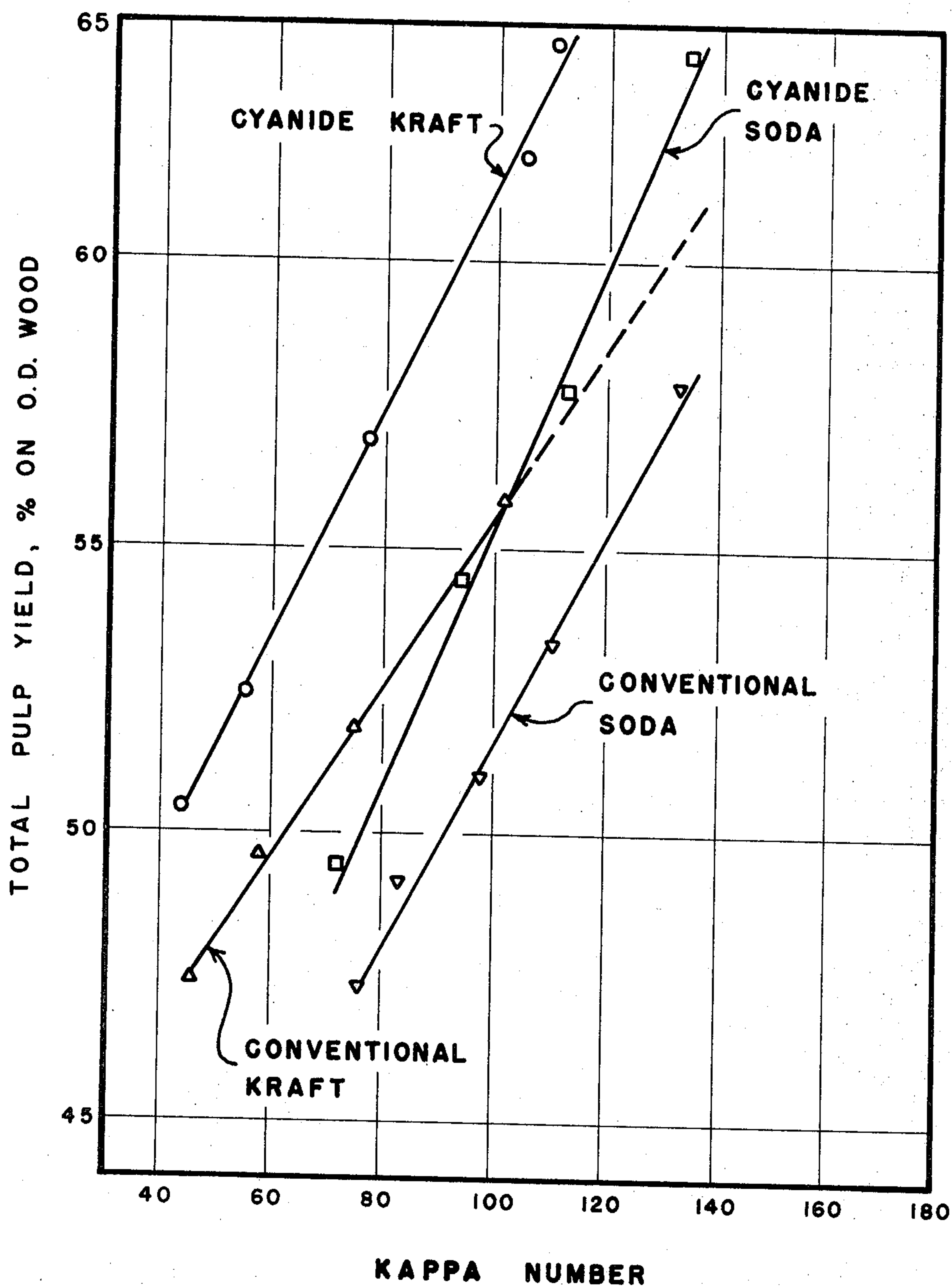


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METHOD FOR STABILIZING POLYSACCHARIDES
AGAINST ALKALINE ATTACK
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INVENTORS

