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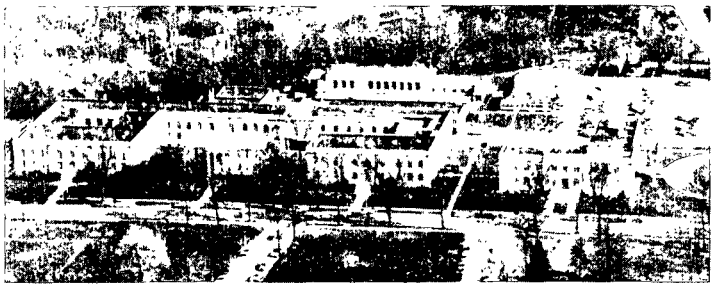

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

RESEARCH PROPOSAL 2068

for

Extension of Group-Sponsored Cooperative
Research Project 2942

on

Increased Yields in Alkaline Pulping

January 29, 1973

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GROUP PROJECT 2942

"Increased Yields in Alkaline Pulping"

BACKGROUND

On April 1, 1970 a group project was established at The Institute of Paper Chemistry directed at conducting fundamental long-range studies on reactions taking place during commercial alkaline pulping conditions. The first phase of this long-range program, a study of the peeling reaction under the conditions of kraft pulping, comprised the initial contract period. This research has been carried on with the cooperation of 15 member companies.

RESULTS OBTAINED

The results obtained in this first phase study on the peeling reaction of carbohydrates under the conditions of kraft pulping were reported in four progress reports, the last of which was dated November 24, 1972. In order to study carbohydrate reactions in alkaline solutions at temperatures up to 170°C. it was necessary to construct a flow reactor capable of operating at very short reaction times and at high temperatures under pressure. The evolutionary development and construction of this flow reactor has been described in detail.

We have been able to follow the alkaline degradation of cellobiose at temperatures up to 170°C. to demonstrate the disappearance of the disaccharide and the appearance of glucose as a product of the peeling reaction. We have been able to obtain quantitative data for these sugars for very short reaction times in the millisecond range and to determine the rates of disappearance and formation of these two sugars, respectively. The data presented in Progress Report Four demonstrated the high precision and accuracy of the flow reactor.

The development and testing of the high temperature-high pressure flow reactor was the most important contribution of the first phase of this long-range program. This remarkable achievement, previously considered unattainable, has given us the means to investigate reactions of both organic and inorganic compounds under the high temperature and high pressure conditions extant during the alkaline (or nonalkaline) pulping of wood. This ability, together with information obtained since our original Research Proposal No. 1612 dated February 12, 1970 for this cooperative research project,

has led us to a reappraisal of this long-range research program directed toward increased yields in alkaline pulping. This situation was anticipated in the original Proposal No. 1612 in which it was noted that "The results, experience, and expertise obtained during Phase One of this program will enable us to outline successive phases in more detail later in the program."

RESTATEMENT OF THE PROBLEM AND APPROACH TO ITS SOLUTION

This project, directed toward the obtainment of high yields in alkaline pulping, is concerned with the investigation of the chemistry of the alkaline degradation of polysaccharides in kraft pulping, especially the peeling reaction, and with the prevention of such degradation. The first phase of this project comprised studies on the peeling reaction which was found to be extremely fast at temperatures of 150 - 170° C. It is well known that carbohydrates are solubilized in kraft pulping liquors at temperatures much below these and that a substantial proportion of possible pulp yield is lost at these lower temperatures in kraft digesters. To counteract these losses in early stages of kraft pulping, various additives have been employed to "bind" or alter the carbonyl end groups which are responsible for the peeling reaction and loss in yield, but their use has been relatively empirical with no knowledge of reaction rates. For optimum use of additives, it is imperative that the following reaction rates be known: 1) peeling reaction; 2) additive reaction; and 3) additive decomposition. These three reactions have been discussed briefly in Progress Report Four under the heading of FUTURE WORK. The figure from Report Four illustrating these reactions is reproduced in the present proposal as Figure 1.

