEACHES

Bleach Designation	Chlorination	Chlorine Consumed, % (Expressed as Cl ₂)		Total	Original Brightness, % G.E.	Standard $\Delta k/s \times 10^4$	Points Bright- ness Drop During Standard Aging
		First Hypo- chlorite	Second Hypo- chlorite				
170-A	5.33	1.45	.36	7.14	81.3	149	4.9
170-B	5.33	1.45	.32	7.10	83.6	97	3.9
170-C	5.33	1.45	.33	7.11	83.7	83	3.4
180	5.42	1.36	.21	6.99	85.2	94	4.2

Maximum and minimum values of the data in Table XXXV are given in Table XXXVI.

TABLE XXXVI

MAXIMUM AND MINIMUM VALUES

	Numerical Value	Bleach Designation
Maximum original brightness	85.2%	180
Minimum original brightness	75.8	103
Maximum standard $\Delta k/s \times 10^4$	307	151
Minimum standard $\Delta k/s \times 10^4$	94	180
Maximum total chlorine consumption	7.74%	164
Minimum total chlorine consumption	5.88%	114

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