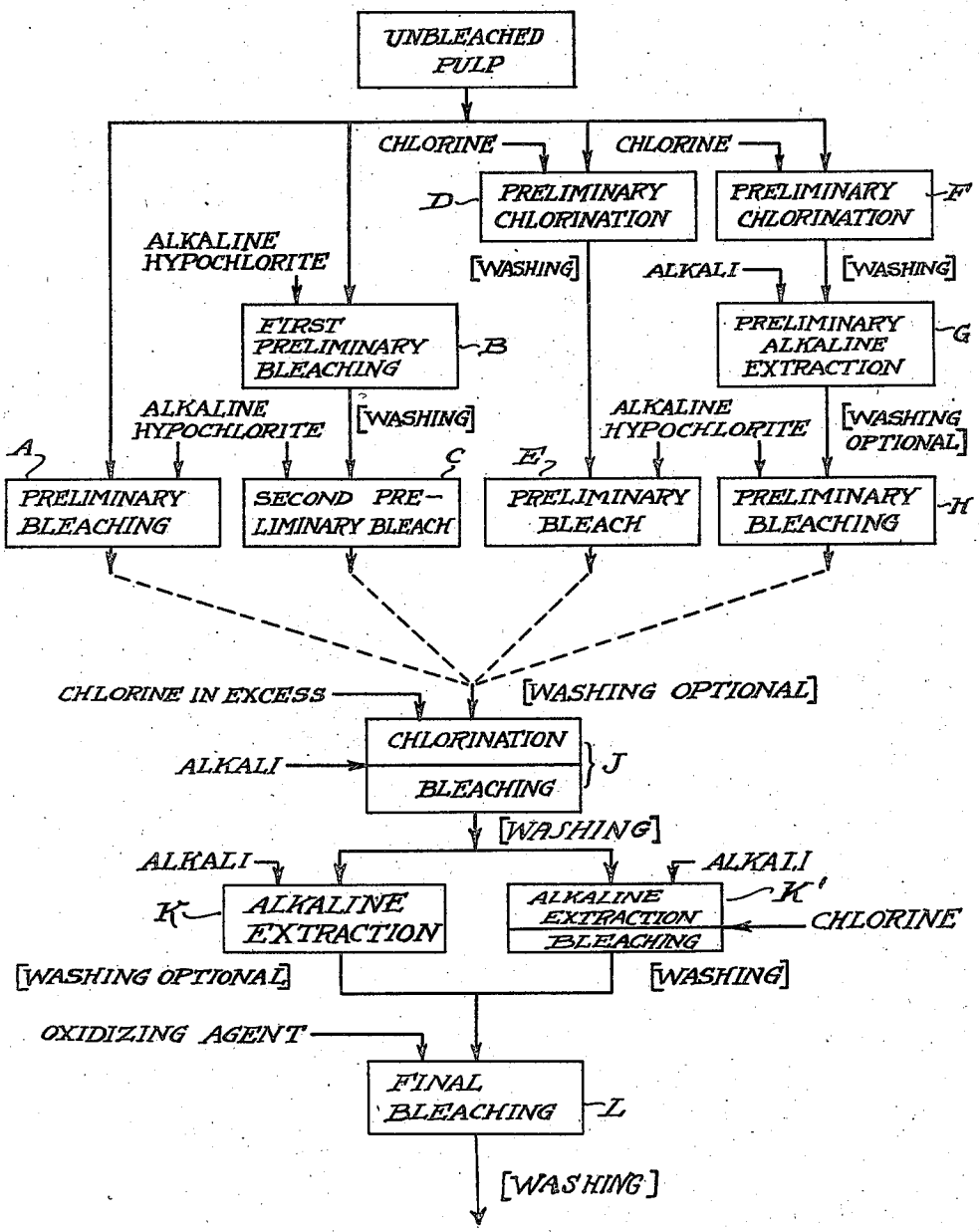
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PROCESS FOR THE PURIFICATION OF CELLULOSIC MATERIAL

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PROCESS FOR THE PURIFICATION OF CELLULOSIC MATERIAL

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This invention relates to an improved process for the purification of cellulosic materials with chlorine and hypochlorite solutions.