ALAN M. BILLS
STEN I. FALKEHAG
PEDER J. KLEPPE

BY *Marion P. Leborg*
AGENT

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3,532,596

METHOD FOR STABILIZING POLYSACCHARIDES AGAINST ALKALINE ATTACK

Alan M. Bills, Summerville, and Sten I. Falkehag and Peder J. Kleppe, Charleston, S.C., assignors to Westvaco Corporation, New York, N.Y., a corporation of Delaware

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7 Claims

ABSTRACT OF THE DISCLOSURE

A process for pulping lignocellulosic material comprising treatment of the material with cyanide ions to form cyanohydrin groups and digesting the thus treated lignocellulosic material with an alkali metal pulping solution containing hydroxyl ions whereby hydrolysis of the cyano groups to carboxyl groups occurs thus retarding alkali degradation.

FIELD OF THE INVENTION

This invention relates to protection of polysaccharides against alkaline attack and particularly relates to neutral and alkaline processes for pulping of lignocellulosic materials for papermaking. It specifically relates to increasing the yield of these processes by increased retention of polysaccharides through pretreating lignocellulosic materials with cyanides, whereby polysaccharides are stabilized against alkaline attack.

Polysaccharides includes starches, gums, sugars, cellulose, and hemicelluloses, all of which are generally repetitions of sugar units, such as anhydro-glucose, mannose, galactose, fructose, xylose, etc., which are themselves five-or-six membered carbohydrates where the resulting polysaccharide chain, of hundreds or even thousands of linked sugar units, has a reducing group of an aldehyde type at one end.

Lignocellulosic materials (such as wood from coniferous and deciduous species of trees, the stalks of bamboo and reeds, bagasse, and cotton fibers) principally contain lignin, cellulose, and hemicelluloses. The lignin and hemicelluloses, such as gluco-mannan chains in softwood or glucurono-xylan chains in hardwood, are located both in the cell wall of the fiber and in the inter-fiber spaces, generally termed the middle lamellae.

In chemical processes for utilizing lignocellulose materials, lignin in the inter-fiber spaces must be dissolved, with as little damage as possible to the fibers, so that the fibers are readily separable. Hemicelluloses can be retained on the surface of the fiber, in which case they can influence the bonding properties of the fibers, and they are also retained in the cell wall of the fiber, improving the flexibility and thereby the papermaking properties of the pulp. It is consequently generally desirable to retain the hemicelluloses in order to produce paper products having superior strength characteristics.

In alkaline pulping processes, a large portion of the hemicelluloses are usually dissolved in addition to lignin, particularly if the digestion is continued long enough to dissolve almost all of the lignin. The soda pulping process, which requires lengthy treatment, causes nearly all of the hemicelluloses to be dissolved and the cellulose chains to be broken at intervals, so that fibers are weakened and relatively little hemicellulose is available for bonding. Kraft and neutral sulfite pulping liquors are more specific toward lignin so that the cellulose is attacked very little, but hemicelluloses are attacked to a high degree, especially when the cook is greatly prolonged in order to remove as much of the lignin as possible before bleaching.

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The dry weight of washed fibers which are recovered after pulping is generally reported as a percentage of the weight of dry lignocellulosic material which was charged to the digestion process. This percentage is termed "yield." Any decrease in yield caused by loss of polysaccharides is generally undesirable in papermaking or in any other use process except production of alpha-cellulose for rayon manufacture. This invention is directed toward retention of hemicelluloses and consequently increasing the yield of neutral and alkaline pulping processes.

In alkaline pulping three types of carbohydrate-dissolving reactions are important: (a) simple dissolution of polysaccharides having very low molecular weight, (b) successive splitting of sugar units from the reducing ends of the polysaccharide chains by means of the "peeling" reaction, and (c) splitting of the polysaccharide chains into shorter fragments by hydrolysis of the ether linkages between the carbohydrate units.