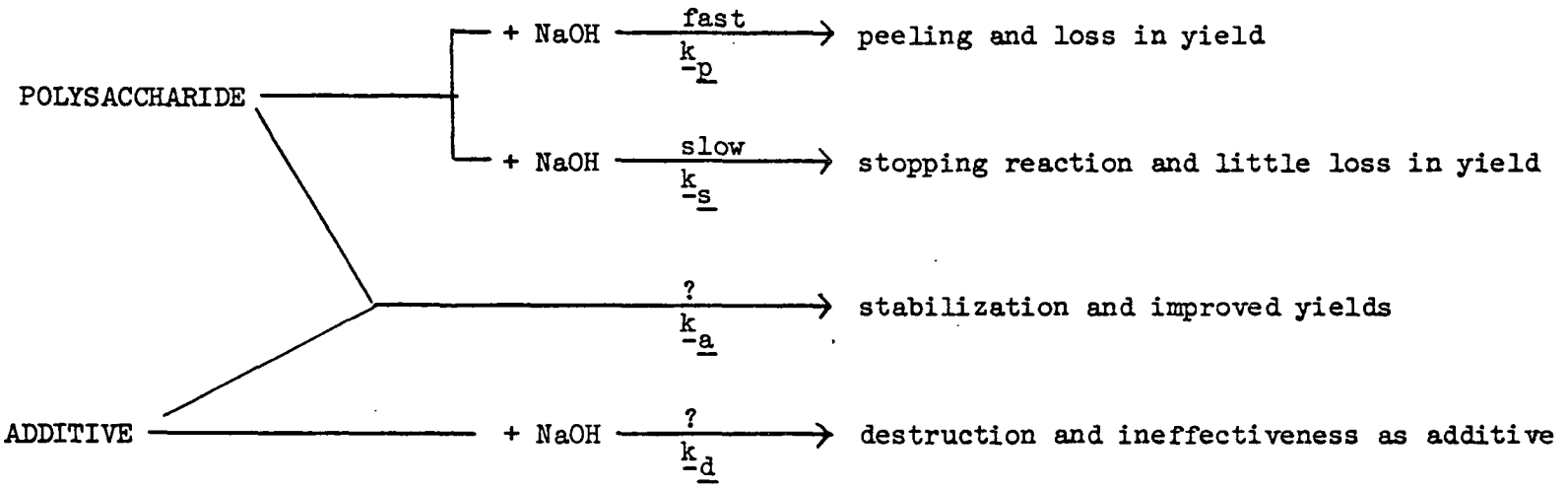
Briefly, we are concerned with finding the optimum conditions for employing these additives during the heat-up period of a kraft cook where ideally the reaction of additives should be rapid and the degradation by peeling should be slow. The industrial literature has noted some attempts to obtain such conditions where preliminary treatments have been carried out at pH values lower than those used in the kraft cook, but investigations have been brief. In the present proposal we are suggesting a study of the several reactions

involved, of the effect of both temperature and pH on the interplay of these competing reactions, and of the best conditions for an economical and efficient use of such additives. In addition, we are proposing an investigation of the stopping reaction, a reaction which has been suggested as a factor in the heat-up stage of the kraft cook. Finally, since the lignin-carbohydrate complex has been related to the peeling reaction, we are proposing an investigation of the kinetics of alkaline decomposition of the model phenyl glucoside.

State of the Art

The carbonyl end group on a polysaccharide chain renders an adjacent glycosidic bond susceptible to alkaline attack and the creation of a new end group. This successive breaking of glycosidic bonds, a "peeling" reaction, can be prevented by alteration of the carbonyl group. The additives employed to effect this alteration are generally either reducing agents or oxidizing agents. In some cases, nitrogen bases have been used, but their action has not been fully explained. Usually the additives have been applied in alkaline solution at a pH of 10 or above, and in most instances in the region of pH 12-14, that of the cooking liquor.

As a functional group reaction site, the carbonyl group is quite susceptible to changes in pH, and most carbonyl reactions are usually performed in the pH range of 4 to 10. Reactions of substituted hydrazins or hydroxylamine with sugars are ordinarily done at pH 4, and borohydride reductions at pH 9 to 10. Only occasionally are reactions with the usual carbonyl group reagents effected outside this pH range.



In heat-up of cook, $k_p >>> k_s$, so mostly peeling and little stopping action at this stage?

What is k_a/k_p ? How is this ratio affected by temperature?

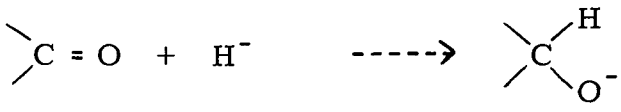
by pH?

What is k_a/k_d ? How is this ratio affected by temperature?

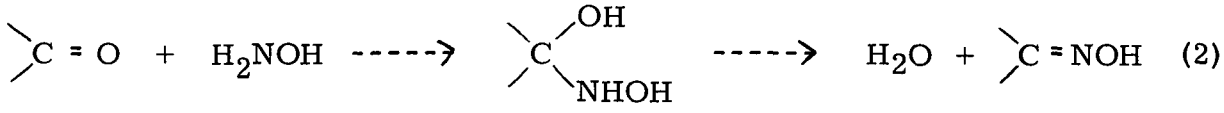
by pH?

