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**Phillips**

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[54] **TREATMENT OF LIGNOCELLULOSIC MATERIAL WITH AN AQUEOUS CONTAINING CYANIDE IONS AND AN ALKALINE EARTH METAL SALT**

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[51] Int. Cl..... **D21c 3/02**

[58] **Field of Search**..... **162/70, 65; 8/116 R**

[56] **References Cited**

UNITED STATES PATENTS

3,532,596 10/1970 Bills et al. .... **162/70**

3,663,358 5/1972 Falkenag et al. .... **162/70**  
3,695,994 10/1972 Worster et al. .... **162/65**

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[57] **ABSTRACT**

A process for increasing the yields in alkaline pulping of lignocellulosic materials, such as by the Kraft process, comprising treatment of the cellulosic materials with cyanide and a water-soluble, alkaline-earth metal salt. The lignocellulosic material is then filtered, washed and digested with an alkali-metal pulping solution having a pH of at least about 7.

**16 Claims, No Drawings**

**TREATMENT OF LIGNOCELLULOSIC MATERIAL  
WITH AN AQUEOUS CONTAINING CYANIDE  
IONS AND AN ALKALINE EARTH METAL SALT**

**BACKGROUND OF THE INVENTION**

Processes have been described for protecting polysaccharides in the pulping of lignocellulosic materials against alkaline attack during processes for converting the lignocellulosic materials into the paper products. One such procedure involves the addition of cyanides, such as sodium cyanide, to the cellulosic material prior to the pulping process to stabilize the polysaccharides against alkaline attack and thereby increase the pulp yields. One such suggestion is found in Bills et al. U.S. Pat. No. 3,532,596, granted Oct. 6, 1970. The patent contains no suggestion that the employment of a water-soluble, alkaline-earth metal salt, in conjunction with cyanide, will enhance yields of pulp.

There is also disclosed in the printed abstract of a paper presented at the 13th International Congress of Pure and Applied Chemistry, held in Stockholm, Sweden, in 1953, by E. Venemark, entitled "A Comparison Between The Influence Of Cyanide And Sulfide On The Alkaline Delignification," a treatment of cellulosic material with cyanide during alkaline delignification.

A paper by D. W. Clayton et al. in *Svensk Papperstidning*, Vol. 69, No. 9, pp. 311-321 (May 15, 1966), entitled "The Effect Of Additives On The Stability Of Polysaccharides In Hot Alkali," is an erudite discussion of the so-called "peeling" reaction. The article of Clayton et al. discusses the cause, chemistry and various suggestions to solve the problem caused by the so-called peeling reaction. Basically these suggestions involve modification of the troublesome aldehyde end group present in polysaccharides. The Clayton et al. article suggests stabilizing wood polysaccharides against the peeling reaction by methods which include the oxidation of the aldehyde end groups to carboxylic acid groups. The conversion of aldehyde groups to carboxylic acid groups by the so-called Kiliani reaction is a well-known means for accomplishing this oxidation. In this reaction cyanide groups react with the aldehyde groups to produce the corresponding cyanohydrin which is then converted to the corresponding carboxylic acid by a treatment under alkaline conditions.

The well-known Kiliani reaction or synthesis has been known for a number of years and it has been studied in connection with aldehydic polysaccharides. Various modifications of the reactions have been proposed. One such modification is disclosed in the chapter by C. S. Hudson in *Advances In Carbohydrate Chemistry*, Vol. 1, pages 1, 23-24 (1945) entitled "The Fischer Cyanohydrin Synthesis And The Configurations Of Higher-Carbon Sugars and Alcohols." This chapter discloses the reaction of glucose with sodium cyanide and calcium chloride to convert glucose to the next higher aldonic acid of glucose. The yields of the next higher aldonic acid of glucose are said to be enhanced. There is no suggestion, however, that the use of these reagents could increase the yield of wood pulp.