Reaction (a) is unavoidable because these very low-molecular-weight polysaccharides are easily dissolved in aqueous alkali and in some instances even in water. However, in a batch cook where the effective alkali is initially high and gradually diminishes to a minimum value, some of the polysaccharides of relatively high molecular weight which were nevertheless dissolved by reaction (a) are later precipitated when the effective alkali has decreased.

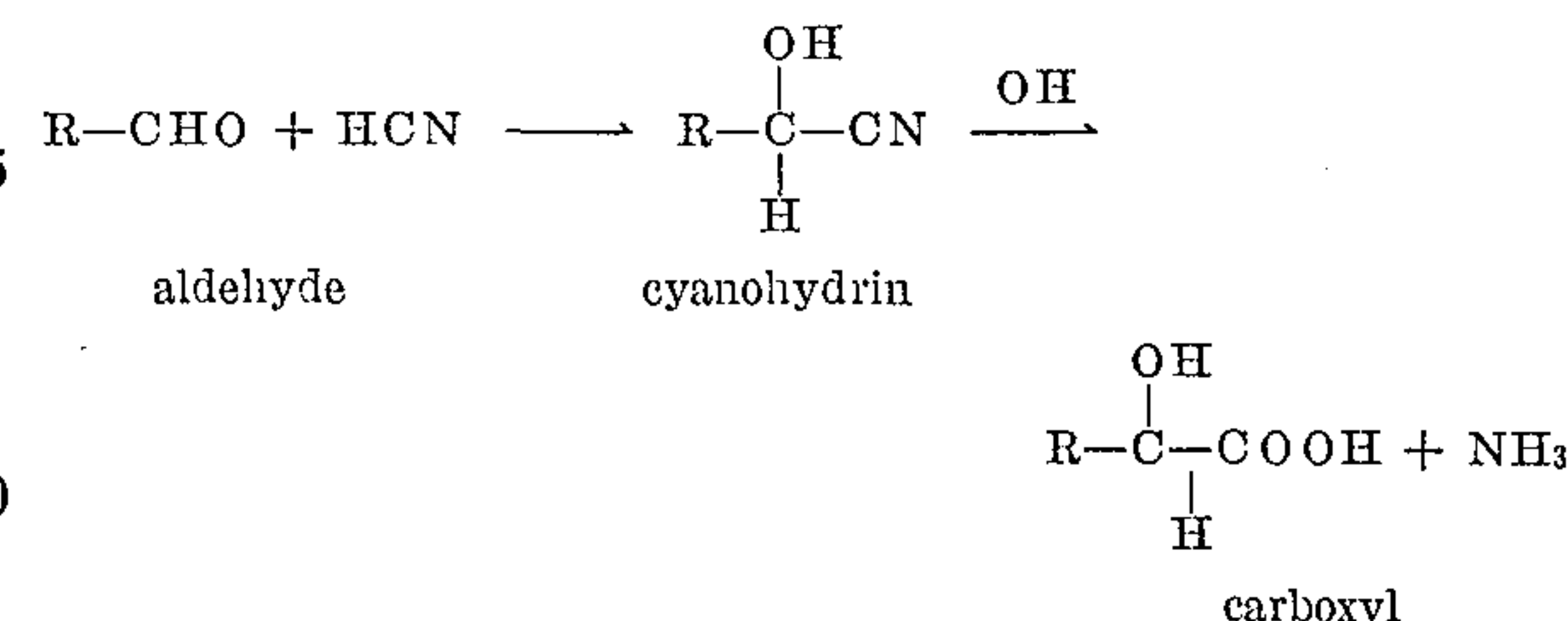
Reaction (b) occurs as lignocellulosic material is being heated in contact with a pulping solution. It is very extensive about 90° C. at a pH above approximately 9 and continues until about sixty carbohydrate units have been successively peeled from the end of a polysaccharide chain; it terminates because of autostabilization by formation of meta-saccharinic acids.