Figure 1. Consideration of Optimum Conditions for Stabilization and Increased Yields

The double bond between the carbon and oxygen of the carbonyl group is a polarized bond creating a positive charge on the carbon atom. The carbon, by virtue of this charge or dipole moment, is electron-deficient and will react with electron-rich reagents. These latter reagents are called nucleophiles because their negative nature causes them to be attracted to the positively charged carbon nucleus. In contrast, the carbon is electrophilic or electron-seeking. Type reactions are shown in equations (1) and (2).



(1)



(2)

In both reactions we have an addition to the double bond with the electron-rich part of the additive attacking the carbon first. In equation (1) the hydride ion (from sodium borohydride*) is bonded to the carbon, and since carbon is normally a "neutral" atom, the negative charge is transferred to the oxygen, and an alcoholate anion is formed. This anion can pick up a proton from the solution to form the corresponding alcohol.

In the reaction of equation (2), while the hydroxylamine molecule is neutral, there are unshared electrons on the nitrogen, so that this compound reacts similarly. The nitrogen is bonded to the carbon, the negative charge

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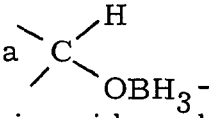
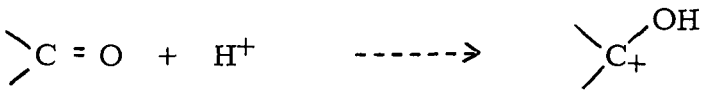
*The BH_4 anion actually reacts to form a  intermediate which decomposes into the alcoholate anion, boric acid, and hydrogen.

from these electrons moves to the oxygen to form the grouping $\diagup$C(OH)NHOH, and this is dehydrated subsequently to give the oxime.

The effect of pH on the reactivity of the carbonyl group is shown in equations (3) and (4).



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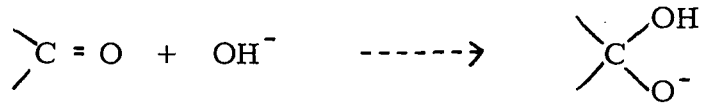


(4)

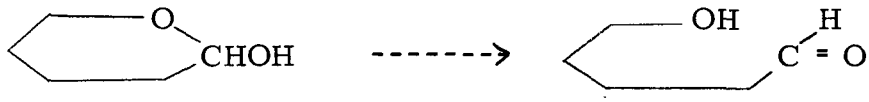
At a low pH (equation (3)), the acidic proton will attack the double bond, link with the oxygen, and cause the carbon to take on a positive charge. In this manner, at the lower pH region the electrophilicity of the carbon is increased and the carbon becomes more reactive. Unfortunately, the attacking nucleophile such as borohydride anion or an hydroxylamine molecule will also pick up a proton at the same time, and by virtue of a lessened negative charge, will become less nucleophilic and less reactive.

A similar effect, but in the opposite direction, is obtained when the pH is increased greatly. As shown in equation (4), the hydroxyl anion adds to the carbonyl creating a negative charge on the oxygen which reduces greatly the electrophilic nature of the carbon and the carbon's reactivity. On the other hand, in alkaline solution a compound such as hydroxylamine will pick up a negative charge and become more reactive.

Thus, in extremely low or extremely high pH regions the reactivity of either the carbonyl group or of the attacking reagent is affected adversely,

and a satisfactory compromise is usually obtained in the pH region of 4 to 10 where both the carbonyl group and the nucleophilic reagent maintain high reactivity toward each other.

Finally, it should be noted that the carbonyl group in a sugar molecule or in an end unit of a polysaccharide chain exists in the form of a hemi-acetal or ring, and this ring is opened readily by a small amount of alkali as shown in equation (5). This accounts for the fact that the carbonyl group in sugars



(5)

and polysaccharide chains is reduced by borohydride only at pH 9 to 10 and not at lower pH values, since the CHOH group is not attacked by the borohydride ion. On the other hand, hydroxylamine or various hydrazine derivatives will react readily with glucose or other sugars at pH 4. It is obvious that a different mechanism is responsible for these reactions than for the borohydride reduction.