The earliest practice in bleaching cellulosic materials was to treat these materials with a solution of calcium hypochlorite in one or two stages. The large amount of hypochlorite required in these treatments resulted in excessive oxidation of the cellulose, thus producing a product of poor quality, especially with kraft pulps.

More recent practice has been to remove a substantial portion of the ligneous material in the pulp by means of a direct chlorination followed by an extraction with an alkali before bleaching the pulp with hypochlorite.

However, most cellulosic materials contain, in addition to ligneous material, a certain amount of coloring matter in nature similar to a dye, which must be removed before a high brightness can be obtained. In most sulfite pulps this matter is not present in large amounts and it is possible to obtain a fairly satisfactory bleaching with hypochlorite solutions alone.

In all kraft or sulfate pulps, however, this coloring matter imparts a very dark color to the pulp and is removed with extreme difficulty. This coloring matter is apparently not affected by the ordinary chlorination and alkaline extraction. In other words, the pulp after this preliminary treatment shows no improvement in brightness. Removal of the coloring matter, therefore, is left entirely to the final bleaching treatment.

Thus, while chlorination reduces the detrimental effect of the hypochlorite solution by virtue of the lower dosage employed, the resulting pulp requires an improvement in brightness fully as large as that required by the original unbleached pulp. Furthermore, the amount of hypochlorite required is still sufficiently great so that, in most applications, it seriously limits the degree of brightness which can be obtained without excessive degradation of the product.

By dividing the hypochlorite treatment into two stages thereby adding another stage to the process, this detrimental effect has been somewhat reduced, but not sufficiently to permit bleaching to substantially higher brightness values.

The need for a more complete chlorination of the ligneous material to permit its more complete removal before final bleaching was met by the introduction of an additional chlorination stage directly following the normal chlorination treatment, as disclosed in my United States Patents Nos. 2,127,765 and 2,203,212. In this second chlorination treatment, a thorough reaction with the

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ligneous material was effected by adding an excess of chlorine to the pulp and reacting for a short time, during which the reaction was primarily one of chlorination. Sufficient alkali was then added to the pulp to produce a pH above 7 and the residual chlorine was permitted to expend itself in oxidizing the readily oxidizable material present.

In this way the pulp, after an alkaline solubilizing treatment, was in a higher state of purity not only in regard to content of ligneous material but also to some extent in respect to its content of coloring matter. The bleaching action which followed immediately upon the second chlorination resulted in a considerable improvement in the brightness of the pulp. There was a consequent reduction in the amount of available chlorine required in the final stage of bleaching and an improvement in the quality of the pulp in bleaching to high brightness values. I now believe that the improved quality of pulp obtained in my earlier processes was due not only to the more complete removal of ligneous matter from the pulp before the final bleaching stage, but also to the oxidation and removal of a portion of the coloring matter before the final bleaching. The results obtained in this manner were a distinct improvement over prior methods, but there was still a substantial attack on the fibre in bleaching to the higher brightness values.

It has been proposed by Sunesson in United States Patent No. 2,140,863 that unbleached kraft pulp should be first treated with a hypochlorite solution and then be treated with an amount of chlorine readily consumed by the pulp. After caustic extraction and final bleaching a product of high brightness is obtained. However, the usefulness of this process is seriously limited by the fact that this treatment always produces a severe degradation of the cellulose.

It is an object of this invention to provide an improved process for the treatment of ligneous cellulosic material with chlorine and hypochlorite solutions in which the cellulose is subjected to conditions such that it is least likely to be degraded.

It is a further object to provide an improved process which will permit the bleaching of ligneous cellulosic material to a high brightness with the maximum retention of desirable paper-making properties.

It is a still further object to provide an improved process which will permit the preparation of pulps of high chemical purity with the mini-

mum degradation in physical and chemical properties of the pulp.

Other objects and advantages of this invention will appear from the following description and claims.

In the process of Sunesson disclosed in United States Patent No. 2,140,863, in order to obtain the desired degree of chlorination of the impurities in the pulp, the cellulose is subjected to prolonged exposure to the chlorination liquor. In investigating the mechanics of this process in the laboratory, I have determined that this prolonged chlorination treatment results in a pronounced attack on the cellulose, as reflected, for example, in the drop in viscosity. Since this marked degradation does not occur when unbleached pulp is chlorinated directly under similar conditions, I have reached the conclusion that preliminary bleaching of the pulp increases greatly the sensitivity of the cellulose to attack by solutions containing chlorine. The preliminary bleaching removes impurities, which serves as a protective coating for the cellulose; and, in so doing, it in effect exposes the cellulose to the harmful oxidizing action of the hypochlorous acid present in the solution of chlorine.