Reaction (c) is of importance at higher temperatures (above 150° C.) but has serious effects because an aldehydic end group is formed every time a chain is split. Thus, reaction (b), the successive peeling of terminal carbohydrate units, can start again.

This invention depends upon the conversion of the aldehyde group on the terminal sugar unit of a polysaccharide chain to a cyanohydrin group and the subsequent hydrolysis of the cyano group to a carboxyl group, as a means of stopping the peeling reaction prior to autostabilization thereof. It is further successful because the pulping solution is more effectively used to dissolve lignin. Consequently, a lower concentration of pulping solution can initially be mixed with the lignocellulosic material or a higher concentration of pulping solution is present when steady cooking temperatures are reached.

DESCRIPTION OF THE PRIOR ART

This invention adds a carboxylic unit to the terminal sugar unit of a polysaccharide chain whereby the aldehydic group is destroyed. The selected reaction for doing so is the well known cyanohydrin synthesis or Kiliani-Fischer Reaction for increasing the length of the carbon chain of the sugars by addition of hydrocyanic acid to aldehydes or ketones, as follows:



The original procedure devised by Kiliani for the sugars required adding a sugar to an aqueous solution of hydrogen cyanide in the presence of a little ammonia. The improved reaction, which goes to completion when buffered at pH 9.0 to 9.1, involves the addition of a sugar to a solution of sodium cyanide and calcium chloride.

Although the original Kiliani synthesis was reported on such monosaccharides as fructose, glucose, arabinose, and galactose as early as 1885, and although improvements as to buffering were reported as late as 1949, there is only one known reference to this reaction being used on a polysaccharide.

As reported in Science, vol. 113, page 532 by H. S. Isbell, C¹⁴-labelled sodium cyanide has been used to convert a 6-carbon reducing end group on a polysaccharide to a 7-carbon unit having a radioactive carboxyl. This reaction was used to determine molecular weights by means of radioactive measurements. No other application to a polysaccharide is known. The extensive literature on cyanohydrin synthesis deals with monosaccharides. For example, John C. Sowden wrote on page 109 of "The Carbohydrates," edited by Ward Pigman, Academic Press, New York, 1957, in chapter II., "Monosaccharides: Occurrence, Properties, Synthesis," that the Kiliani cyanohydrin synthesis had been used to build up synthetic sugars having as many as ten carbons in a straight chain but made no comment about polysaccharides.

SUMMARY OF THE INVENTION

The process of this invention comprises the steps of (a) diffusion, at a pH between 7.0 and 12.0, of cyanide ions and hydroxyl ions into a polysaccharide material; (b) formation of cyanohydrin groups by reaction with aldehydic end groups; and (c) hydrolysis of the cyano groups into carboxyl groups, whereby the polysaccharide material is protected against alkaline attack when the pH is subsequently raised above 12.0. Greatly superior results are obtained when the pH of the pretreatment is held between 8.5 and 10.5.

DETAIL DESCRIPTION OF THE INVENTION

Cyanohydrin is formed more rapidly at higher temperatures, but hydrolysis of cyanide ion directly into ammonia is also accelerated at higher temperatures. To avoid competition between these reactions for available cyanide ion, diffusion should occur at relatively low temperatures, such as, below 75° C. The reaction to form cyanohydrin can take place at considerably higher temperatures.

However, as a practical digestion procedure for wood chips, diffusion and cyanohydrin formation must generally proceed simultaneously. If wood chips are pre-steamed to drive out air and thoroughly wet the wood structure, about 70% of the possible reaction occurs in three hours at a temperature of 95° C. At a temperature of 130° C., approximately five minutes is sufficient, but control and uniformity of cooking conditions are not reliable. An economic penalty must also be paid for cyanide ion which becomes unavailable for cyanohydrin formation because of hydrolysis directly into ammonia.