Generally, reactions of carbonyl compounds with amine derivatives are not conducted in strongly alkaline solutions such as those employed in kraft pulping, although Anderson and Jencks (1) investigated the reaction of substituted benzaldehydes with hydroxylamine at pH 7 to 10 and found an increase in reaction rate with increasing pH. This was a base-catalyzed dehydration as pictured in the second step of equation (2). It should be pointed out this investigation was carried out with carbonyl groups of simple aromatic aldehydes, whereas the carbonyl groups of polyhydroxy compounds such as those

of sugars comprise much more complex reacting entities and give rise to other reactions. A common example is the decomposition of sugar hydrazones in hot alkaline solution to give chain splitting and small fragments (2).

This is an oversimplified picture of the effect of pH on reactions of the carbonyl group, but it will serve to impress the reader with the importance of pH and why the rate of such reactions should be studied under varying conditions of temperature and pH.

Types of Additives Used in Alkaline Pulping

The additives used to alter the carbonyl group in polysaccharides and thus prevent peeling fall into four general classes as follows:

(a) reducing agents that convert the end unit into an alditol;

(b) oxidizing agents that convert the end unit into an aldonic acid;

(c) compounds that add to the double bond and create new groups which are stable to alkali; and

(d) conditions or ions that cause the end unit to rearrange into a metasaccharinic acid (the "stopping reaction").

Screening tests carried out with hydrocellulose or with wood have demonstrated that sodium borohydride, sodium polysulfide, hydroxylamine, hydrogen sulfide, and anthraquinone sulfonic acids are the most effective additives (3, 4, 5). These additives are generally used in an amount of 1 to 5% based on the polysaccharide or on the wood. Cyanide has also been employed as a preliminary treatment at low temperature and at a low pH of 9 to 10 (6). Surprisingly, the strong reducing agent, hydrazine, is quite ineffective, and must be employed in large amounts in order to exert any protective action.

Reducing Agents

Sodium borohydride. Reduction with sodium borohydride is conducted generally in aqueous solution at pH 9 or above. Below this pH the reagent is unstable, and hydrogen is evolved. Davis and Swain (7) demonstrated that the decomposition is catalyzed strongly by hydrogen ion ($k = 10^6$ mole^{-1} sec^{-1} at 25°C.) and only weakly by water ($k = 10^{-9}$). Thus, in strong alkali, where the (H^+) concentration is very small, the hydrolysis will be very slow. However, at higher temperatures, catalysis by water becomes more effective, and Hartler (8) found the half-life of sodium borohydride in normal sodium hydroxide at 100°C. and at 170°C. to be about 40 minutes and 40 seconds, respectively. (The latter value was determined by extrapolation.) Messmer and Jolly (9) obtained a rate expression for the decomposition of sodium borohydride at lower temperatures for the pH range of 4 to 14. Application of this rate expression to Hartler's conditions gives approximately the rates found by Hartler (8).

An aqueous solution of sodium borohydride has a pH of about 10, and this pH may be the optimum for reduction. It is sufficient for ring opening of a sugar, but not high enough to place a negative charge on the carbonyl group and thus reduce its reactivity. At higher pH values the reactivity of the carbonyl group, and the rate of peeling will definitely increase (k_a and k_p in Figure 1). In preliminary studies along this line we have found that reductions of cellobiose with sodium borohydride at pH 10 gave only the reduction product cellobiitol, but reductions at pH 13 yielded, in addition, a small amount of reduced glucose, a product of peeling. The k_a/k_p ratio has decreased in the change from pH 10 to pH 13.

The literature is rather vague about the rate of borohydride reduction of carbonyl groups. One of the hydrogens is more reactive than the other three in reactions with water. Thus, $NaBH_4$ readily forms $NaB(OH)H_3$, but later steps give only $NaB(OH)_4$ and no $NaB(OH)_2H_2$ or $NaB(OH)_3H$. Since the first hydrogen is lost so readily in reaction with water, a similar pattern might follow in reductions, giving a fast initial reduction and a slow reaction of the $NaB(OH)H_3$ with the water present.

Hydrogen sulfide. The use of hydrogen sulfide for increasing the yields in kraft pulping has been explored extensively by investigators of MacMillan Bloedel Inc. (5, 10, 11). Hydrogen sulfide has the advantage of being essentially one of the ingredients of a kraft cook so that no foreign ions are introduced to complicate the recovery process. Its action is to convert the carbonyl group into a thio-alcohol group, $-CH_2SH$, which is stable toward alkali (11). Hydrogen sulfide is applied in a pretreatment of the chips in a weakly alkaline buffer. The reagent is stable, so there is no problem of its loss. The buffer system is prepared with hydrogen sulfide supplied under pressure (10), and an optimum temperature of 125°C. is employed to compromise between reductive action and rate of alkaline degradation.