I have discovered that this serious attack on the cellulose can be avoided by applying the principles of "excess chlorination" as embodied in my earlier patents, United States No. 2,127,765 and No. 2,203,212 to the pre-bleached pulp. The procedure comprises treating the pre-bleached material with an amount of chlorine substantially in excess of that required for the chlorination reaction and limiting the time of the reaction to a period of only a few minutes by abruptly changing the pH of the solution to a value above 7 by the addition of an alkali. The resulting hypochlorite is then permitted to react with the impurities in a normal hypochlorite bleaching reaction. Operating in this manner, I obtain a relatively small drop in viscosity and a material which can be further purified and bleached to yield a final bleached product of exceptionally high brightness with a minimum degradation of the cellulose.

This combination of the preliminary oxidation or bleaching of the coloring matter followed by the short chlorination with an excess of chlorine makes possible the substantially complete removal of colored impurities while retaining the desired physical and chemical properties of the pulp to an extent which was hitherto impossible.

The accompanying drawing illustrates, by way of example, the flow of material in the carrying out of my process.

Stated generally my invention includes the following treatment of cellulosic material suspended in water to obtain a bleached product:

(1) A preliminary bleaching to a brightness substantially lower than that desired in the final product.

(2) A thorough chlorination of the residual ligneous material by treatment with an amount of chlorine substantially in excess of the amount required in the chlorination reaction. After a short reaction time, the pH of the mixture is increased to a value greater than 7 and additional time is allowed for the available chlorine to react with the oxidizable material in the pulp.

(3) After washing the pulp either with water alone or with water followed by an extraction with an alkaline solution, a final bleaching with an oxidizing agent.

The following description will illustrate the application of the principles of my invention. The reference letters refer to the various steps in the accompanying flow diagram.

I. *Preliminary bleaching*

In its simplest form, the preliminary bleaching may consist of a single-stage treatment A with calcium hypochlorite solution prepared by absorbing chlorine gas in a milk of lime solution. The most favorable conditions for the attainment of a high quality product are those described in my co-pending application Serial No. 486,657, in which the pH of the bleaching solution is controlled at a certain fixed value throughout the treatment. However, desirable results are obtained in the present invention even when such control is not exercised over the pH of the solution and I do not wish to be limited to these conditions.

Neither do I wish to be limited to the pH conditions ordinarily employed in hypochlorite bleaching. Normally it is essential that too high pH conditions be avoided so that the bleaching time is not unduly prolonged. However, in the preliminary bleaching employed in my invention, the time is usually very short, and therefore it is practical to use higher than normal pH conditions without unduly prolonging the reaction time. Improved quality may sometimes be obtained in this way.

The preliminary bleaching may, if desired, consist of two or more treatments, step B and step C, with a hypochlorite solution separated by a washing. In this case, because of the very short reaction period involved in step B, it may be feasible and desirable to employ still higher pH conditions than those in step C without unduly prolonging the bleaching time.

If a product of exceptionally high brightness is desired, together with economy in chemical consumption, the preliminary bleaching may consist of two stages of treatment in which the first is the ordinary chlorination step D with a solution containing chlorine followed by a water wash, and the second, a bleaching treatment, step F with a solution of a hypochlorite. In the second or bleaching stage, it is preferable to add sufficient alkali at the start to give a final pH of not less than 7. In fact, sufficient alkali can be added at the start to permit the addition of the desired amount of chlorine as elemental chlorine, thus forming hypochlorite in the presence of the pulp; and to provide the excess required to give a final pH not less than 7. While I have stated the conditions most desirable in the second or bleaching stage, I do not limit myself to the conditions named and wish to be free to carry out this stage of the process with no control of pH if I so desire.

With still another form of pre-bleaching, a further improvement in pulp quality and an additional economy in chemical consumption is achieved by performing the preliminary bleaching in three stages by interposing a solubilizing treatment step G with a solution of an alkali between a chlorination step F and the bleaching step H.