EXAMPLES 1-22

The stabilization of pure cellulose against alkaline degradation in hot-alkali purification of dissolving pulps is an example of a practical use to which this invention can be put. To explore its utility, a sample of hydrocellulose was prepared from a high-viscosity cotton linters pulp by partial hydrolysis with 2.5 N HCl at 60° C. for 2 hours. The product was washed with water until acid-free and then solvent exchanged with ethanol followed by light petroleum ether. The thus treated hydrocellulose was air-dried, ground in a Wiley mil and then kept in air-tight storage.

The final hydrocellulose product was 100% of the initial cotton linters, its 0.5% CED viscosity (TAPPI T 230 SM-50) was 2.5, and its copper number (TAPPI T 215

M-50) was 5.1. This hydrocellulose product was used for Example 1-22.

After 2.000 g. had been treated with 25 ml. of a selected KCN solution at a selected temperature for a selected time, 125 ml. of boiling 1.2 N NaOH solution were added (bringing the concentration to 1.0 N NaOH), and the mixture was refluxed for 2.5 hours.

The hydrocellulose was then filtered hot in a tared glass crucible and washed, in small quantities with careful stirring, according to the following sequence: 100 ml. of distilled water, 100 ml. of 1% acetic acid, 100 ml. of distilled water, 50 ml. of ethanol, and 50 ml. of petroleum ether. After drying and cooling, the crucibles were re-weighed to determine yield.

A sample of untreated hydrocellulose yielded 69.4%. After pretreatment as 25° C. for 23 hours with 10% KCN on the hydrocellulose at indicated buffered pH and after subsequent alkali extraction, the yields are as given in Table I.

TABLE I

Example	Pretreatment pH	Yield of hydrocellulose, percent
1	5.0	70.5
2	6.7	70.7
3	8.6	90.4
4	9.6	91.4
5	10.7	85.4
6	12.1	71.1

Pretreatments without buffering (pH 10.7) gave the results in Table II for additional runs at 10% KCN on another sample of similarly prepared hydrocellulose. This sample yielded 64.8% without pretreatment.

TABLE II

Example	Pretreatment		Yield of hydrocellulose, percent
	Time, hours	Temperature, ° C.	
7	1	25	68.5
8	3	25	72.5
9	12	25	79.6
10	23	25	84.6
11	23	55	89.9
12	1	95	76.9
13	3	95	82.9
14	23	95	92.3
15	1	120	79.5
16	3	120	83.4
17	23	120	86.2

The consumption of cyanide ion as HCN is given in Table III for three of the foregoing runs in Table II.

TABLE III

Example	Pretreatment		Consumption of HCN, percent of hydrocellulose
	Time, hours	Temperature, ° C.	
10	23	25	0.15
11	23	55	0.30
13	3	95	0.90

Additional examples of hydrocellulose were pretreated at 95° C. for 23 hours without buffering and at indicated KCN concentrations and pH levels, with yield results shown in Table IV.

TABLE IV

Example	Pretreatment		Yield of hydrocellulose, percent
	pH	KCN conc., percent of hydrocellulose	
18	10.4	1	80.4
19	10.5	5	86.0
20	10.7	10	92.3
21	11.4	25	89.0
22	11.4	50	89.0

It is clearly apparent from the foregoing results that polysaccharides can be protected to a remarkable degree against alkaline attack by the methods of this invention.

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EXAMPLES 23-30

The digestion of lignocellulosic materials under alkaline conditions obviously presents a very large-scale field for utilizing the present invention. Kraft, soda, and neutral sulfite digestion processes are currently being used for converting large quantities of lignocellulosic materials, particularly wood-derived materials, into paper and paper-board products. The method and results given in Examples 23 through 30 established the practical utility of this invention for treating commercial wood chips. Only treatments of softwood chips are herein described, but it is known that hardwood chips can be beneficially treated by the methods of this invention if adequate diffusion techniques are employed.