Thioglycollic acid. The proposed use of thioglycollic acid by Fisher, Lenz, and Hider (12) might be considered analogous in its effect to hydrogen sulfide (5, 10), especially at lower pH values.

Other Reducing Agents. Catalytic hydrogenation and the use of hydrazine have been suggested for increasing yields in kraft pulping, but these reagents will not be considered here as applicable reducing agents.

Oxidizing Agents

Sodium polysulfide. This additive has been investigated extensively, and many reports have appeared on its preparation and use for increasing yields in kraft pulping (13). Polysulfide acts to convert the end units to aldonic acids, and Alfredsson and Samuelson (14) have found mannonic acid to be the main acid present in polysulfide black liquor.

Sodium polysulfide is not very stable at higher temperatures. According to Sanyer and Laundrie (15) the half-life is about 40 minutes at 140°C. and only 10 minutes at 160°C. Teder and co-workers (16) have explored in depth the chemical reactions involved in the decomposition of the polysulfide system.

Anthraquinone sulfonates. Recently Bach and Fiehn (4) suggested the use of various anthraquinone sulfonic acids as oxidants in alkaline solution. These additives appear to be quite efficient in amounts up to 5% based on the wood. The stability of these compounds in alkali is good, so that they can be added directly to the pulping liquor.

Other Oxidizing Agents. Many other oxidants such as chlorite and peroxides have been investigated. These will not be given attention here. The action of hydroxylamine, which may be considered to be an oxidizing agent, is discussed in the next section under nitrogen compounds which add to the double bond of the carbonyl group.

Nitrogen Compounds Which Add to the Carbonyl Double Bond

Hydroxylamine. This amine derivative is usually used as a salt, the sulfate and hydrochloride being the most common commercial ones. The free

base is relatively unstable and gradually decomposes into ammonia, nitrogen, and water. This decomposition is favored by alkali.

Hydroxylamine is more effective in stopping the peeling reaction than are sodium borohydride and other reagents (4). However, the end group formed, presumably an oxime (see equation (2)), is probably converted by hot alkali into two products:

(a) hydrolysis to regenerate the carbonyl group (reversal of equation (2)) and

(b) dehydration of the oxime to give the nitrile which decomposes in the presence of water and alkali to give the aldonic acid and ammonia (equation (6)).

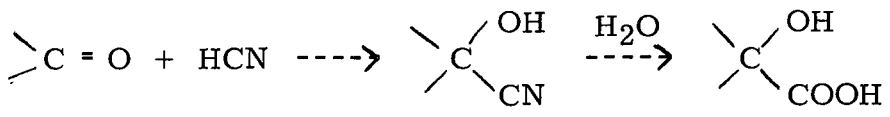
Thus, the formation of the aldonic acid via the nitrile is actually an oxidation,

$$-CH=NOH \longrightarrow H_2O + -C\equiv N \xrightarrow{OH^-} -COOH + NH_3 \qquad (6)$$

with the original hydroxylamine being reduced to ammonia. Undoubtedly, the nitrile or aldonic acid groups are stable groups which are resistant to peeling. Clayton and Jones (17) noted that a very high pH and a temperature near 100°C. were required to form the oxime of hydrocellulose. In contrast, cellobiose did not react with hydroxylamine in hot aqueous alkaline solution to form the oxime, but yielded a dark product instead. Better results were obtained in alcoholic alkaline solution.

Hydrogen cyanide. The well-known Kiliani reaction comprising the addition of hydrogen cyanide to a sugar for the purpose of increasing the length of the carbon chain (equation (7)), is the subject of a patented

pretreatment for increasing the yield of kraft pulps (6). The pretreatment is

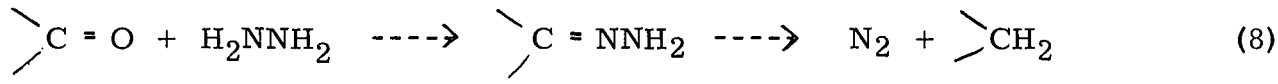


(7)

conducted at pH 9 to 10 at temperatures below 90°C. In subsequent hot alkaline treatments the cyanohydrin, or the C_7 hydroxyacid formed by saponification, is a stable end group and a good protection against peeling.

This type of stabilization might be considered similar to the action of hydroxylamine noted above in that both reactions involve an intermediate nitrile. The hydroxylamine forms a C_6 nitrile and then a C_6 aldonic acid, whereas the cyanide forms a C_7 nitrile and then a C_7 aldonic acid. In addition, both reagents are relatively unstable in alkaline solution, and the intermediates formed, the oxime and the cyanohydrin, are both subject to hydrolysis to regenerate the original carbonyl compound.