II. *Excess chlorination*

The pulp obtained from any of the four preliminary bleaching steps which have been described is then subjected to the excess chlorination step J. This step includes in every case the treating of pulp in water suspension with a solution of chlorine preferably at a pH below 3, said

solution containing an amount of chlorine in excess of that required for the chlorination reaction. This excess is usually about 50% but may in some cases be much greater, and in other cases it may be as little as 20%. The reaction or chlorination time will usually be less than five minutes and will seldom be more than ten minutes. After this short reaction time, the pH of the pulp is abruptly changed to a value above 7 by adding an alkaline reagent, such for example as milk of lime. After the addition of the alkaline reagent, the resulting hypochlorite solution is allowed to react with the impurities and the pulp is then washed.

The pH value below 3 which is desired for the chlorination reaction is usually obtained simply by the addition of the required amount of chlorine gas or chlorine water to the pulp. However, where the amount of chlorine being added is very small, it may be necessary to supplement it with an amount of an acid, such as a solution of HCl or H_2SO_4, to obtain the desired pH.

While I prefer to wash the pulp after the preliminary bleaching treatment and before the treatment with an excess of chlorine, step J, nevertheless, it is by no means necessary to do so. I have found that good results can be obtained by omitting the washing after the preliminary bleaching and simply lowering the pH to a value below 3 by the addition of elemental chlorine either alone or supplemented by a solution of an acid such as HCl or H_2SO_4 and proceeding with the chlorination in the manner just described.

III. *Alkaline extraction*

After step J, the washed pulp may be treated with a solution of an alkali such as caustic soda, step K, to solubilize most of the remaining impurities in the pulp. In making a product for normal paper-making purposes, the amount of alkali used in this stage may be very small, in some cases only enough to prevent the pH of the solution dropping below 7 during the treatment. In other instances, where a product of high alpha cellulose content is desired either for use in special paper products or for purposes of chemical conversion into other products of cellulose, the alkali treatment may be much more energetic, and may comprise a treatment with much stronger caustic soda solutions up to mercerizing strength. This stage may or may not be carried out at elevated temperature. After this treatment it is usually preferable to wash the pulp before the final bleaching stage, but there may be instances in which it is not necessary to do so.

The alkaline extraction stage may be modified by treating the unwashed alkali-treated pulp with a hypochlorite solution, step K'. This may conveniently be done by adding a small amount of chlorine to the alkaline pulp. The pulp is then washed and given a final bleaching treatment.

IV. *Final bleaching*

The final bleaching stage L will usually consist of a treatment with sufficient hypochlorite solution to give the desired brightness, followed by a washing with water. Any solution containing available chlorine may be used for this purpose, although it is usually preferable to employ a solution of calcium or sodium hypochlorite at a pH not less than 7. If desired, the final bleaching can be performed by other oxidizing agents such as a solution of a chlorite, or a peroxide.

The small amount of bleaching agent required in this final treatment makes it economically feasible to use an expensive chemical if desired. While I have referred here to the final bleaching as a single treatment with an oxidizing agent, it is possible to employ more than one stage for this purpose with one or more of the above-mentioned oxidizing agents.

Example

The following example of an embodiment of my invention will further illustrate its application in a four-stage process. The raw material used in this example was an unbleached kraft pulp having a brightness of 21.5 and a cuprammonium viscosity of 68.5 (centipoises).

Stage 1.—A sample consisting of 1000 grams air-dry weight of this kraft pulp suspended in water at a pulp consistency of 4% and a temperature of 75° F. was treated with 5.5% of available chlorine by the addition of a quantity of calcium hypochlorite solution containing 55 grams of available chlorine. The pH of the pulp mixture, which was 8.9 at the start, was permitted to drop to 8.25 at which point it was held practically constant by the frequent addition of caustic soda solution in small doses. After 1.5 hours of treatment, the residual chlorine was 0.2% or 2 grams and the pulp was washed with water.

At this point the brightness of the pulp was 40.5 and its viscosity was 47.6.

Stage 2.—The pulp was then treated with 42.5 grams or 4.25% of elemental chlorine at a pulp consistency of 4% and a temperature of 75° F. After five minutes reaction time, at which point the pH was 1.6, the pulp was abruptly made alkaline by the addition of a quantity of milk of lime containing 45 grams or 4.5% of calcium hydroxide. The pH of the mixture after the addition of lime was about 8.5. After one hour's reaction time, the residual chlorine was 2 grams or 0.2% and the pulp was washed with water.

The brightness of the resulting pulp was 65 and its viscosity was 35.5.

Stage 3.—The pulp was treated with 20 grams or 2.0% of caustic soda for one hour at a pulp consistency of 15% and a temperature of 150° F. The treated pulp, containing 15 grams or 1.5% of unconsumed caustic soda, was diluted and washed with water.

The brightness was now 58 and the viscosity was 32.3.

Stage 4.—In the final treatment 7.5 grams or 0.75% of available chlorine was added in the form of calcium hypochlorite solution. The treatment was carried out at a pulp consistency of 6% and a temperature of 95° F. The pH which was 8.5 at the start was allowed to drop to 8.0 at which point it was maintained by the frequent addition of caustic soda solution. After 3.25 hours of bleaching, the amount of residual chlorine was 2.5 grams or 0.25%, after which the pulp was washed with water.

The brightness of the final product was 83.3 and its viscosity was 19.2. This high quality of product is very unusual, and highly desirable.

To better illustrate the advantages of my invention, I have prepared a table listing the properties of two bleached kraft pulps prepared from the same raw material and bleached to the same final brightness but by different four-stage processes. Column A represents the pulp bleached by the process of my invention as described in the example. Column B represents the pulp bleached by me according to the conditions em-

ployed in the example disclosed in United States Patent No. 2,140,863.

	A (present invention)	B (U. S. 2,140,863)
Brightness	83.3	83.2
Loss in Brightness on Fading	7.8	9.0
Alpha Cellulose Content	86.8	84.4
Cuprammonium Viscosity	19.2	9.75
Bursting Strength—at 75% Freeness	173	144
Bursting Strength—at 50% Freeness	185	160
Tearing Resistance—at 75% Freeness	190	172
Tearing Resistance—at 50% Freeness	181	150

It will be readily seen that the product resulting from the application of the process of my invention is distinctly superior in quality to that obtainable by the method of Patent No. 2,140,863. My process produces a pulp which is more stable in color, is higher in chemical purity (as shown by the alpha cellulose content), is much less degraded (as shown by both alpha cellulose content and cuprammonium viscosity), and is superior in paper-making strength characteristics (as shown by bursting and tearing values).

The determination of pulp quality involving the properties of brightness, alpha cellulose content, cuprammonium viscosity, bursting strength, and tearing resistance were all run according to the standard methods of the Technical Association of the Pulp and Paper Industry. The loss in brightness on fading was determined by testing the brightness of a sample handsheet of the pulp before and after a two-hour exposure at a distance of 16 inches from a G. E. type H–5 mercury vapor lamp.

The following terms where they appear in the specifications or claims are to be understood to have the following meaning:

"Cellulosic material" comprises kraft pulps, soda pulps, sulfite pulps, and other ligneous materials such as jute, hemp, flax, bagasse, bamboo, straw or recovered waste ligneous cellulosic materials.

"Bleaching" consists of a treatment with an oxidizing agent such as a hypochlorite solution in which colored impurities are oxidized and the brightness of the pulp is increased.

"Single treatment" means the application of a chemical reagent to the pulp at one time or in several doses, but the doses are not separated by a washing.

"Hypochlorite solution" is any solution containing the hypochlorite ion and it may also contain hypochlorous acid.

The term "chlorine" where used in reference to the chlorination reaction refers to free chlorine in solution as distinguished from chlorine in combined form such as hypochlorous acid and hypochlorite ion. The solution of chlorine may be prepared from elemental chlorine or by the acidification of hypochlorite solutions to a pH below approximately 4.

"Alkaline reagent" refers to sodium hydroxide, calcium hydroxide, sodium carbonate, or any other suitable material which has an alkaline reaction.

While I have described several forms of my invention, in its broad form I do not wish to be limited to the specific forms described herein.

I claim as my invention:

1. A process for the purification of cellulosic material in the form of a pulp in water suspension, which comprises the steps of: preliminarily bleaching the pulp to a brightness substantially lower that that desired in the final product by contacting the pulp with a hypochlorite solution; washing the pulp with water; adding to the pulp chlorine substantially in excess of the amount required for complete chlorination of residual liqueous material; reacting on the impurities in the pulp with a part of said chlorine for a period of time not materially in excess of approximately ten minutes; adding sufficient alkaline reagent to the reaction mixture to obtain a pH above 7 in the pulp; allowing the hypochlorite solution thus formed to react with the impurities in the pulp; and washing the pulp with water to remove soluble reaction products.

2. A process for the purification of cellulosic material in the form of a pulp in water suspension, which comprises the steps of: preliminarily bleaching the pulp to a brightness substantially lower than that desired in the final product by contacting the pulp with a hypochlorite solution as the bleaching agent; washing the pulp with water; adding to the pulp chlorine substantially in excess of the amount required for complete chlorination of residual ligneous material; reacting on the impurities in the pulp with a part of said chlorine for a period of time not materially in excess of approximately ten minutes; adding sufficient alkaline reagent to the reaction mixture to obtain a pH above 7 in the pulp; allowing the hypochlorite solution thus formed to react with the impurities in the pulp; washing the pulp with water to remove soluble reaction products; treating the pulp with an alkaline reagent to render soluble additional impurities; and washing the pulp with water.

3. A process for the purification of the cellulosic material in the form of a pulp in water suspension, which comprises the steps of: preliminarily bleaching the pulp to a brightness substantially lower than that desired in the final product by contacting the pulp with a hypochlorite solution; washing the pulp with water; adding chlorine to the pulp; reacting on the impurities in the pulp with a part of the chlorine for a period of time not materially in excess of approximately ten minutes; adding sufficient alkaline reagent to the reaction mixture to obtain a pH above 7 in the pulp; allowing the hypochlorite solution thus formed to react with the impurities in the pulp; washing the pulp with water to remove soluble reaction products; treating the pulp with an alkaline reagent to render soluble additional impurities; washing the pulp with water to remove such additional impurities; bleaching the pulp by treatment with an oxidizing agent; and washing the bleached pulp.

4. A process for the purification of cellulosic material in the form of a pulp in water suspension, which comprises the steps of: preliminarily bleaching the pulp to a brightness substantially lower than that desired in the final product by contacting the pulp with a hypochlorite solution; adding to the pulp chlorine substantially in excess of the amount required for complete chlorination of residual ligneous material; reacting on the impurities in the pulp with a part of said chlorine for a period of time not materially in excess of approximately ten minutes; adding sufficient alkaline reagent to the reaction mixture to obtain a pH above 7 in the pulp; allowing the hypochlorite solution formed in the preceding step to react with the impurities in the pulp; washing the pulp with water to remove soluble reaction products; treating the pulp with an alkaline reagent

to render soluble additional impurities; bleaching the pulp by treatment with an oxidizing agent; and washing the bleached pulp.

5. In the purification of a cellulosic material as a pulp in water suspension, which cellulosic material has received a preliminary bleaching, the process which comprises: adding to the prebleached cellulosic material chlorine substantially in excess of the amount required for complete chlorination of residual ligneous impurities; reacting on the impurities in the pulp with a part of the chlorine for a period of time not materially in excess of approximately ten minutes; adding sufficient alkaline reagent to the reaction mixture to obtain a pH above 7 in the pulp and to form with the remaining chlorine a hypochlorite solution; and allowing the hypochlorite solution thus formed to react with the impurities in the pulp.

6. A process according to claim 4 in which the preliminary bleaching of the pulp consists of: treating the pulp with an amount of chlorine not substantially in excess of that required for the chlorination of the impurities in the pulp; washing the pulp with water; treating the pulp with an alkaline reagent; and treating the pulp with a solution of hypochlorite.

7. A process according to claim 4 in which the treatment of pulp with an alkaline reagent, immediately preceding the final bleaching step, comprises the steps of: reacting the alkaline reagent with the pulp; treating the pulp with hypochlorite solution; and washing the pulp with water.

FERRI CASCIANI.

REFERENCES CITED

The following references are of record in the file of this patent:

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