While treatment with cyanide is a means of increasing the yields of pulp by alkaline pulping processes, the paper industry has sought further means of providing substantial increases in the yields of pulp during alkaline pulping processes.

It is therefore an object of the present invention to provide processes for increasing the yields of pulp ob-

tained during alkaline pulping processes of lignocellulosic materials.

It is also an object of the present invention to provide for improving the stability of polysaccharides in the alkaline pulping of lignocelluloses.

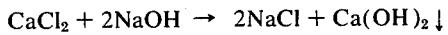
Other objects will be apparent to those skilled in the paper making art from the present disclosure.

**GENERAL DESCRIPTION OF THE INVENTION**

The process of the invention comprises an initial treatment of lignocellulosic materials at a pH of at least about 7.0, up to about 12.0, preferably 8.5 to 10.5, in an aqueous solution containing cyanide ions, hydroxyl ions, along with a water-soluble, alkaline-earth metal salt. The cellulosic material is removed from the aqueous initial treatment solution and digested in an alkaline-metal pulping solution having a pH of at least about 7, preferably not higher than 12.0.

The alkaline earth metal salt employed is desirably soluble in water at 25°C. to the extent of at least about 50 grams per liter.

The water-soluble, alkaline-earth metal salt is desirably employed in an amount of at least about 0.1 percent, preferably at least about 1.0 percent, by weight of the treatment solution. A treatment solution of at least about 0.25 molar with respect to calcium chloride has been shown to provide excellent increase in pulping yields. The amount of alkaline-earth metal salt addition should take into account the realization that metal ion residing in the chips following pretreatment by the cyanide solution will consume active alkali in the subsequent kraft cook by the reaction:



The amounts of cyanide, preferably introduced as alkali-metal cyanide, such as sodium cyanide, may vary widely, but amounts of between 0.25 and 2.0 percent by weight of treatment solution are preferred, with the optimum between about 1 and 1.5 percent.

The pretreatment with the cyanide and water-soluble, alkaline-earth metal salt over a broad range of temperatures, such as from ambient temperature to about 130°C. is satisfactory. Temperatures in excess of 130°C., while providing improvement, are less desirable than temperatures below 130°C. The preferred temperatures are between about 75°C. and 95°C.

Among the alkaline earth salts which may be employed are calcium chloride, which is preferred, calcium acetate, calcium bromide, calcium hypochlorite, calcium cyanide, calcium ferrocyanide, calcium hydrosulfide, calcium bisulfite, calcium dithionate, calcium thiosulfate, barium bromate, barium bromide, barium chlorate, barium chloride, barium cyanide, barium ferrocyanide, barium hydrosulfide, barium silicate, strontium chloride, strontium chlorate, etc.

**DETAILED DESCRIPTION OF THE PROCESS**

In order to disclose more clearly the nature of the present invention, the following examples illustrating the invention are given. It should be understood, however, that this is done solely by way of example and is intended neither to delineate the scope of the invention nor limit the ambit of the appended claims. In the examples which follow, and throughout the specification, the quantities of material are expressed in terms of parts or percent by weight, unless otherwise specified.

## EXAMPLES I TO IX

In Examples I-IX, hydrocellulose, in the amount of 1.0 grams, was used as a model of the cellulosic substrate to ascertain the improvement in yields under varying conditions and amounts of sodium cyanide and calcium chloride. In these examples, an aqueous suspension of the hydrocellulose powder was first treated at 75°C. for 2 hours in 150 ml. of aqueous solution containing the additives set forth in Table I below. The treatment was continued for 2.0 hours. The hydrocellulose was then filtered, washed with water, then acetic acid, followed by water. The washed powder was transferred to a flask containing 150 ml. of one normal sodium hydroxide. The contents of the flask were then boiled under reflux conditions for two hours. The thus treated hydrocellulose was then filtered, washed with water, then acetic acid, followed by water. The resulting hydrocellulose powder was dried overnight and the yield determined. The results are set forth in Table I below:

TABLE I

STABILIZATION OF HYDROCELLULOSE WITH NaCN - CaCl<sub>2</sub>

Example No.	Pretreatment		% Yield After Boiling In One Normal Sodium Hydroxide for 2 Hours
	Molarity of HCN	Molarity of CaCl <sub>2</sub>	
I	0.0	0.0	46.90
II	0.0	0.0	47.10
III	0.0	0.0	48.92
IV	0.25	0.0	64.69
V	0.25	0.0	65.67
VI	0.25	0.25	75.33
VII	0.25	0.25	76.15
VIII	0.0	0.25	47.50
IX	0.25	2.5	100.0

Examples I-III, above, involving no pretreatment with cyanide or calcium chloride, show that the unstabilized and unpretreated hydrocellulose gave a consistent yield of about 47-48 percent after boiling in one normal sodium hydroxide for two hours. Examples IV and V indicate that pretreatment with sodium cyanide alone (0.25 molar) increased the stability of the hydrocellulose so that after treatment in boiling one normal sodium hydroxide for two hours, the yield obtained was in the order of 65 percent. Examples VI and VII

75-76 percent. Example VIII shows that the increase in yield in Examples VI and VII was due to the combined presence of cyanide and calcium chloride, and not one of these reagents alone. Example IX shows that yields can be increased to the order of about 100 percent by increasing the amount of calcium chloride to about 2.5 molar in combination with the 0.25 molar concentration of cyanide in the pretreatment.

## EXAMPLES X-XX

In Examples X-XX a series of pulping experiments was conducted using southern pine chips. In these experiments, a one cubic foot digester was used in some cases, while in others a four liter digester was used. The results were found to be unaffected by the size of the digester.

In the latter experiments, 400 grams (oven-dry basis) of chips were charged to the four liter digester. Following steaming of the chips for five minutes, a pretreatment liquor containing 1.41 percent hydrogen cyanide (an oven-dry wood) in the form of a sodium cyanide was added to the digester so that a liquor-to-wood ration of 6:1 was present. After capping the digester, 50 psig nitrogen pressure was introduced to improve penetration of the pretreatment liquor into the chips. Pretreatment was conducted for 42 minutes at 75°C. after which the liquor was allowed to drain from the chips. Two liters of fresh water were circulated over the chips for two minutes, then drained. This washing procedure was then repeated. Analysis for hydrogen cyanide was made in the pretreatment liquor, as well as both wash waters, and the results used to determine the "% HCN Recovered." In cases where CaCl<sub>2</sub> was present the desired amount was added along with the NaCN.

After completion of the pretreatment and washing stages, sufficient kraft cooking liquor (27-28 percent sulfidity) was introduced to give a predetermined percentage of active alkali at 4:1 liquor: wood ratio. A cooking schedule was employed of approximately 65 minutes to reach a temperature of 171°C. after which the temperature was maintained at 171°C. for 35 minutes, with an H-factor of 950. After completion of the digestion, the softened chips were defibrated, washed, and centrifuged. Portions were taken for pulp yield and kappa number determinations.

The results of Examples X-XX are set forth in Table II below:

TABLE II

STABILIZATION OF SOUTHERN PINE CHIPS WITH NaCN-CaCl<sub>2</sub>

Example No.	% HCN on Oven Dried Wood Applied	%, CaCl <sub>2</sub> on Oven Dried Wood Applied	%, Active Alkali on Oven Dried Wood	Total Pulp Yield, %	Kappa No.
X	1.41	0.60	150	—	N.D.*
XI	1.41	0.92	5.74	13.1	57.3
XII	1.41	1.04	5.74	13.1	59.95
XIII	1.41	1.04	5.74	13.6	53.3
XIV	1.41	0.96	5.74	13.6	56.2
XV	1.41	0.87	5.74	14.1	55.1
XVI	1.41	0.91	5.74	14.1	56.4
XVII	1.41	1.10	0.00	14.1	53.1
XVIII	1.41	1.09	0.00	13.6	53.3
XIX	0.00	0.00	0.00	14.1	55.3
XX	0.00	0.00	0.00	15.1	52.1

