Nov. 3, 1942. L. M. SHELDON 2,300,733

CELLULOSE PULPING SYSTEM

Filed May 21, 1937

Fig. 1.

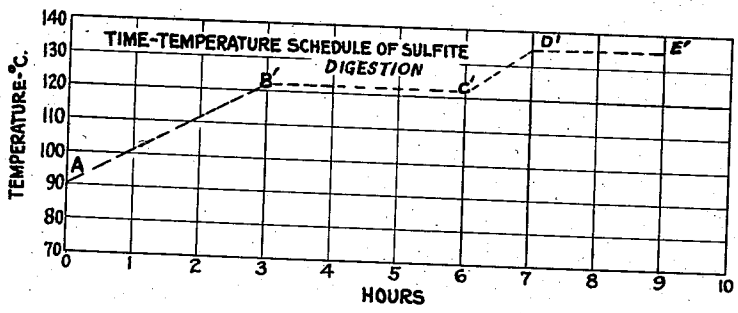


Fig. 2.

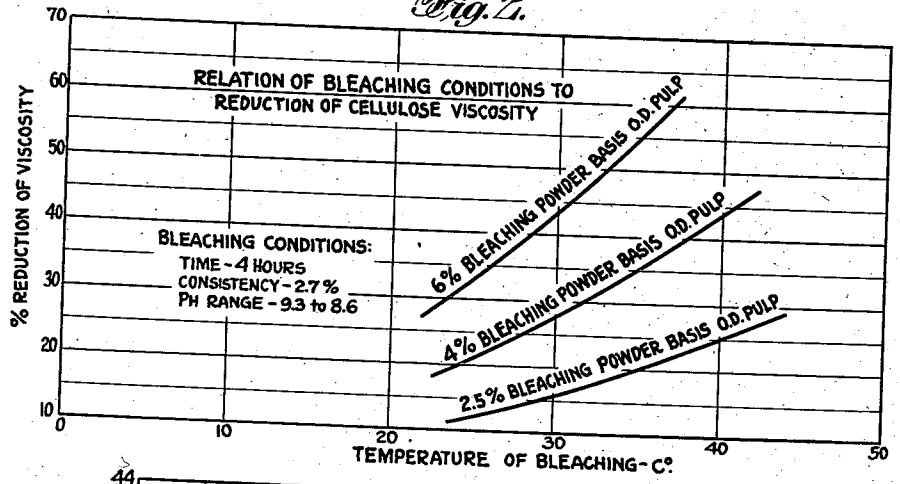
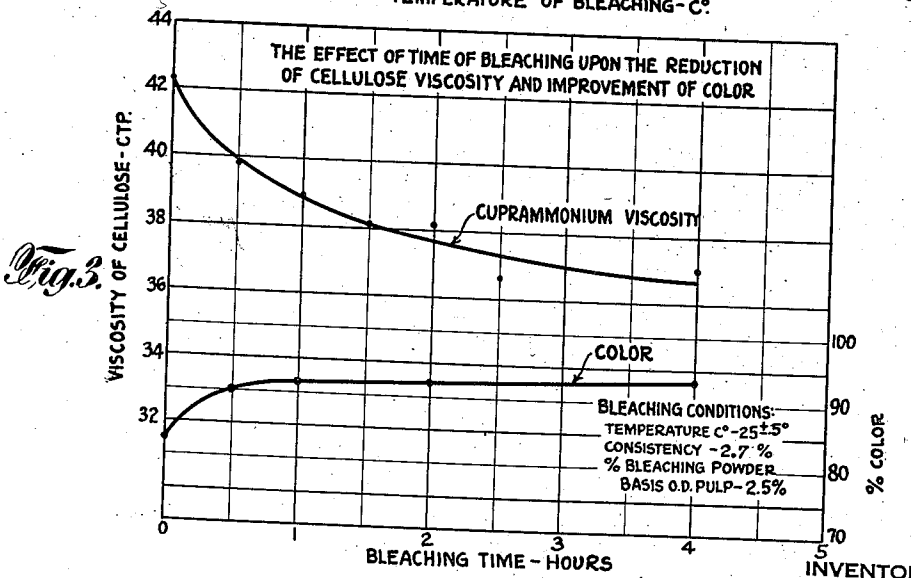


Fig. 3.



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CELLULOSE PULPING SYSTEM

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2 Claims. (Cl. 92—11)

This invention relates to the production of cellulosic pulp from resinous woods and in particular to the removal of resinous materials therefrom.

A primary object of the invention is to provide a process for producing purified cellulosic pulp suitable for conversion into cellulose esters, particularly acetate, ethers, viscose and other derivatives from resinous woods, such as the southern pine species; said purified cellulosic pulp being capable of very close duplication with respect to its physical and chemical properties between successive batches.

Another object is the provision of an economical process employing selected wood from the various species of trees known collectively as southern pines as a base raw material to produce purified wood cellulosic pulp capable of acetylation, xanthation and conversion into other derivatives, which wood has heretofore been considered unsuitable for the satisfactory production of purified cellulosic pulp of the class described; said process providing means for the removal of impurities, such as resins, which are characteristic of said southern pine species.

A further object is to provide an economical process for producing sulfite pulp for paper, employing the selected wood for use from the various species of trees known collectively as southern pines as the base raw material, which woods have been heretofore regarded as unsuitable for this purpose; said process providing the means for removing impurities such as resins and pitch.

In the accompanying drawing which illustrates several features of the present invention:

Figure 1 is a typical time-temperature impregnation and digestion schedule.

Figure 2 shows the relation of bleaching temperature to viscosity reduction.

Figure 3 shows the relation of bleaching time to viscosity reduction and color of cellulose.

The advisability of confining the raw material for the manufacture of chemical cellulose to one genus or to one species of trees from which the base wood material is derived has been suggested. In treating even single species of wood there is a tremendous distinction within each species of the factors affecting pulping and purification of the wood, the amount of recoverable alpha cellulose and the economy with which the process may be carried out.

In the process of the present invention there is employed a certain group of trees not heretofore known to be capable of yielding cellulosic pulp suitable for derivative purposes. The primary advantage found in this group is the almost complete absence of heartwood. For example, the group of trees, known collectively as southern pine (which include the individual species of *Pinus palustris,* long leaf; *Pinus taeda,* loblolly; *Pinus echinata,* short leaf; and *Pinus caribead,* slash pine), grow in such a manner that if they are cut before they reach the age of about 25 to 35 years, they consist of substantially all sapwood. At the age of 20 years, for example, slash pine will produce logs in excess of 8"–10" in diameter, which obviously may be economically chipped by the customary practices.

The southern pine wood species have heretofore proven unsatisfactory for pulping by the sulfite processes owing to the serious operating difficulties encountered because of their high pitch or resin content. The pitch and resin content is frequently as high as 5%–10% and when permitted to solidify before pulping, as by evaporation and prolonged storage, is quite difficult to remove. In the manufacture of pulp for paper purposes by the prior practices the resin exhibits a strong tendency to agglomerate, clog the screens and wires of the paper machines and form very undesirable defects in the paper.

I have discovered, however, that by selecting southern pine wood substantially free of heartwood and defective material, including pitch pockets, before the pitch or resin content has had an opportunity to solidify and preferably before any substantial amount of fungus growth such as "blue stain" develops, a highly uniform cellulosic pulp suitable for conversion into cellulose derivatives may be economically prepared according to the process hereinafter set forth. I have also found that such selected woods may be satisfactorily and economically used for producing strong sulfite paper pulp.

The logs are debarked, washed and chipped by the customary practices. The chips are preferably of the order of ¼" in length, but the standard ¾" to ⅞" chips may be employed, if desired.

The suitably divided wood is impregnated with the selected delignifying reagent. Normally, it is preferred in connection with the present invention to use a sulfite delignifying solution, such as ammonium, calcium or sodium bisulfite. The chips are impregnated and thoroughly saturated with the delignifying liquor at a temperature of 100° C. or less, while at the same time substantially their entire air content is removed. At a temperature of the order of 100° C. there is but slight tendency for delignification to take

place, hence the saturation of the chips is accomplished before the delignification of the wood proceeds. By this provision a far more uniform treatment of the woody material is insured.

Impregnation of the wood with the digesting liquor may be accomplished, for example, by boiling the chips in a freely vented tank or digester filled with the treating solution and then allowing the surrounding liquor to flow into the interstices of the wood either by increasing the pressure on the liquor or by cooling the mass slightly below 100° C. In either case, the steam within the interstices of the wood is condensed, thus forming a partial vacuum which draws the surrounding liquor into all the capillaries and interstices.

Removal of the air from the subdivided wood and impregnation with the digesting liquor may also be accomplished by a preliminary boiling of the wood with water to remove the air and then adding the delignifying liquid to the chips and providing a sufficient time to permit diffusion of the delignifying chemical through the water saturated chips.

Regardless of the particular digestion procedure, the character of the raw material employed together with the advantageous presaturation of the chips with the delignifying solution makes it possible to carry out the digestion under such mild and lenient conditions that substantially no chemical degradation of the cellulosic material in the wood is encountered and a high yield results.

The mild and lenient digestion results in the production of pulp wherein the cellulosic fibers have a gradually increased porosity and permeability over their original condition and which are relieved of the greater portion of their ligneous impurities. The digestion moreover reduces the pitch content of the pulp to less than the order of about 1.5%.

At the completion of the digestion, the treating solution is drained and the reaction products washed from the pulp, preferably with hot water and with air excluded. This treatment not only improves the color of the pulp but also aids in removing a part of the residual pitch and other hot water soluble impurities from the fibers, such for instance as hydrolyzed hemicelluloses and mineral constituents composed mostly of calcium, magnesium, iron, manganese, sodium, potassium and silicon salts. The pitch content of the digested pulp may be reduced even further by adding ¼% or less caustic soda, based on the dry weight of the pulp, to the hot water used in washing.

Upon the completion of the thorough washing of the crude pulp, it is screened to remove knots and other fragment material and then completely defibered by any suitable mechanical means; the defibered pulp may be screened, if necessary, to remove any neps or bundles of fibers which may have survived the defibering process.

Regardless of the ultimate use of the cellulosic pulp, whether for cellulose acetate, viscose products or for bleached paper pulp, the first step in the purification is a uniform chlorination of the defibered pulp. The chlorination may be accomplished by introducing a known amount of chlorine gas into a water slurry of the pulp under highly efficient agitation. For economy and to insure complete delignification of the pulp, the gas is added to the pulp slurry in as short a time as possible consistent with uniform distribution. An amount of chlorine in pounds for each 100 pounds of pulp (oven dry basis), equivalent to 14%–18% of the bleach value of the pulp is employed. The control of the distribution and amount of chlorine results in a maximum purification of the pulp with an almost complete absence of chemical degradation.

Following the chlorination, the pulp is treated with either hot or cold alkaline solutions to remove the reaction products. The result of the chlorination and causticizing treatments is to reduce the bleach value of the pulp to between the order of 1.0% and 5%, depending upon the kind of alkaline treatment given, and to reduce the pitch content to less than the order of 0.3%.

Regardless of the bleachability of the washed pulp after the chlorination and causticizing treatment within the range of 1% to 5%, it is bleached in a dilute hypochlorite solution containing 1% to 6% bleaching powder based on the pulp. A sufficient amount of alkali is added to the bleach solution to bring its pH value to approximately 8.0 or above. Under these treating conditions the residual oxidizable impurities remaining in the pulp are reacted upon in the early stages of the bleaching, for example, in from ½ to 1½ hours or less.

The treatment is continued for an additional time, usually from 2 to 3 hours, to reduce the cuprammonium viscosity of the cellulosic pulp to the desired value. By reference to Figure 3 it will be observed that the cuprammonium viscosity of the pulp is rapidly reduced during the early stages of the bleaching treatment. This is followed by a period in which the rate of reduction is relatively small. For example, it will be seen that the viscosity is reduced from 42 centipoises to about 39.0 centipoises in 1 hour, but in the succeeding 3 hours the value is reduced only an additional 2.2 centipoises. Thus by continuing the hypochlorite treatment until the relatively level portion of the viscosity curve is reached, the treatment may be readily terminated at the desired viscosity level, since the rate of reduction is relatively small and the desired time to give the required value may be calculated with precision.

The desired reduction in the cuprammonium viscosity of the pulp may also be effected by varying the temperature of the hypochlorite bleach treatment and holding the time, concentration, and consistency of the solution constant.

Upon the completion of the bleaching treatment the pulp is thoroughly washed with water until free of available chlorine, preferably until neutral.

At the end of the bleaching treatment the cellulosic pulp will have an alpha cellulose content of about 90%–94%, depending upon the time, temperature and concentration of alkali used in the treatment after chlorination. The resin content will be reduced to the order of 0.3% or less. The material is very satisfactory for use in preparing viscous products and is characterized by its nearly invariable physical and chemical properties between successive batches. It is also very satisfactory for paper purposes since it possesses unusually high strength properties, a high white color, and the resin content is in such condition and of such low value as to cause none of the usual clogging of the screens or other operating difficulties.

For attaining a more highly purified quality, the pulp is next given a treatment in alkali at elevated temperature. This may be conveniently accomplished by the following method: The

washed, bleached pulp is boiled in a sodium hydroxide solution having a concentration in the range of about 5%–10%, preferably of the order of 7%, for from 1–3 hours during continuous agitation. It is desirable to carry out the operation under conditions which exclude atmospheric oxygen. Upon the termination of the treatment the solution is drained and the pulp washed with water until substantially free of the alkaline solution. This step effects a reduction in the soda soluble content of the pulp to less than 3% and a corresponding increase in the alpha cellulose content.

The washed pulp may be given a second hypochlorite bleach employing less than 1% bleaching powder based on the dry weight of the pulp. The time, temperature and consistency are controlled substantially as described for the first hypochlorite treatment. The pulp is again washed until free of available chlorine, preferably until neutral.

The cellulosic pulp at this stage of its purification is of exceptionally high quality for use in the preparation of viscose products. The alpha cellulose content is approximately 95%–97%, its soda solubility less than 4% and the resin content is reduced to the order of 0.25% or less. It may also be used to advantage in the preparation of acetate where exceptionally low color and haze in solvent solutions are not essential.

When the cellulosic pulp is intended for conversion into cellulose acetate of high quality, the pulp obtained by the treatments above is mercerized in a strong sodium hydroxide solution.

Upon the completion of the mercerization it is important to wash the caustic reagent from the cellulose as rapidly as possible and in the absence of atmospheric oxygen. With suitable equipement, this may be and is desirably accomplished in 30 minutes or less.

Cellulose acetate of lower cost may be obtained from the use of the purified pulp of the present invention since the base raw wood material is not only cheaper than other available supplies of raw cellulosic material, but its ready response to chemical treatment permits important economy in the process of its conversion to acetylatible quality.

In order to more particluarly describe the present invention and manner of attaining uniformity in the reactions, the following example sets forth a typical embodiment thereof:

Example A

A very satisfactory treating liquor consists of ammonium bisulfite having a total SO_2 content of 6.0% and a combined SO_2 content of 1.1%.

The chips are charged into the digester and water, preferably at or near 100° C., is added in sufficient quantity to completely immerse the chips. When they have become partially saturated, steam is admitted into the digester by means of suitable ports located in the bottom of the digester and the mass of water and chips is boiled for 30 minutes under freely vented conditions. It is important that the chips be maintained completely immersed in the water during the boiling. At the end of 30 minutes boiling, the relief valve or other outlet to the atmosphere at the top of the digester is closed and the steam supply to the bottom ports is cut off. A suitable outlet in the bottom of the digester for draining is then opened and steam is admitted at the top of the digester through a suitable port above the water level. This forces the water surrounding the chips out of the digester. After all of the water has been drained from the chips in this manner, the water outlet at the bottom and the steam inlet at the top of the digester are both closed. This leaves the digester and the voids around the chips, the capillaries and interstices within the chips completely filled with steam at approximately 100° C.

The ammonium bisulfite liquor previously preheated to a temperature of the order of 90° C. is then pumped into the digester in sufficient quantity to attain a ratio of liquor to oven dry wood of the order of 6:1. When the liquor comes in contact with the chips the steam with which they are saturated is forced to condense. This creates a partial vacuum which acts to draw the cooking liquor into all the capillaries and interstices of the chips. In a short time, for example, 15 minutes or less, the chips become completely saturated with treating liquor. Thus, by first removing all of the air from around and within the chips by the boiling and steaming practice, the chips become completely saturated with treating solution at a temperature just under 100° C.

Steam is now admitted into the digester and the temperature raised at a uniform rate to the order of 121°–123° C. over a period of 3 hours, as shown by reference to curve AB', Figure 1. The temperature is held within this range for approximately 3 hours (curve B'C', Figure 1). During this period the sulfonation of the noncellulosic components of the wood takes place. Owing to the completeness with which the air has been evacuated from the digester and the chips before the temperature is raised to above 100° C., the pressure within the digester during the sulfonation cycle (curve B'C', Figure 1) will be due solely to the heated treating solution and should not exceed 85 pounds per square inch. Gas reliefs to prevent the pressure exceeding the customary limit in the conventional digester equipment are consequently usually unnecessary. Thus, the usual variability in the concentration of the treating liquor during the sulfonation period, occasioned by the loss of sulfur dioxide gas by venting, is avoided and a treatment of the woody material with a liquor of nearly invariable composition between successive batches is insured.

At the end of the 3 hour sulfonation period, the temperature is raised to the order of 135° C. at a uniform rate over a period of 1 hour (curve C'D', Figure 1) and maintained closely at this level for from 2–4 hours (curve D'E', Figure 1), depending upon the bleachability and viscosity desired in the digested pulp. The effect upon the bleachability and viscosity by varying the period of treatment at a temperature of the order of 135° C. will be described later in this example.

Hydrolysis of the sulfonated, non-cellulosic material takes place satisfactorily during the treatment at temperatures in excess of 130° C., and in the present example the digestion is terminated at the end of 2 hours treatment at 135° C. Gas relief to control the pressure in the digester below the permissible limit of the equipment may be practiced during the hydrolyzing cycle. Care is exercised that the venting is carried out in such a manner as to avoid reducing the temperature appreciably below the preferred level of the order of 135° C., since the rate of hydrolysis of the sulfonated, ligneous material is affected by variations in temperature. Short gas reliefs of

less than 30 seconds each will accomplish the desired reduction in pressure without substantially lowering the temperature, except in the final stages of digestion where gas relief is practiced to effect as complete recovery of sulfur dioxide as possible.

Upon the completion of the digestion schedule, the pulp is blown from the digester in the customary manner into a blow pit and washed with water, preferably as near 100° C. as possible until it is neutral to litmus. The washed pulp is screened through a 0.012"–0.015" screen and passed over a riffle box for further removal of heavy foreign material, such as knots, particles of bark, dirt and the like.

By the foregoing digestion schedule, from 50–52 pounds or more of oven dry pulp are obtained from each 100 pounds of oven dry slash pine wood used. An actual analysis of a typical screened pulp showed the following:

	Per cent
Alpha cellulose	87.9
Soda solubility	24.6
Ash	0.76
Cuprammonium viscosity (ctps.)	41.1
Bleachability	22.7
Pentosans	6.8
Resins (ether extract)	1.1

It will be noted that the retention of the native alpha cellulose is 44–46 pounds of each 100 pounds of oven dry slash pine wood used. The resin content is reduced to the order of 1% and is in a condition which permits its ready removal to an inconsequential residue devoid of objectionable agglomerating tendency in the first step of purification to be presently described.

The digestion schedule just described is designed to produce a high yield of raw pulp of relatively high viscosity and bleachability. The same schedule and liquor composition applied to other coniferous woods such as spruce, or to deciduous woods such as black gum, yellow birch and the like will result in raw pulps whose viscosities and bleachabilities may vary to some extent from the above values. These variations will also occur with wood of the same species obtained from different geographical areas and of varying growth conditions. Consequently, it is usually necessary to determine the precise adjustment of the time-temperature schedule to give a pulp of the desired bleach and viscosity characteristics by carrying out one or more experimental digestions on the quality of wood to be used in continuous operation. The adjustments in the digesting practice for controlling the bleachability and viscosity of the raw pulp are conveniently made by varying the time or the temperature, in some cases both. To obtain a maximum yield of raw pulp together with high cuprammonium viscosity, the average cooking temperature should be held as low as possible and the time of treatment prolonged by experiment to give a pulp that can be readily and completely defibered.

High cuprammonium viscosity in the raw pulp is quite necessary where it is intended that the purified cellulose shall have a viscosity in excess of the order of 25 centipoises. There are certain types of cellulose acetate, however, for which it is necessary to provide a purified cellulose having a relatively low cuprammonium viscosity, for example, below the order of 10 centipoises. For this purpose it is more convenient to produce a raw pulp with a cuprammonium viscosity less than the order of 25–30 centipoises. To accomplish this the digestion schedule, represented by curve DE, Figure 1, is carried out at a somewhat higher temperature, for example, 140°–145° C., the time being held constant. This treatment appreciably lowers the cuprammonium viscosity and also effects a considerably smaller proportional reduction in the bleach value. The purpose of providing a relatively low raw pulp viscosity as the starting material to produce purified cellulose of less than 10 centipoise viscosity will be explained in the description which follows of the hypochlorite bleach treatment.

After the washed, digested pulp has been thoroughly defibered, the consistency is adjusted to 3%–10% and the pulp slurry pumped to a gas tight chlorination tank equipped with an efficient agitation device. The pulp is now treated with an amount of chlorine gas equal (in pounds per 100 pounds of oven dry pulp) to 16% of the bleachability value of the pulp as determined by the permanganate number method. This amount will just satisfy the demand of the immediately reactive lignin and should be controlled within 3% or less. Larger amounts of chlorine are uneconomical and tend to cause chemical degradation of the cellulose, while smaller amounts result in incomplete chlorination.

The required amount of chlorine gas is incorporated in the pulp slurry at a uniform rate of flow in between 20 and 30 minutes. The chlorine will be substantially exhausted in an additional 5 to 15 minutes but the treatment is allowed to continue for a total of 45 minutes (after all of the chlorine has been added) in order to allow the acids formed by the chlorination treatment to act upon the ash content of the pulp. The chlorine should be added in a manner that will insure a uniform distribution of gas with the unchlorinated fibers; otherwise an increased loss of chlorine may occur due to reaction with material already chlorinated and result in an incomplete chlorination of part of the fibers. It has been found desirable to effect the incorporation of the required amount of chlorine gas into the pulp slurry in as short time as possible consistent with such uniform distribution as will avoid the beforementioned undesirable localized action.

At the end of the 45 minute chlorination treatment, a sufficient amount of sodium hydroxide is added to the chlorinated pulp to bring the concentration of the solution to about 1% and the treatment consistency preferably to about 2%–4%. It is desirable to add a sodium hydroxide solution to the pulp slurry at a concentration of not more than 7%, as stronger solutions have a tendency to "set" the chlorinated compounds and make them more difficult to remove.

The pulp slurry is now brought to about 100° C. in 20 to 30 minutes and held at about 100° C. for 30 minutes. It is then promptly transferred to a continuous filter or centrifuge and washed thoroughly with water, preferably until neutral. A typical sample of the chlorinated and causticized pulp has the following analysis:

	Per cent
Alpha cellulose	94.9
Soda solubility	6.5
Cuprammonium viscosity (ctps.)	54.0
Bleachability	1.1
Pentosans	5.4
Resins	0.3
Ash	0.40

The washed pulp is now ready for a hypochlorite bleach, the purpose of which is twofold: (1) to eliminate the residual, oxidizable material remaining in the pulp; (2) to adjust the viscosity of the cellulose to the proper level required at this stage of its purification in order to yield the desired viscosity at its final stage of refinement. It has been found that the viscosity of the final purified cellulose will be approximately 75%–85% of its value at the end of the hypochlorite bleach treatment. In general, the higher the viscosity of the purified end product, the greater will be the spread between the vsicosity value at the end of the hypochlorite treatment and such final viscosity. For example, if a viscosity of 30 centipoises for the final purified cellulose is desired, the pulp viscosity should be reduced in the hypochlorite treatment to approximately 35 centipoises. If an end product of 18 centipoises is desired, the cuprammonium viscosity of the cellulose should be reduced by means of the hypochlorite treatment to approximately 20 centipoises.

In carrying out the bleaching step of this example, the required volume of hypochlorite solution to give 2.5 pounds of bleaching powder (calculated on the basis of 35% available chlorine) for each 100 pounds of pulp is added to the pulp slurry which has previously been adjusted to a consistency of 2.7%. This addition of reagent will give a concentration of bleaching powder in the treating solution at the start of the reaction of 0.067%. The hypochlorite is added in the form of a solution containing 60–70 grams of bleaching powder per liter and saturated with lime. The bleaching reaction is allowed to proceed for 4 hours at a temperature of 25° C. which results in a consumption of approximately 50% of the active reagent present. Control and close duplication of the pH conditions during the bleaching step of successive batches is essential for reproduction of the rate and extent of viscosity reduction. The preferred practice is to have the pH at the start of the reaction at about 9.4 and allow it to decrease uniformly to a value about 8.7 at the end of the treatment. The lower limit of pH for satisfactory bleaching of pulps intended for use in derivatives is of the order of 8.0.

The bleaching treatment just described affects primarily the cuprammonium viscosity, the color of the cellulose and the amount of oxidizable material present. During the course of the bleaching step, the cuprammonium viscosity will be reduced to about 43 centipoises, the color of the cellulose improved from a reflectance value of about 82.4% to a value of about 93.4% and the bleachability reduced to a value of about 0.4% or less.

If a greater reduction in the viscosity of the pulp is desired than illustrated by the present example, this may be effected by employing higher bleaching temperatures or by adding a greater percentage of bleaching powder. However, either practice tends to undesirably impair the properties of the pulp and furthermore are less economical than providing a raw pulp of lower initial viscosity obtained by proper adjustment of the digestion conditions.

Figure 3 shows the nature of the changes in these properties of the celluloses, which are appreciably affected during the bleaching treatment, produced by varying some of the conditions of the hypochlorite bleach. The property most difficult to control is the cuprammonium viscosity. Variations such as the rate and degree of agitation, pH during bleaching, size of batch, direct or indirect heating, rate of heating, presence of metallic contaminants etc. are factors in the control of viscosity during bleaching. I have found a control viscosity determination to be a practical method for obtaining a substantially constant cuprammonium viscosity of successive batches of pulp after the completion of the hypochlorite bleach. A curve showing the change in viscosity with time of bleaching should first be determined on a number of successive lots from the same wood supply going through the process. This is desirable in order that the cumulative effects may be known of the natural variations in the raw material and the minor unavoidable variations in the processing steps arising from the limitations of accuracy in measuring the weight and consistency of pulp, weight of reagents and the like. When these curves are established, a single control viscosity determination, made after some selected elapsed time of bleaching, will suffice for each lot of pulp in process. From this control value, the curve may be extrapolated and the proper adjustment in the bleaching time made to insure the desired viscosity of the pulp upon the termination of the bleaching. Reference to Figure 3 shows that although in the last two hours of the bleaching the change in viscosity with time is small, proper adjustments in time can be made to readily overcome differences of for instance, 2 to 4 centipoises between successive lots. These adjustments in time may be made with no deteriment to the other pulp properties for the oxidizable material in the cellulose has been substantially reacted with during the first hour of the treatment and there is practically no change in the alpha cellulose and soda soluble contents even though the bleaching treatment should be prolonged 2 hours or more beyond the 4 hours preferably chosen and used in this example.

A typical analysis of the cellulose after bleaching is:

	Per cent
Alpha cellulose	94.6
Soda solubility	7.9
Cuprammonium viscosity (ctps.)	43.0
Bleachability	0.35
Pentosans	5.2
Resins	0.3
Yield (based on oven dry wood)	42–45, or more
Ash	0.35

The cellulose at this stage of its purification may be used to prepare viscose products; however, to obtain a higher quality of cellulose further purification treatments may be given. It is also of excellent quality for use in the manufacture of paper. It should be noted that the resin content of the pulp has been reduced to a negligible value and furthermore, it has been found that the condition in which the residue exists is such that it has no tendency to agglomerate and cause the objectionable clogging of the wires and felts, typical of pulps produced from resinous woods by the prior practices when such pulps are used for the manufacture of paper. This is considered an important feature of the invention since it makes possible the use of the abundant supplies of low cost southern pines for paper purposes.

After washing until free of available chlorine, the consistency of the pulp slurry may be adjusted to about 4%–12% and the pulp treated

with a 7% caustic soda solution for 1½ to 3 hours at about 100° C. under conditions which allow a minimum amount of atmospheric oxygen to come in contact with the pulp. Following this treatment the pulp is drained free of excess solution and washed thoroughly with water until the pH has been reduced to between 7.0 and 8.0 units. An analysis of a typical sample of the cellulose at this stage of purification is as follows:

	Per cent
Alpha cellulose	96.6
Soda solubility	3.1
Viscosity (ctps.)	34.0
Bleachability	0.3
Pentosans	2.8
Ash	0.30
Resin	0.1
Yield (based on oven dry wood)	38–40, or more

This cellulose may be acetylated according to the practice disclosed in Letters Patent No. 2,187,710 of Lionel Goff et al., granted January 16, 1940; or, it may be used as a high quality raw material for preparing viscose products.

A further variation of the purification practice consists in omitting the calcium hypochlorite bleaching treatment and proceeding directly to the 7% sodium hydroxide boiling treatment as soon as the chlorinated compounds have been washed from the pulp. In this case, after the caustic boiling treatment, the pulp is thoroughly washed in purified water, preferably until neutral, and given a 0.5% to 1.0% calcium hypochlorite bleach treatment in which the concentration of active reagent and/or temperature is adjusted to give the desired reduction in viscosity. The analysis of the pulp will be similar to that produced by the first described practice and is a particularly desirable quality for xanthation purposes, as well as for conversion into useful acetate and other esters.

Where the highest qualities of acetate or other esters are desired, particularly those acetates for use in film and sheeting, the pulp is next mercerized.

When the treatment has been completed, the caustic soda solution is drained from the cellulose in a settling tank or other suitable apparatus and the caustic soda still retained by the pulp washed out under carefully controlled conditions with purified water, preferably until neutral. The properties of the cellulose are especially affected by the procedure followed in removing the alkali from the cellulose at the completion of the mercerizing treatment. The time employed to remove the caustic soda from the pulp should be no more than the order of 30 minutes and is preferably 15 minutes or less.

The mercerization (and classification, if employed) completes the chemical purification of the cellulose, a typical sample of which will then analyze as follows:

	Per cent
Alpha cellulose	99.0
Soda solubility	2.5
Resins	0.10
Ash	0.15
Bleachability	0.30
Viscosity (ctps.)	30.0
Yield (based on oven dry wood)	36–38, or more

The above highly purified cellulose can now be dried and acetylated by the wellknown methods ordinarily practiced. It is, however, preferably maintained in a wet condition a[illegible] acetylated even more economically and satisfactorily by the method set forth in copending application of Lyle Sheldon et al., S. N. 70,372, filed March 23, 1936, which has become abandoned. It should be noted that the resin content has been reduced to the low value of 0.1%.

A more thorough understanding of the advantages inherent in the use of sapwoods with substantially complete exclusion of heartwood and compression wood as a raw material for the production of chemical cellulose can possibly be derived by considering the morphological differences between sapwoods and heartwoods.

Sapwood may be considered as that portion of the xylem nearest to the bark which contains living cells and which serves for the conduction, support, and storage of food; while the heartwood functions mainly as mechanical support, after all active growing ceases in the sapwood and it serves only as mechanical tissue, it becomes heartwood which is composed of dead wood cells and contains a greater amount of resin, gums, etc. than is present in sapwood.

Sapwood may be distinguished from heartwood in most species of wood by the difference in color; usually the latter is of a much darker color. The infiltration of the cell walls with such substances as oils, resins, and coloring matter and the plugging or filling of the lamina of the cells with gums, resins, and waxes are largely responsible for the change in color. The heartwood of the southern pines, particularly long leaf and slash pines, is impregnated with resin which solidifies in the lumen of the tracheids, resin ducts, and parenchyma cells. The resin of the sapwood of these species is in the liquid state and is confined for the most part in the resin canals. In and around injuries and knots, the wood is often saturated with resin, even in the sapwood portion.

In the transforation of sapwood into heartwood a number of important changes occur; all living cells lose their protoplasts; the cell sap is withdrawn and commonly the water content of the cell walls is greatly reduced; food material present in the living cells is removed; and the partly lignified walls or parenchyma cells may become more strongly lignified. There are formed within, or brought into the changing cells, certain substances new to the tissues such as oils, gums, resins, tannin compounds, and various achromatic and coloring substances, the achromatic substances being such as the colorless salts of metals magnesium, silicon, calcium, sodium and potassium, as well as some colorless organic compounds. The so-called pit membranes, in the case of coniferous species, which act as valves permitting the flow of fluids to and from the interior of the individual wood or cell fibers becomes fixed in a closed position.

By virtue of having used only selected sapwood as the starting material in the present process and the careful control of the conditions under which each step of the digestion of the wood and the purification of the pulp are carried out, an end cellulosic pulp product is produced having any desired degree of purity and distinguished by the nearly invariable chemical and physical properties between successive batches.

The control of the chemical treatment in each purification step almost completely avoids chemical degradation of the cellulosic fibers and effects a gradual increase in the purity of the product as measured by the alpha cellulose and soda soluble contents. At the same time, pitch, resins and

other objectionable impurities are almost completely eliminated with the result that the cellulosic pulp product of the present invention possesses a homogeneity combined with high purity and permeability which renders it a nearly ideal product for conversion to cellulose derivatives.

The alkaline treatment of the chlorinated pulp is quite effective in removing the residual pitch and resin compounds which have heretofore been a troublesome problem in the use of highly resinous wood pulps in paper making. Furthermore, the process of the present invention not only removes these objectionable resinous materials, but produces substantially resin-free pulp of high whiteness with a yield considerably higher than that ordinarily obtained by the prior practices in producing similar pulp from the non-resinous wood species.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results obtained.

As many changes could be made in carrying out the above compositions and processes without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Since no published methods have been found which clearly define certain measurements used herein, the following definitions of such treatments are given.

Soda soluble material is defined as that portion of a cellulosic sample dissolved when it is subjected to the action of 7.14% sodium hydroxide solution at the boiling point of water for 3 hours by a refinement of the method of Griffin, "Technical Methods of Analysis," 492 (1927 ed.), described in Letters Patent of Sheldon et al. No. 2,185,776 granted January 2, 1940, page 2, column 2.

Alpha cellulose is defined as that portion of a sample of cellulose material not dissolved by 17.5% sodium hydroxide solution at 20° C., determined by a refinement of the method described by H. F. Lewis in "Technical Association Papers," Series XVII, #1, 436 (1934), described in Letters Patent of Sheldon et al. No. 2,185,776 granted January 2, 1940, page 2, column 1.

Bleachability of cellulose, as used herein, is a measure of the materials oxidizable by potassium permanganate in the presence of an acid under specific conditions, and is expressed in terms of standard bleaching powder containing 35% available chlorine. A detailed description of the method, including the conversion table for expressing the permanganate number in terms of per cent bleaching powder of 35% available chlorine, was published by T. A. P. P. I., Series XVII, #1, 146 (1934), "Permanganate Number of Pulp" by R. N. Wiles.

Cuprammonium viscosity, as used herein, means the viscosity number or value obtained according to the following method: The cuprammonium solution was prepared by the action of air on electrolytic copper in the presence of strong ammonia water. The copper concentration of the solutions employed for viscosity determinations was 30, ± 2 g. per liter and the ammonia content was 165 g., ± 2 g. per liter. The concentration of cellulose employed was 0.6 g. (oven dry basis) per 100 cc. of cuprammonium solution. The cellulose sample for this determination was dried at 70° C. to 4% moisture content. After weighing out 0.6 g. (oven dry basis), the sample was moistened, squeezed to a uniform weight of 2 g. and then dispersed in cuprammonium solution in an atmosphere of hydrogen from which oxygen has been completely removed. The viscosity measurements were made at 25° C. with a modified Ostwald pipet, constructed according to the specifications of the American Chemical Society Committee on the Viscosity of Cellulose (Journal of Industrial & Engineering Chemistry, I, #49; 1929). The time of flow in seconds was converted to centipoises on the basis of the calibration of the pipet with oils of known viscosity in centipoises obtained from the United States Bureau of Standards.

Color and haze.—The measurements referred to herein of the color and haze of the acetic acid and acetone solutions of the acetate were made by comparisons with standards of known color and also turbidity expressed in parts per million. The standards are those used for water analysis recommended by the American Public Health Association and consist of platinum cobalt (for color determinations) and fuller's earth (for turbidity comparisons). With the materials recommended by the American Public Health Association, a series of standard solutions ranging from 10 p. p. m. to 200 p. p. m. inclusive at intervals of 10 p. p. m. were prepared for both color and haze. 100 cc. of each of these solutions was hermetically sealed in an 8-ounce, wide-mouth, glass-stoppered bottle having an internal diameter of $2\frac{7}{16}$ inches. The acetate dope samples to be measured were prepared in bottles identical with those employed in making the color and haze standards and compared under a controlled source of light, first with the color standards until the particular solution of each which most nearly corresponded to the dope under comparison was found, and then with the haze standards in conjunction with the most appropriate color standard. The measurements of the color and turbidity of the acetate dope are made exactly 1 hour after the dope has been killed by the addition of the dilute acetic acid. At the time of measurement, the dope must be absolutely free from air bubbles and at a temperature of 25° C., and the quantity of dope under comparison in the bottle must not be less than 100 cc. It has been found that color and haze ratings by this method can be made to an accuracy of approximately 10 p. p. m.

Color of cellulose.—The color of the cellulose is measured by the amount of light reflected from a pad of cellulose. This is determined by using a photo-electric cell and is expressed as per cent of the range from black to the white of a magnesium carbonate block.

I claim:

1. The process of producing cellulose pulp from highly resinous wood such as Southern pine, comprising providing fresh Southern pine in desired subdivisions having their resin content in a liquid state in the natural resin solvent, impregnating the subdivisions with a sulphite digesting liquor by heating the subdivisions to a temperature at which steam is formed within the subdivisions and condensing the steam while the subdivisions are submerged in a liquid solvent of the sulphite liquor, then progressively raising the temperature to the order of 121°–123° C., maintaining the temperature in the range below 130° C. for at least three hours with substantially no gas relief, thereafter raising the temperature above 130° C. and continuing the digestion for at least two hours at the higher temperature to

simultaneously reduce the resin content to less than one-third of the original resin content of the wood, washing with hot water and pulping the digested wood with relatively slight reduction in the resin content of the wood below that attained during digestion, subjecting the pulp to treatment with chlorine gas in amount (in pounds per 100 pounds of oven dry pulp) equal to about 16% of the bleachability value of the pulp as determined by the permanganate number method, substantially exhausting the chlorine in chlorinating the immediately reactive lignin in said treatment, then treating the pulp in a caustic solution to remove the reacted products of the chlorination and simultaneously reducing the resin content to 0.3% or less, and then bleaching said pulp to desired whiteness with hypochlorite.

2. The process as set forth in claim 1 in which the hypochlorite bleach is followed by a treatment of the pulp with a 7% caustic soda solution at elevated temperature for from one to three hours further to reduce the soda soluble content of the pulp to less than 3%.

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