Hydrazine. This amine derivative has proved relatively ineffective in preventing peeling during kraft pulping unless extremely large amounts are employed (for example, 25% compared with 5% for hydroxylamine based on the wood) (3, 4, 5). However, the reagent is stable in alkaline solution. The action of this reagent is possibly that of a reducing agent in the manner of the Wollf-Kishner reaction (18) often employed to convert carbonyl groups to methylene groups in synthetic organic chemistry (equation (8)). At higher temperatures, about 170°C. in high boiling solvents, nitrogen is evolved, and a methylene group is formed. The Wollf-Kishner reaction is usually



(8)

carried out in high boiling nonaqueous solvents such as ethylene glycol, and it is entirely possible that the same reaction may not occur in an aqueous system such as that of the kraft cook.

The Lignin-Carbohydrate Complex

Although the suppression of the peeling reaction has beneficial effects relating to yields in alkaline pulping, adverse effects with respect to delignification have been noted (19). Presumably, the lignin is linked to the hemicellulose polysaccharides by glycosidic and/or ether linkages, and peeling of the polysaccharide facilitates breaking of the lignin-carbohydrate bond. A lignin unit, linked to the polysaccharide in the vicinity of a carbonyl end group, could be split off by alkali in a β-elimination in a manner similar to the splitting off of the glucose unit in cellobiose or the splitting off of the bulk of a polysaccharide chain from the end group unit in a peeling reaction.

The rate of hydrolysis of phenyl and other glucosides with potassium hydroxide solution at 100°C. has been studied by Dyfverman and Lindberg (21), and Kenner and Richards (22) have investigated the cleavage of a benzyl ether group from carbon-3 of glucose under mild alkaline conditions.

The Stopping Reaction

The alkaline rearrangement of the end unit in a polysaccharide to form a metasaccharinic acid, commonly referred to as the stopping reaction, is relatively slow compared with the peeling reaction. Lindberg and co-workers (23) demonstrated that the stopping reaction was favored relative to the peeling

reaction by lower temperatures and by the use of calcium hydroxide instead of sodium hydroxide. These investigators did not compare the rates of the two reactions directly, but reported only the yield of stopped material, a glucosyl-metasaccharinic acid formed from cellobiose. These studies were performed in dulute alkali (0.02 Molar sodium hydroxide and calcium hydroxide), and no information is available for higher alkali concentrations or on the effect of buffer solutions.

Although the formation of glucosyl-metasaccharinic acid in support of the stopping reaction has been reported both in alkaline solution (23) and in polysulfide cooking liquor (24), Rowell (25) treated cellobiose with aqueous alkali and could find no glucosyl-metasaccharinic acid.

The greater effect of calcium over sodium ions was studied by LeMon and Teder (26) in an investigation of polysulfide pulping in calcium and in sodium systems.

PROPOSED RESEARCH PROGRAM

The flow reactor constructed during the first phase of this group cooperative research program will enable us to measure reaction times from minutes to as small as the single digit millisecond range at temperatures either above or below 100°C. We will employ this reactor in the studies outlined below.

The proposed program is divided into three parts. The first two, comprising the stopping reaction and the stability of additives and the rate of their reaction with carbohydrates, respectively, are closely related. Both are concerned with carbohydrates and additives, and both relate directly with yields in alkaline pulping. The third part pertains to the lignin-carbohydrate complex and the relation of peeling to delignification. The relevancy of the third part to alkaline pulping yields is more indirect than those of the first two parts.

I. The Stopping Reaction

The rate, k_s, of the stopping reaction, the rearrangement of the end sugar unit into a metasaccharinic acid, will be studied in alkaline solutions of varying concentrations and types and at various temperatures.

The work of Lindberg and co-workers (23) will be repeated initially, first with a small excess of alkali, and then with more concentrated solutions. We will try to establish the presence of an alkali-stable gycosidic bond after the action of alkali for extended periods of time. Reactions will be monitored for glycosidic bonds by the phenol-sulfuric acid procedure of

Painter (27) and for cellobiose left in the alkaline system by derivatized gas chromatography.

If this approach is successful and the stopping reaction can be demonstrated under the conditions employed by Lindberg and co-workers, we will use more concentrated alkaline solutions and higher temperatures. In addition, we will try both sodium and calcium based systems.

II. The Stability of Additives and the Rate of Their Reaction with Carbohydrates

This program will be confined to sodium borohydride, hydroxylamine, sodium polysulfide, anthraquinone sulfonates, and possibly hydrazine. The use of hydrogen sulfide with a gaseous atmosphere of this additive above the aqueous buffer system would be extremely difficult with our new flow reactor in its present arrangement, and experiments with hydrogen sulfide will not be included in the present program. However, if considered important enough, analogous reactions with thioglycolic acid can be included in the present program, and studies under hydrogen sulfide pressure can be conducted in the next phase of our long-range program on reactions under specific gaseous pressures of oxygen, hydrogen sulfide, etc. with a modified flow reactor.

The stability of the several additives to alkali of varying concentrations and at varying temperatures will be conducted in the flow reactor. The reaction with alkali can be stopped in three ways, all three of which will be examined for best results:

(a) Lowering the pH by addition of an acid such as boric acid.

(b) Lowering the temperature by addition of a cold aqueous solution to give thermal mixing. Thus, five volumes of water at 0 to 5°C. added to one volume of reaction solution at a higher temperature would slow the reaction rapidly.

(c) The addition of a reagent that will react with the additive. For example, a known excess of potassium iodate can be added to a reaction solution containing borohydride. The remaining iodate can be titrated to determine the amount of borohydride present in the solution at the moment the potassium iodate was added. Similar oxidants can be used with hydroxylamine or with hydrazine. Of concern here is the rate of reaction of these quenching solutions. Ionic reactions, such as the neutralization of sodium hydroxide with boric acid, are very fast, but the decomposition of sodium borohydride by an acid solution or by potassium iodate may be slower. Reaction of various oxidants with hydroxylamine or with hydrazine may also take appreciable time. These facts will have to be ascertained.

As long as the time of quenching is small compared with the time of decomposition by alkali of the additive under study (expressed by rate constant k_d), we anticipate no difficulties in the analysis of these systems and in the determination of rates.

It should be pointed out that Hartler (8) analyzed for borohydride in alkaline systems by treatment with acid and evolution of hydrogen. This method is not applicable to alkaline sulfide systems because of simultaneous evolution of hydrogen sulfide upon acidification. In addition, the use of oxidants in sulfide-containing systems may cause difficulties due to possible oxidation of sulfide.

The rate of additive reaction with carbohydrates, primarily cellobiose, will be studied and analyzed in a similar manner. The removal of excess additive from the system by use of an oxidant may give rise to problems, because the oxidant may react with either the sugar or other reaction product

formed (such as an oxime). Ideally, the additive and excess carbohydrate should be removed, and the glycosidic bond remaining in the reaction product determined.

The extent of additive reaction will then be determined in one of the following three manners:

(a) Change in concentration of the additive.

(b) Change in concentration of the original carbohydrate.

(c) Amount of alkali-resistant glycosidic linkage present.

For method (a) a correction will be made for reaction of additive with alkali. For method (b) a correction will be made for loss of carbohydrate due to the peeling reaction. For method (c) the system will be treated with alkali, and after removal of the additive, the amount of glycosidic linkage remaining will be determined by the method of Painter (27).

III. The Relationship of the Peeling Reaction to the Lignin-Carbohydrate Complex

Three types of sugar derivatives are subjects for model compound investigations. These three types are (a), a benzyl derivative of glucose or cellobiose; (b), a phenyl derivative of glucose or cellobiose; and (c), phenyl glucoside. These three types will be treated with various alkaline liquors at various temperatures. In addition, the effect of additives on the prevention of peeling and on the loss of benzyl or phenyl groups will be investigated.

(a) Kenner and Richards prepared the 3-O-benzyl derivative of

glucose and noted the rate of its alkaline degradation. The 6-O-benzyl derivative of cellobiose could possibly be prepared by a procedure of tosylation on carbon-6, replacement of the tosyl group with iodide, and then with the benzyl group. Preparation of the 3-O-benzyl cellobiose would be more difficult.

(b) The 3-O-phenyl derivative of glucose could be prepared by reaction of diacetone glucose (with carbon-3 unsubstituted) with sodium in liquid ammonia, and then with iodobenzene. The carbon-6 derivative of cellobiose could be prepared by reaction of the 6-iodo derivative with sodium phenoxide.

(c) While the studies under (a) and (b) model a lignin-carbohydrate ether linkage, phenyl glucoside studies serve as models for glucosidic or acetal linkages. The half-life of phenyl glucoside in normal sodium hydroxide at 100°C. is approximately 130 minutes (21). Rates have not been determined at higher temperatures or in alkaline sulfide systems.