\* Not Determined

were 0.25 molar calcium chloride was employed in addition to the 0.25 molar cyanide solution, show that yields were further substantially increased to about

As shown from the results in Table II, the presence of calcium chloride decreases the amount of cyanide recovery, indicating either of the desirable phenomena

of improved penetration of that reagent into the chips or increased efficiency of reaction. The results also show that there is a clear tendency for higher yields at any given Kappa number when calcium chloride is used in conjunction with sodium cyanide in the pretreatment. This demonstrates the validity of the conclusion that the addition of a water-soluble alkaline earth metal salts to the cyanide produces enhancement of yields of wood pulp from lignocellulosic materials.

In the foregoing examples, the calcium chloride employed may be replaced by equivalent amounts of other watersoluble, alkaline-earth metal salts such as, calcium acetate, calcium bromide, calcium hypochlorite, calcium cyanide, calcium ferrocyanide, calcium hydro-sulfide, calcium bisulfite, calcium dithionate, calcium 15 thiosulfate, barium bromate, barium bromide, barium chloride, barium chloride, barium cyanide, barium ferrocyanide, barium hydrosulfide, barium silicate, strontium chloride, strontium chlorate, etc.

The terms and expressions which have been employed are used in terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible 20 within the scope of the invention claimed.

What is claimed is:

1. A process for increasing the yields of alkaline pulping of lignocellulosic material comprising treatment of the lignocellulosic material with an aqueous solution 30 containing cyanide ions and a water-soluble, alkaline-earth metal salt.
2. A process in accordance with claim 1, wherein the lignocellulosic material is in the form of wood chips.
3. A process in accordance with claim 1, wherein said treatment is conducted at temperatures of at least about room temperature and up to about 130°C.
4. A process in accordance with claim 1, wherein the cyanide ion is obtained from sodium cyanide.
5. A process in accordance with claim 1, wherein the 40 cyanide ion containing solution shall contain at least about 0.25 percent by weight of cyanide and up to

about 2 percent.

6. A process in accordance with claim 1, wherein the water-soluble, alkaline-earth metal salt is present in an amount at least about 0.1 weight percent of the aqueous solution.

7. A process in accordance with claim 1, wherein the water-soluble, alkaline-earth metal salt is a salt of calcium.

8. A process in accordance with claim 1, wherein the water-soluble, alkaline-earth metal salt is calcium chloride.

9. A process for increasing the yields of alkaline pulping of lignocellulosic material comprising treatment of said lignocellulosic material with an aqueous solution containing cyanide ions and a water-soluble, alkaline-earth metal salt, removing the lignocellulosic material from said aqueous solution, and digesting the thus treated lignocellulosic material with an alkali-metal pulping solution having a pH above about 7 and up to about 12.

10. A process in accordance with claim 9, wherein the lignocellulosic material is in the form of wood chips.

11. A process in accordance with claim 9, wherein said treatment is conducted at temperatures of at least about room temperature and up to about 130°C.

12. A process in accordance with claim 9, wherein the cyanide ion is obtained from sodium cyanide.

13. A process in accordance with claim 9 wherein the cyanide ion containing solution shall contain at least about 0.25 percent by weight of cyanide and up to about 2 percent.

14. A process in accordance with claim 9, wherein the alkaline earth metal salt is present in an amount at least about 0.1 weight percent of the solution.

15. A process in accordance with claim 9, wherein the water-soluble alkaline-earth metal salt is a salt of calcium.

16. A process in accordance with claim 15, wherein the alkaline earth metal salt is calcium chloride.

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