In conventional soda pulping, the lignocellulosic material is digested with an aqueous solution of sodium hydroxide at 165-180° C. according to a cooking schedule which varies with the type of pulp desired. Similarly, conventional kraft pulping utilizes an aqueous solution of sodium hydroxide, containing sodium sulfide. The presence of sodium sulfide considerably increases the rate of delignification of the lignocellulosic material and hence results in shorter cooking schedules for kraft pulps compared to soda pulps. Therefore, kraft pulps are generally stronger than soda pulps, probably because briefer cooking produces a less degraded product.

The so-called "neutral" sulfite process actually utilizes a liquor which is alkaline (pH 9-10) at the beginning of the digestion process. This sulfite liquor consists mainly of an aqueous solution of sodium sulfite. During the cook, the pH can drop to about 7 because of consumption of the chemical and production of acidic materials from the wood. The pulping action is very mild and hence a considerable amount of time is necessary to pulp to a reasonably low lignin content.

GENERAL OUTLINE OF EXPERIMENTAL PROCEDURE

In two comparable kraft cooks which are described hereinafter, Examples 25 and 26, 100 grams of oven-dry loblolly pine chips were digested with a kraft liquor containing 17.5% effective alkali (as NaOH on O.D. wood) at a sulfidity of 25.0% in a small digestion bomb for one hour at 170° C. maximum temperature. The chips which were digested in one of these cooks had been pretreated for 18 hours after vacuum impregnation with a cyanide solution, made by dissolving 2.5 g. KCN in one liter of water, as a convenient source of cyanide ion, at a 5:1 liquor:wood ratio.

In four comparable kraft cooks which are described hereinafter, 1500 grams of wood chips (commercially chipped loblolly pine from a different wood sample) were pretreated at 100° C. for 30 minutes with 15 p.s.i.g. steam to open up the wood structure and to drive out the air in order to improve the accessibility of the wood chips to cooking liquor. Before cooling, 8 liters of an aqueous cyanide solution were drawn into the wood chips and then circulated through the chips for 3 hours at 50° C. At the end of this time, the excess cyanide liquor was withdrawn. The cooking liquor was then added and the subsequent digestion was continued in the conventional manner. Examples 23 and 24 show kraft cooks. Examples 27 and 28 show soda cooks.

The yields of pulp from these cooks are shown as a function of Kappa number in the accompanying figure. The calculation of effective alkali in the kraft cooks was based on the NaOH and one-half of the Na₂S expressed as NaOH. Sulfidity was calculated as the molecular ratio of Na₂S to the sum of the NaOH and the Na₂S, expressed as a percentage.

EXAMPLE 23

1500 g. (O.D.) of loblolly pine chips were presteamed for 30 minutes, then pulped by a normal kraft process in a 22-liter stationary digester using forced liquor circulation. (See Table V.)

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EXAMPLE 24

1500 g. (O.D.) of loblolly pine chips were presteamed for 30 minutes and then treated with 8 liters of an aqueous cyanide solution containing 7.8 grams per liter of cyanide, calculated as HCN. The chips were treated at 50° C. for 3 hours by circulating the liquor continuously through the chips. After the 3-hour pretreatment, the liquor was withdrawn and titrated to determine the amount of cyanide consumed. The chips were then pulped by a kraft process as in Example 23. (See Table V.)

EXAMPLE 25

100 g. (O.D.) of loblolly pine chips were pulped by a normal kraft process in a 1-liter bomb in a steam jacketed rotating digester. (See Table V.)

EXAMPLE 26

100 g. (O.D.) of loblolly pine chips were vacuum impregnated with 500 ml. of an aqueous cyanide solution containing 2.1 grams/liter of cyanide, calculated as HCN. The chips were treated at room temperature (22° C.) for 18 hours. At the end of the 18-hour treatment, the excess cyanide liquor was drained off and the chips were then pulped by a normal kraft process as in Example 25. (See Table V.)

EXAMPLE 27

1500 g. (O.D.) of loblolly pine chips were presteamed for 30 minutes and then pulped by a normal soda process in a 22-liter stationary digester using forced liquor circulation. (See Table V.)