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PROJECT DIRECTION

The research project will continue to be centered in the Division of Natural Materials and Systems, the Director of which is Dr. John W. Swanson. The research project will be under the general supervision of Dr. Irwin A. Pearl, Group Coordinator, and technical supervision will be the responsibility of Dr. John W. Green, Project Leader, with whom you may correspond directly concerning progress of the work.

REPORTS

The Institute shall render technical reports at the end of each six-month period throughout the course of this extension. In addition, informal reports or memoranda may be submitted at interim periods as progress of the work so dictates.

BUDGET AND TIME SCHEDULE

This proposed extension is planned for a two-year effort. As with the initial phase of the project, this proposed research extension is such that it can be pursued at various levels of activity and the amount of research accomplished would be dependent upon the total budget available. The Institute would prefer to continue at the present level of about $65,000 per year for the two-year period, but it feels it can continue with the research at a level of about $50,000 per year. It is quite likely that the desired level will be obtained in the light of the current support.

GENERAL PROVISIONS

The general provisions relating to authorization, joining the project, technical representative, patents, publication, concurrent research and continuation, and use of reserve account shall be the same as set forth in the initial proposal for this project, No. 1612 dated February 12, 1970, and for this extension are incorporated herewith and set forth in Exhibit A attached to this proposal.

SIGNATURE PAGE

THE INSTITUTE OF PAPER CHEMISTRY

Irwin A. Pearl
Group Coordinator
Division of Natural
Materials and Systems

John W. Swanson
Director
Division of Natural
Materials and Systems

Wendall H. Smith
Secretary

PATENTS

The purpose of this program is to advance scientific insights and understanding in the area of alkaline pulping and it is not contemplated, therefore, that the Institute or any of the participating companies in the program will be concerned with the patenting of any discoveries or inventions. However, it is conceivable that the Institute as a participating company may deem it advisable to seek patents for the purpose of protecting certain work as for the purpose of keeping fields "open." In such event, the Institute shall have exclusive right to said patents and shall further grant to all the initial and/or subsequent participating companies in the project a nonexclusive, royalty-free license under said patents.

PUBLICATION

It is understood that if any or all of the participating companies wish to publish, or publicly refer to, the results developed under such cooperative research projects, The Institute of Paper Chemistry reserves the right to edit, and to approve or disapprove, such reports, references, or papers. The Institute shall not publish said results without prior approval of all of the participating companies. However, the Institute shall have the right to publish the results of the investigations and researches after a period of two years from the date of transmittal of the results to the companies participating in the research program, provided that if the Institute finds after consultation with said companies that publication after the expiration of the two-year period would prove detrimental to the best interest of certain companies, the Institute shall delay such publication a reasonable time.

CONCURRENT RESEARCH

It is understood that the Institute and/or any or all of the participating companies shall have the privilege of carrying on similar, related, or collateral research and investigations concurrently on their own behalf or for companies or organizations having similar objectives and interest in the field covered by the proposed program.

CONTINUATION OF RESEARCH

If it is decided that this proposed research will not be pursued after the termination of this project, the Institute reserves the right to pursue the particular investigation and research itself, or if the occasion arises, to pursue such investigation and research in cooperation with others. The Institute shall have the right to use or otherwise refer to, any information developed on this proposed research project in connection with any continued research in this area whether an extension of the same project or the initiation of a related project or projects. This right, however, shall not be exercised so as to derogate from the rights of the participating companies which may accrue under "Patents" and "Publications" above.

INVOICING PROCEDURES

The Institute of Paper Chemistry is a nonprofit organization and as such our charges are based upon the actual cost of the work performed. Invoices are submitted monthly while the work is in progress and cover Personal Services, which are the major charges and include staff time on an hourly basis chargeable directly to the project, direct research and departmental overhead costs, general and administrative costs; and Disbursements, which pertain

directly to the research project, and comprise authorized travel by our staff, telephone and telegraph, samples, supplies, and special equipment procured for such project, consultants and attorney fees. Any equipment necessary for a cooperative research project not already a part of the Institute's facilities is to be provided by your company at your expense and will remain a part of the Institute's facilities upon termination of the project. However, no major pieces of equipment will be purchased nor traveling done by our staff unless so approved by your company.

MEMBERSHIP RESERVE ACCOUNT

The balance accumulated in your reserve account will be utilized to defray the personal services charges in connection with this project. The disbursements will be billed for cash payment. If the balance in the member's reserve account becomes exhausted during the period of the membership agreement or is "expired" at the termination of the membership agreement pursuant to such agreement, the member company, of course, would be billed for cash payment for the personal services charges also.