EXAMPLE 28

1500 g. (O.D.) of loblolly pine chips were presteamed for 30 minutes and then treated with 8 liters of an aqueous cyanide solution containing 7.8 grams/liter of cyanide, calculated as HCN. The chips were treated at 50° C. for 3 hours by circulating the liquor continuously through the chips. After the 3-hour treatment, the liquor was withdrawn and titrated to determine the amount of cyanide consumed. The chips were then pulped by a normal soda process as in Example 27. (See Table V.)

TABLE V.—COMPARISON OF KRAFT AND SODA PULPING WITH AND WITHOUT CYANIDE PRETREATMENT

	Example No.					
	23	24	25	26	27	28
Pretreatment time, hours.....	0	3	0	18	0	3
Equilibrium concentration of HCN, g./l.....	0	6.5	0	2.1	0	6.5
Amount of HCN, percent on O.D. wood.....	0	4.15	0	1.05	0	4.15
Effective alkali, percent NaOH.....	17.0	17.0	17.5	17.5	19.0	19.0
Sulfidity, percent.....	25.0	25.0	25.0	25.0	0	0
Liquor: wood ratio.....	4:1	4:1	4:1	4:1	4:1	4:1
Time to 170° C., min.....	45	45	60	60	45	45
Time at 170° C., min.....	60	38	60	50	240	120
Total pulp yield, percent on O.D. wood.....	55.9	61.8	48.9	51.2	53.4	57.8
Kappa number.....	102	105	59	56	111	113
G.E. brightness, percent.....	15.2	18.0	21.0	23.4	14.5	17.7
Yield increase, percent on O.D. wood.....		5.9		2.3		4.4
Consumption of cyanide as HCN, percent on O.D. wood.....		1.3		0.4		1.3

EXAMPLE 29

1500 g. (O.D.) of loblolly pine chips were presteamed for 30 minutes and then pulped by a normal neutral sulfite process in a stationary 22-liter digester using forced liquor circulation. (See Table VI.)

EXAMPLE 30

1500 g. (O.D.) of loblolly pine chips were presteamed for 30 minutes and then treated with 8 liters of an aqueous cyanide solution containing 7.8 grams/liter, calculated as HCN. The chips were treated at 50° C. for 3 hours by circulating the liquor continuously through the chips. After the 3-hour treatment, the liquor was withdrawn and titrated to determine the amount of cyanide consumed. The chips were then pulped by a normal neutral sulfite process as in Example 29. (See Table VI.)

After cyanide liquor has been withdrawn from a digester, it can be reused if fortified by adding additional quantities of a selected cyanide compound. In order to maintain selected cyanide concentrations as percentages of hydrocellulose in Examples 1-22 while maintaining the desired ratio of 25 ml. of liquor to 2.000 grams of hydrocellulose, solution concentrations ranging from 0.8 gram of KCN per liter to 40.0 grams of KCN per liter were used. In the wood cooks, a solution containing 7.8 grams of cyanide per liter, calculated as HCN, was used, but in equilibrium with water in the presteamed wood, the solution became 6.5 grams of cyanide calculated as HCN per liter.

TABLE VI.—CYANIDE TREATMENT IN NEUTRAL SULFITE PULPING

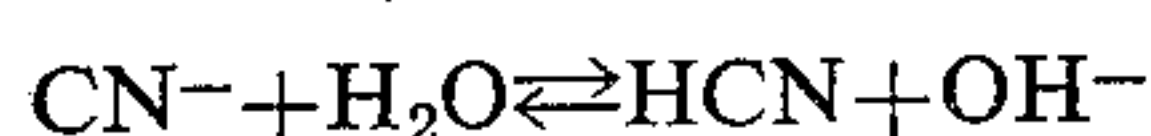
	Example	
	29	30
Pretreatment time, hours.....		3
Concentration of cyanide, g./l. calculated as HCN.....		7.8
Amount HCN, percent on O.D. wood.....		4.15
Percent Na ₂ SO ₃ on O.D. wood, as Na ₂ O.....	15.0	15.0
Liquor to chip ratio.....	4:1	4:1
Time to 170° C., min.....	90	90
Time to 170° C., min.....	240	120
Total pulp yield, percent on O.D. wood.....	68.5	75.6
Total lignin.....	19.0	19.3
Yield increase, percent on O.D. wood.....		7.1
Na ₂ SO ₃ as Na ₂ O consumed, percent on O.D. wood.....	10.9	8.2

Another practical advantage in producing unbleached pulp from lignocellulosic materials in accordance with this invention, in addition to increased yield, is a lighter-colored pulp, commonly measured as larger numbers of "G.E. Brightness, Percent," as shown in Table V. This beneficial characteristic may be caused by higher effective alkali.

This invention may be practiced in continuous or batch digester operations. A very useful modification of the invention, which is also suitable for batch or continuous operation, is: (a) presteam chips to drive out air, soften wood, and fill pores with liquid; (b) soak chips with an alkaline solution, such as aqueous NaOH, at a temperature below 90° C. for a first pretreatment; (c) withdraw excess alkaline solution; (d) introduce gaseous HCN at a convenient low pressure and at a temperature below 110° C. for a second pretreatment which varies inversely in duration with the temperature; and (e) introduce cooking liquor at a pH above 9.

As another alternative, lignocellulose can be treated with a first pretreatment solution only up to the absorptive capacity of the lignocellulose. The alkali-pretreated lignocellulose can then be stored at a temperature below 90° C. for inward diffusion of alkaline ions before introduction of HCN gas.

In the practice of this invention, any aqueous solution containing a cyanide ion may be used. When KCN, for example, is added to water, it readily dissociates into K⁺ ion and CN⁻ ion. The cyanide ion then reacts with water:



Whether derived from HCN gas, liquid hydrogen cyanide, an inorganic compound or an organic compound, any

treatment solution therefore contains reactive CN⁻ ion so that it is immaterial how the cyanide ion is added to the treatment solution.

The unbuffered dissociation constant of HCN in water is 7.2×10^{-10} at about pH 9. Because HCN is known to be effective in cyanohydrin reactions with polysaccharide materials, it is clear that the dissociation constant of a cyanide-supplying compound is not controlling. Consequently, any water-soluble, cyanide-releasing compound may be used to form pretreatment solutions containing cyanide ion in practicing this invention.

It is apparent that other modifications may be made without departing from the spirit and scope of the novel concepts of this invention. The invention is defined in the following appended claims.

We claim:

1. A process for pulping lignocellulosic material comprising treatment of the lignocellulosic material with an aqueous solution containing cyanide ions to form cyanohydrin groups, withdrawing excess cyanide ion containing solution and digesting the thus treated lignocellulosic material with an alkali metal pulping solution having a pH about 7 containing hydroxyl ions whereby said hydroxyl ions hydrolyze the cyano groups into carboxyl groups thereby retarding degradation of the lignocellulosic material.

2. The process of claim 1 wherein the lignocellulosic material is in the form of wood chips.

3. The process of claim 1 wherein said alkali metal pulping solution contains sodium sulfides.

4. The process of claim 1 wherein said alkali metal pulping solution contains sodium sulfite.

5. The process of claim 1 wherein said treatment is conducted at temperatures below 75° C.

6. The process of claim 1 wherein said cyanide ion is obtained from sodium cyanide.

7. The process of claim 1 wherein said lignocellulosic material is treated with a solution of an alkali metal hydroxide at a temperature below 90° C. prior to treatment with said cyanide ions.

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S. LEON BASHORE, Primary Examiner

T. G. SCAVONE, Assistant Examiner

U.S. Cl. X.R.

8-116.2; 162-72, 86; 260-229

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,532,596

Dated October 6, 1970

Inventor(s) Alan M. Bills et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 71, "mil" should read -- mill --.
Column 4, line 16, "as" should read -- at --. In the
seventh line of claim 1, "about" should read -- above --.

Signed and sealed this 29th day of December 1970.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents