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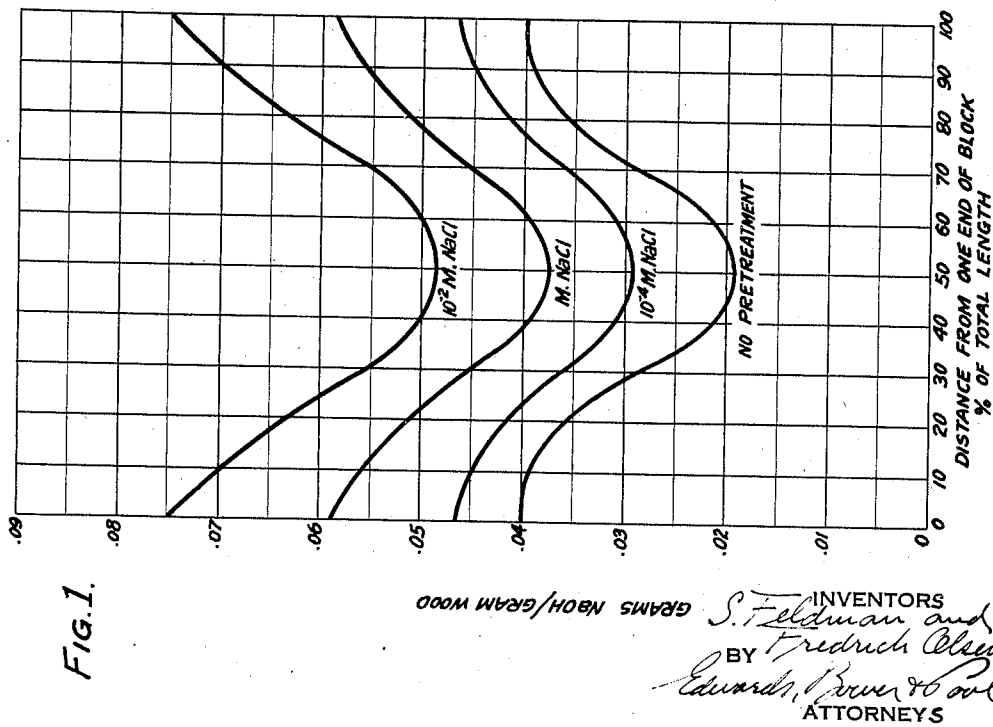
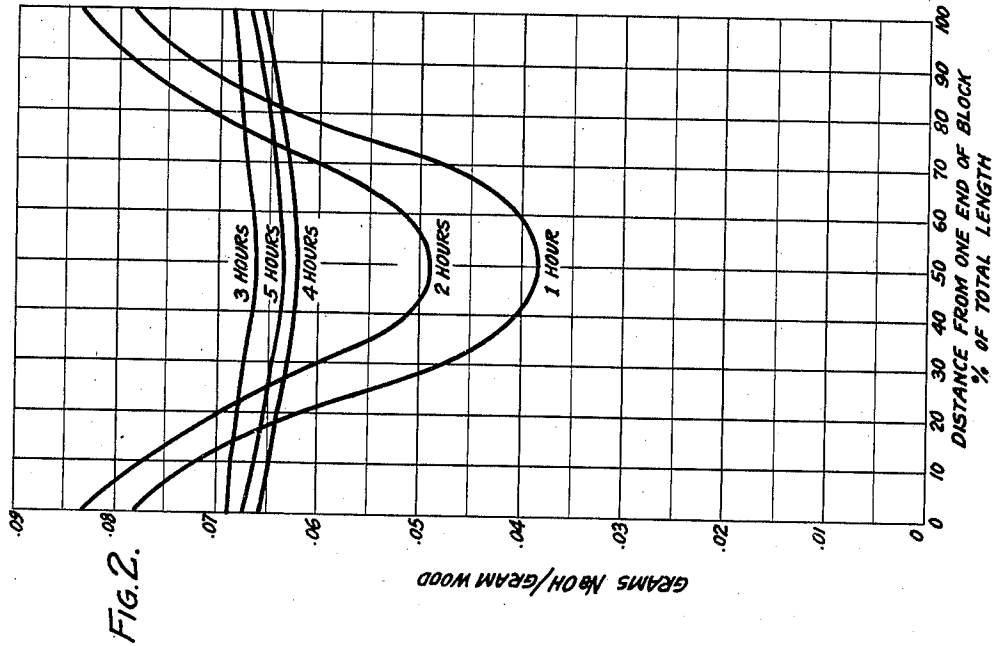
S. FELDMAN ET AL

2,228,349

TREATMENT OF WOODY MATERIAL

Filed Nov. 28, 1936

2 Sheets-Sheet 1



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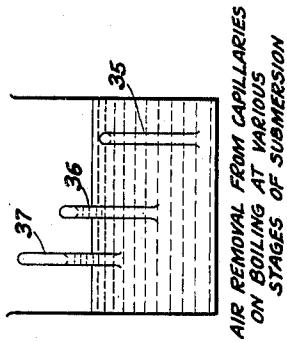
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TREATMENT OF WOODY MATERIAL

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FIG. 4.



SHOWING INCOMPLETE REMOVAL OF AIR FROM CAPILLARIES UNDER PRESSURE ALTHOUGH SAID CAPILLARIES HAVE YET FREE TO ALLOW REMOVAL.

FIG. 5.

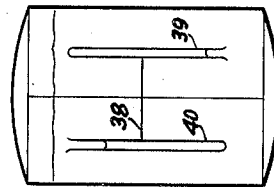
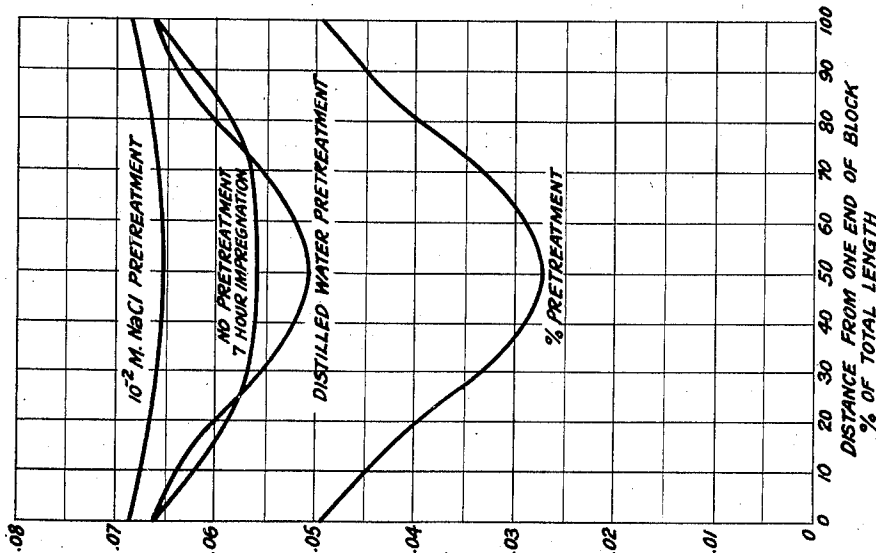


FIG. 3.



GRAMS NaOH/GRAM WOOD

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## UNITED STATES PATENT OFFICE

2,228,349

## TREATMENT OF WOODY MATERIAL

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Application November 28, 1936, Serial No. 113,124

5 Claims. (Cl. 92-13)

This invention relates to the impregnation of wood and woody material and more particularly to the impregnation and pulping of wood with alkaline reagents.

A primary object of the invention is to provide a process for uniformly impregnating wood and woody materials with liquids, chemical reagents, dyestuffs, preservatives and the like.

Another object is to provide a process for the treatment of wood which includes a means for facilitating the uniform distribution of an alkaline reagent throughout the wood subdivisions prior to the attainment of temperatures at which substantial rates of delignification of the wood are obtained.

A further object is to provide a process whereby the substantially uniform removal of any desired proportion of non-cellulosic substances from the raw material can be accomplished by digestion with alkaline liquors.

A still further object is to provide a process for the alkaline pulping of wood whereby a given extent of delignification can be obtained in a shorter digestion period and with a lower consumption of chemical than is demanded by the prior practices.

A further object of the invention is to provide means for facilitating the uniform distribution throughout the woody material of such predetermined amount of reagent as is required for the treatment of its non-cellulosic components so that on attainment of reactive temperatures the necessity for the transfer of chemical from the liquor surrounding the wood subdivisions will be obviated.

A further object is to provide a process for treating wood which minimizes the conditions which normally hinder or prevent uniform impregnation with treating solutions and more especially, the uniform digestion of reagents, preservatives, dyestuffs, or other substances throughout the wood and each subdivision thereof.

The natural morphological structure of wood presents serious difficulty to its uniform penetration by liquids. It comprises a highly complex structure of capillary passage and interstices which are normally filled with air and encrusting substances in a variety of forms, ranging from more or less freely flowing liquid to a state of semi-immobility, or even complete immobility. This condition renders it quite difficult to impregnate and evenly distribute liquids throughout the subdivisions of the wood by the usual methods. In addition, the wood preferentially adsorbs certain reagents, preservatives, dyestuffs,

and other substances held in solutions. Consequently, in many cases, even where it may be possible to effect impregnation of the solutions, the reagents and other substances which it is desired to uniformly distribute may be largely deposited on the exterior portions of the subdivisions; therefore, little, if any, of said substances reach the interior portions of the subdivisions.

In the accompanying drawings which illustrate various features of the invention:

Figure #1 is a graph illustrating the effect of a pretreatment of the present invention with special attention to the concentration of the pretreating electrolyte.

Figure #2 is a graph illustrating the effect of a pretreatment of the present invention with special attention to the subsequent time of impregnation with a delignifying solution.

Figure #3 is a graph illustrating the effect of a pretreatment of the present invention as compared to certain prior practices.

Figure #4 is a diagrammatical representation of capillary tubes containing air under conditions of freely vented boiling.

Figure #5 is a diagrammatical sketch similar to Figure #4 illustrating the action of air in similar tubes where the heating is under pressure conditions.

It has long been known that the conventional processes for reducing wood to cellulosic pulp in which the wood subdivisions are charged into a digester, delignifying solutions added and heating of the mass started, are far from ideal since the delignification reaction starts on the outer exposed surfaces of the wood subdivisions and gradually proceeds to the inner regions. Since the delignifying reactions under such conditions are relatively slow, the outer portions of the wood subdivisions are the first to be delignified and are subjected to the chemical action of the treating liquors for increasingly longer periods of time than other areas progressively distant from the outer surfaces of the subdivisions. Furthermore, the concentration of the delignifying reagents progressively decreases during the course of the reaction so that when the delignifying liquors finally reach the innermost portions of the wood subdivisions the concentration of the reactive chemicals in the solution has been greatly depleted.

These unfavorable conditions provided by the prior processes are further accentuated by the tendency of the wood to preferentially adsorb the reagent from some of the commonly used treating solutions, such as, for example, sodium hy-

droxide solutions. In such cases, a large excess of reagent, for example, 90% of the total reagent, will be accumulated on the exterior portions of the wood while the interior portions will have an insufficient amount, for instance, 10% of the total reagent or even no reagent at all.

Still another factor contributing to the unequal distribution of reagent is the pronounced swelling effect of some of the usual treating solutions, such as sodium hydroxide and kraft liquors. When the chips come in contact with such solutions, the swelling of the exterior portions thereof tend to constrict or even close the capillary passages and channels existing in the woody structure, so that penetration of liquids into the interior portions becomes even more difficult. Furthermore, the delignifying action of the treating liquors itself tends to obstruct penetration by producing colloidal substances capable of mechanically blocking or plugging the membranes or capillaries and interstices of the wood through which the liquors must penetrate.

The combined effect of such adverse conditions is to reduce the yield and quality of pulp since the portions of the pulp delignified first are in contact with the delignifying solutions at reactive temperatures for considerable periods of time. It is a well known fact that cellulosic materials are rapidly degraded and pass into solution under such conditions. Furthermore, since various portions of the pulp are exposed to this action for widely varying lengths of time, a predominating characteristic of the resulting pulp product is non-uniformity.

The ideal condition and one of the important features of this invention is uniform and intimate association of all parts of each wood subdivision with the required amount of delignifying reagent before reactive conditions are attained, so that the reaction may proceed uniformly, rapidly, and simultaneously throughout the mass of wood subdivisions under treatment. These conditions are provided by treating the wood subdivisions in a boiling solution of a non-delignifying electrolyte of very dilute and critical concentration under freely vented conditions for about 30 minutes, or until all of the air within the capillaries and other interstices of the wood subdivisions has been removed. During the boiling period the chips are maintained submerged and upon the termination of the boiling, the temperature is allowed to drop a few degrees, the chips still being maintained submerged, with the result that the condensable vapors within the chips are condensed. This creates a partial vacuum within the wood which causes the surrounding non-delignifying electrolyte solution to saturate the wood. The treated chips are maintained submerged in the solution for approximately 30 minutes after the termination of the boiling. The excess water is then drained from the chips, care being taken to maintain them saturated to prevent the reentry of any air and a delignifying solution, for example, sodium hydroxide, at a temperature preferably just under and not exceeding the order of 100° C., is added. The caustic reagent becomes uniformly distributed throughout the wood and the wood is then in an ideal condition for pulping.

An illustration of the concentration of the electrolyte solutions which we may employ is  $1 \times 10^{-5}$  molar for aluminum sulfate and  $1 \times 10^{-2}$  molar for sodium chloride, both being the types of electrolytes satisfactory for the purpose.

Accordingly, the process of this invention as

applied to the pulping of wood provides for the uniform distribution of delignifying reagents through the wood prior to attaining active digestion conditions by removing substantially all of the air from the wood and thereafter pretreating it with a non-delignifying electrolyte solution within a critical range of concentration and subsequently treating the wood with a delignifying reagent.

By this process, saturation of the wood with digestion liquors is attained under conditions which insure uniform distribution of the required amount of treating reagent throughout each subdivision of the wood at temperatures not greater than 100° C. This permits the adjustment of the pulping conditions to a lenient character which results in the production of higher yields of pulp of exceptional uniformity and higher quality. A characteristic feature of the pulp products resulting from the process is their substantially undegraded cellulosic content.

These enhanced results are due primarily to the following factors:

A more rapid rise and greater uniformity of the temperature within the chips is attained due to the marked increased thermal conductivity over unimpregnated chips.

The uniform availability of the required amount of chemical permits the chemical action with the encrustants of the wood to proceed at the maximum rate, simultaneously in all portions of the wood subdivisions.

The wood subdivisions may be provided with just the requisite amount and no more of delignification reagent to remove the desired amount of ligneous material and then removed from the presence of additional delignification reagent so that continued or excessive degrading action of the delignifying reagent on the cellulose after the desired amount of delignification is accomplished can not occur.

The above factors permit less drastic cooking conditions, i. e., lower chemical to wood ratios and decreased time and temperature of digestion with consequent less chemical action on the cellulose itself than can be obtained in the prior practices.

Saturation of the wood with the treating liquor can be accomplished only after the thorough removal of the air and other gases which normally occupy a large portion (50%–80%) of the volume of wood as usually prepared for pulping. An important feature and one of the objects of this process is the substantially complete removal of air from the chips by submerging them in an aqueous, non-delignifying chemical solution which is maintained in a state of active ebullition. A boiling period of 15–30 minutes is sufficient to effect air removal in the case of most deciduous woods, for example, yellow birch, aspen, soft maple and black gum, which constitute the usual raw materials for so-called soda pulps. Slightly longer boiling periods are required for the coniferous woods commonly used for kraft and sulfite pulps such as spruce, the hemlocks and pines, and for woods which contain a high percentage of heartwood.

An explanation of this method of air removal from the wood subdivisions is that under conditions of active ebullition in the surrounding liquor, the total pressure within the capillaries of the wood, i. e., the sum of the partial pressure of air and water vapor is greater than the external pressure as long as any air is present and water vapor and air escape from within the chips

because of the existence of this pressure differential, the air being carried off in the current of steam generated. The presence of liquid insures the rapid and uniform distribution of heat to the chips during the boiling process and makes possible the efficient and complete removal of air. This result can not be obtained by the use of steam alone or the use of pressure, vacuum and other means as has been suggested in prior practices. The ineffectual action of steam has been substantiated by an experiment in which a 30 minute treatment of spruce chips in freely boiling water removed 208 cubic centimeters of air from 100 grams of dry wood while a steaming treatment of the same amount of wood for an equal period of time removed only 145 cubic centimeters. Experiments have shown that pressure treatments, vacuum, and alternate use of vacuum and pressure likewise fail to accomplish complete air evacuation of the wood.

After the removal of the air, saturation of the wood with liquid can be effected by cooling the mass slightly below the boiling point, followed by a soaking period of 1 hour or less. When the temperature of the chips is thus reduced slightly below atmospheric boiling, the water vapor within the wood chips condenses and the capillaries become filled with liquid which is drawn into the wood from the surrounding supply. The thoroughness of air removal by this procedure is illustrated by the following percentages of weight increase on the dry weight of wood on immersing chips in boiling water for 30 minutes and thereafter soaking at 30° C. for 60 minutes: yellow birch, 130%; and a mixture of hemlock and balsam, 255%. The corresponding values at saturation obtained after extended boiling and soaking until equilibrium conditions were established were, respectively, 130% and 250%.

When the wood chips are accordingly subjected to a boiling and soaking treatment with an aqueous solution of an alkaline delignifying reagent, such as sodium hydroxide, an increase in weight is obtained which substantially corresponds to the saturation value. However, it has been found that the distribution of the chemical retained by the chips under such practice is far from uniform even after extended soaking periods, the greater proportion of reagent being present in the outer portions of the chips while the centers, although saturated with liquid, contain relatively small amounts of alkali or may be even entirely free of reagent. The inequality of distribution of reagent between the exterior and interior of the chips may be as great as 10:1 or even greater.

We have discovered that if wood chips are first saturated with a very dilute non-delignifying solution of an electrolyte, uniform distribution of chemical reagent can be obtained on subsequent impregnation with solutions of alkaline delignifying chemicals such as sodium hydroxide or kraft liquor. Any aqueous, non-delignifying solution of any electrolyte can be used for the pretreatment, each electrolyte having an optimum range of concentration for the purpose which can be readily determined by the method to be described below.

For instance, we have found that calcium chloride, sodium chloride, aluminum sulfate, sodium benzene sulfonate, and aluminum tartrate are very satisfactory when used alone or as mixtures in the proper concentration. The action can be explained as probably due to the effect of the adsorption of the ions of the pretreating

non-delignifying electrolyte on the surfaces within the wood structure which prevent the adsorption of the ions of the delignifying reagent, thereby minimizing the usual swelling of the wood and the formation of electrical double layers of the ions of the alkaline reagent. The observed fact that a specific optimum concentration exists for each different electrolyte is an excellent indication that the effect is based on electrokinetic phenomena.

The optimum concentration or range of concentration for pretreating wood with any given non-delignifying electrolyte may be determined by any convenient method. The following method has been found quite satisfactory for investigating the proper concentration of sodium chloride electrolyte for use with black gum wood:

Black gum sapwood blocks, 1 inch long (in the fiber direction) by 1 inch wide by  $\frac{3}{8}$  inch thick, are saturated with 1 molar (5.845% by weight),  $1 \times 10^{-2}$  molar,  $1 \times 10^{-4}$  molar, sodium chloride solutions by submerging and boiling the blocks in the respective solutions for 1 hour, then cooling to room temperature, and thereafter allowing them to soak for 1 hour. The blocks are then drained, weighed to determine the absorbed moisture and their volumes measured. They are then uniformly impregnated with sodium hydroxide by immersing them in a quantity of sodium hydroxide solution, so adjusted that the total caustic to wood ratio is 0.23 and the water to wood ratio is 4.0, and maintaining the liquid and submerged wood at 95°-100° C. for 2 hours. A control block, which has not been pretreated with sodium chloride electrolyte, is treated under like conditions with sodium hydroxide. After cooling, the excess caustic solution is removed, the volumes of the blocks measured and all of the blocks then cut into five equal sections (in the direction of the grain). The weights of caustic soda, water and wood are then determined in each section. The data obtained are tabulated in Table I and is shown graphically in Figure #1.

TABLE I  
Grams sodium hydroxide per gram of wood  
(O. D. basis)

| Pretreating-non delignifying solution | Wood section |              |        |              |       |
|---------------------------------------|--------------|--------------|--------|--------------|-------|
|                                       | End          | Intermediate | Center | Intermediate | End   |
| None                                  | 0.039        | 0.029        | 0.020  | 0.028        | 0.034 |
| 1 molar NaCl                          | .057         | .045         | .038   | .045         | .060  |
| $1 \times 10^{-2}$ M. NaCl            | .071         | .056         | .048   | .049         | .066  |
| $1 \times 10^{-4}$ M. NaCl            | .045         | .035         | .030   | .034         | .041  |

By referring to either Figure #1 or Table I, it will be seen that  $1 \times 10^{-2}$  molar (0.0585% by weight) sodium chloride solution pretreatment resulted in the penetration of the greatest amount of caustic soda reagent into the blocks and is therefore considered in the optimum concentration range. However, the penetration of the caustic soda was not uniform with respect to the cross section of the blocks and it was then necessary to treat wood pretreated with  $10^{-2}$  molar sodium chloride solution as above described for various lengths of time in the sodium hydroxide solution at the ratios and temperatures above described in order to establish the length of time required for uniform penetration of the caustic reagent. These results are tabulated below in Table II and are shown graphically in Figure #2.

TABLE II  
Grams sodium hydroxide per gram of wood  
(O. D. basis)

[All samples pretreated with  $1 \times 10^{-2}$  molar NaCl]

| Time of caustic treatment | Wood section |               |        |               |       |
|---------------------------|--------------|---------------|--------|---------------|-------|
|                           | End          | Inter-mediate | Center | Inter-mediate | End   |
| 1 hour.....               | 0.073        | 0.049         | 0.039  | 0.048         | 0.061 |
| 2 hours.....              | .076         | .057          | .050   | .045          | .076  |
| 3 hours.....              | .073         | .067          | .066   | .067          | .068  |
| 4 hours.....              | .064         | .060          | .062   | .057          | .066  |
| 5 hours.....              | .070         | .064          | .063   | .064          | .074  |

Thus, it may be seen that by pretreating the blocks with  $10^{-2}$  molar sodium chloride solution, a 2 hour treatment in caustic soda solutions at  $100^{\circ}$  C. results in but little improvement in uniformity of distribution of the reagent over a 1 hour treatment, but such treatment for 3 hours results in substantially uniform distribution as evidenced by the nearly straight line concentration of the reagent through the cross section of the block.

It should be noted that in determining the optimum concentration of the electrolyte to be used by the method described above, the precise optimum concentration may not have been determined since sodium chloride concentrations slightly above or slightly below  $1 \times 10^{-2}$  molar might prove somewhat more efficient. However, it is considered that  $1 \times 10^{-2}$  molar concentration lies in the optimum range of concentration for all practical purposes.

Similar experimentation has shown the optimum concentration of aluminum sulfate as a non-delignifying pretreating solution for black gum sap wood to be of the order of  $1 \times 10^{-5}$  molar, uniform impregnation with sodium hydroxide then being achieved in the order of  $3\frac{1}{2}$  hours.

Figure #3 shows the distribution of caustic soda throughout the wood when a proper electrolyte pretreatment is given as compared with pretreatment with distilled water alone before treating the wood at  $100^{\circ}$  C. in caustic soda for 3 hours. It should be noted that the electrolyte pretreatment results not only in a very uniform distribution of the caustic reagent, but also in a higher total reagent on the wood content than either distilled water pretreatment or no pretreatment. It has further been found that with no pretreatment, even 7 hours treatment at  $100^{\circ}$  C. with sodium hydroxide solution fails to give uniform distribution of the caustic reagent in the wood.

Volume measurements of the blocks show that the wood swells in caustic solution without pretreatment to as much as 27% greater than the original volume of the wood, while with electrolyte pretreatment the increase is only 14%. This reduction in swelling is considered an important aid to uniform penetration.

In practice, the time required for treating the wood chips with delignifying solutions at below  $100^{\circ}$  C. is much less than that described above with the use of blocks 1 inch by 1 inch by  $\frac{3}{8}$  inch. It is a well established fact that penetration proceeds much more rapidly with the grain of wood than at right angles thereto. Commercial wood chips usually range from  $\frac{3}{8}$  to  $\frac{3}{4}$  inch in length. Consequently, they are much more rapidly penetrated than the blocks used in illustrating the operation of the principles of our invention. For example, a soaking time of chips pre-impregnated

with a non-delignifying electrolyte solution with a caustic soda solution of 30-60 minutes is usually found ample to effect the uniform distribution of reagent.

After the wood chips have thus been saturated with a solution of a non-delignifying electrolyte according to the method described, and if the avoidance of undue dilution of subsequent delignifying solutions is desired, removal of the residual non-delignifying liquid in which the boiling and soaking has taken place may be accomplished by drainage, preferably in the presence of steam at a somewhat higher temperature than that employed during the air removal treatment. This permits the displacement of excess surface liquid from the chips and may also serve to boil off some of the liquid held internally in the wood. However, under these conditions care must be taken to avoid any exposure of the chips to air.

To the saturated, drained chips a delignifying solution such as, for example, sodium hydroxide, may then be added at a temperature preferably just under its boiling point. In calculating the concentration of the delignifying reagent in such solutions, account should be taken of the amount of water held by the saturated chips. This will vary over a considerable range such as, for example, 100% or less of the weight of the wood to 250% or more, depending on the species of wood being treated. It will also vary with the proportions of different kinds of growth of the tree such as sap wood, heart wood, springwood, and summerwood. The chips are thereafter allowed to soak in a delignifying solution for about 1 hour or less while the temperature is preferably maintained close to  $100^{\circ}$  C. to provide the best diffusion conditions without substantially exceeding a temperature of  $100^{\circ}$  C.

The wood, after being uniformly penetrated with alkaline cooking liquors by this process, is then capable of being delignified more economically to a more homogeneous pulp than is possible by processes in which uniform association of the alkaline reagents prior to providing reactive temperatures is not attained. The present process can be readily carried out in the equipment in general use in the pulping industry with the important advantages of the use of milder digesting conditions and a smaller requirement of delignifying chemicals.

The reaction between sodium hydroxide, for example, and the ligneous component of the wood at temperatures in the range of  $150^{\circ}$ - $175^{\circ}$  C. is quite rapid, so that when the lignin demand of reagent has been uniformly distributed throughout the woody structure in accordance with the provisions of our invention, the required reaction not only proceeds uniformly but quite rapidly. As a result, the time for completing the reaction may be very much reduced with consequent minimum amount of degradation to the cellulose itself. A further advantage accruing from the discoveries of the present invention is the use of a lower delignifying temperature with consequent milder conditions to which the cellulose itself is subjected. Both shorter time of digestion and lower temperatures may be employed with marked beneficial effect over prior practices.

The pulp derived from the modified cooking schedules, made possible by the uniform association of the proper amount of reagent with the wood prior to the attainment of pulping conditions, is not only an improvement over alkaline pulps by prior processes with respect to homogeneity and substantial freedom from degrada-

tion, but the yield is higher by usually 3%-5% than the yields ordinarily resulting from the best conventional practices.

The following are examples of the application of the principles of the present invention to the pulping of yellow birch chips with a sodium hydroxide solution carried out in standard pulp mill equipment. It must be understood, however, that the invention is not limited to the reagent, species of wood, nor specific conditions set forth in these examples.

#### EXAMPLE A

Yellow birch chips, preferably free of dirt and knots, are charged into a conventional digester and covered with a dilute, non-delignifying electrolyte solution at optimum concentration, for example,  $1 \times 10^{-2}$  molar sodium chloride or  $1 \times 10^{-5}$  molar aluminum sulfate. Steam is admitted through the distributing mains provided for that purpose near the bottom of the digester, and the solution is boiled for 30 minutes under freely vented conditions to accomplish the removal of air from the chips. During this boiling all of the chips should be kept under the surface of the liquid.

An alternate practice is to supply steam to the sealed digester until a temperature slightly in excess of  $100^{\circ}\text{C}$ . is attained and then to relieve air and steam from the top of the digester intermittently over a 30 minute period. Upon the completion of the boiling treatment, the steam relief valves are closed and a 30 minute period is allowed for the saturation of the chips with the dilute sodium chloride solution. During this time steam under pressure may be admitted above the liquor level to facilitate the impregnation.

The excess solution is then drained from the digester and may be used for the treatment of subsequent batches of chips. In the case of pretreating highly resinous woods, the resins tend to float up to the liquid surface during the boiling period and form a layer on the surface which is very sticky and tends to adhere to the walls of the digester, the wood, or anything else with which it comes in contact. This layer of resins may be removed by any convenient means, such as drawing off the upper layer of the liquid above the chips before draining the mass of electrolyte solution from the digester.

Caustic soda solution at a temperature of about  $70^{\circ}\text{--}100^{\circ}\text{C}$ ., but preferably not exceeding  $100^{\circ}\text{C}$ ., is then added to the digester at a concentration and in an amount which is adjusted to bring the proportion of wood (oven dry basis): caustic soda: water equal to 100:18:400. For example, 293 pounds of 8.5% sodium hydroxide solution will be required for each 100 pounds of wood if a 130% increase in weight on the original dry weight of wood has occurred during the boiling and soaking treatment with the dilute, non-delignifying electrolyte solution heretofore described. The wood is allowed to soak in the cooking liquor for 30-60 minutes, preferably at not more than  $100^{\circ}\text{C}$ . The digester is then sealed and steam is added to raise the temperature to  $170^{\circ}\text{C}$ . as rapidly as possible. Digestion is continued at  $170^{\circ}\text{C}$ . for about 2 hours, and the digester contents then discharged into a blow pit where it is thoroughly washed. A yield of 53% of screened pulp is thus obtained, having a single-stage bleachability requirement of about 26% bleaching powder, containing 35% active chlorine, as determined by the permanganate

titration method described by R. N. Wiles in "Technical Association Papers of the Paper Industry", Series XVII, #1, 146 (June, 1934).

If a pulp with lower bleachability, such as 17%-19%, is desired, it can be obtained by lengthening the time of digestion treatment at maximum temperature to about  $2\frac{1}{2}$  hours.

#### EXAMPLE B

Yellow birch chips, preferably free from dirt and knots, are charged into a digester and covered with an optimum concentration of a dilute, non-delignifying electrolyte solution such as, for example,  $1 \times 10^{-2}$  molar sodium chloride or  $1 \times 10^{-5}$  molar aluminum sulfate. The solution is brought to the boiling point by direct steam and boiled for 30 minutes under freely vented conditions to accomplish the removal of air from the chips. On the completion of the boiling period, the heating is discontinued and the chips allowed to soak for about 30 minutes in order to saturate them with the electrolyte solution. During the boiling and soaking, all of the chips should be kept under the surface of the liquid.

The alternate practice described in Example A of sealing the digester and supplying steam until the temperature of the mass of chips and electrolyte solution slightly exceeds  $100^{\circ}\text{C}$ . and then to relieve the air and steam from the top of the digester intermittently over a 30-minute period may be practiced if desired.

The excess solution is then drained from the chips as in Example A and 310 pounds of 12.8% sodium hydroxide solution for each 100 pounds of wood (oven dry basis) are then added to the pretreated chips. The chips are allowed to soak in this caustic soda solution for 30-60 minutes at a temperature of  $95^{\circ}\text{--}100^{\circ}\text{C}$ . The excess solution is then drained from the chips and may be utilized for impregnating subsequent batches of chips with delignifying solution. 60%-65% of the weight of caustic soda solution originally added can be recovered in this manner.

The treatment described leaves each chip in the batch thoroughly and uniformly impregnated with the caustic soda reagent in the ratio of 18-19 parts of NaOH for each 100 parts of wood (oven dry basis). The chips are therefore in an ideal condition for subsequent delignification when heated to reactive temperatures, especially in continuous digestion equipment, since they are impregnated with sufficient delignifying reagent to insure complete pulping without the necessity of subsequent diffusion of reactive chemical from the usual pool of surrounding liquor, as is common practice in conventional processes.

Furthermore, when subjected to reactive temperatures, the chips are pulped very much more rapidly than in conventional processes, for example, the impregnated and drained chips, as described above, may be heated to  $170^{\circ}\text{C}$ . in 15 minutes and maintained at that temperature for 25 minutes or even less. At the end of this treating period a yield of 52%-53% of screened pulp having a bleach value of 20%-25% may be obtained.

Consideration of the theoretical aspects of the present invention and the reason it offers the very considerable advantages that it does involves, first, an understanding of

a. The removal of air from small capillaries, and

b. Certain aspects of the direct impregnation of wood with caustic delignifying solutions as practiced in prior processes.

By "direct impregnation" is meant the treatment of wood with a caustic delignifying solution without using the pretreatment step with a non-delignifying solution as described in connection with this invention.

#### a. Removal of air from small capillaries

Since the structure of wood is known to involve the presence of not only microscopic pores and capillaries, but also submicroscopic pores, the problem of the retention of air in very small cavities is one of fundamental importance. The air is held in these cavities with great tenacity and its displacement is exceedingly difficult because of the minute dimensions which prevent the easy flow of liquid and gas through these pores. We have found that the use of strong suction or various low pressure devices does not effectively remove the adsorbed air. Therefore, in practice we depend upon the preferential wetting of the surfaces of the wood cavities by water or other treating liquids to thereby displace the adsorbed air film.

The nature of the problem of the removal of air from the pores and capillaries of wood is illustrated by reference to Figure #4 showing a set of three small test tubes, 35, 36 and 37. These tubes are inverted and placed in water to varying depths, one of the tubes being completely submerged. When the water is heated, the air inside the tubes will expand and bubbles of air will be noticed leaving the tubes. The amount of air which can be removed in this way will depend on the temperature of the bath. As the temperature increases, the vapor pressure of the gases within the tube is the sum of the partial pressure of the air and water vapor at a given temperature. Hence, as the temperature increases, the effect of the water vapor upon the total vapor pressure of the system becomes more and more significant, and at boiling temperature the pressure of the water becomes equal to the pressure at the mouth of the tube. In each bubble which leaves the tube there will therefore be a portion of air and a portion of water vapor.

Since the amount of air is limited by that quantity which originally filled the tube, and also since there is an unlimited amount of water vapor obtainable (from the supply of liquid water present in the tube), there will be a constant tendency to remove air from the tube, displacing same with water vapor. This displacement will occur as long as any air is present because the pressure within the tube will always be greater than the atmospheric pressure at the mouth of the tube at the time of boiling by an amount that is equal to the partial pressure within the tube. The development of water vapor at a pressure corresponding to the temperature of the bath provides a means therefore of flushing the air completely from the tube. If it is desired to have the tube filled with water in the liquid phase, it is only necessary to either cool the system sufficiently to allow the water vapor within the tube to condense thereby sucking water in the liquid phase from the surrounding reservoir, or to subject the system to a slight increase in pressure which will cause the water vapor in the tube to condense.

When the experiment described above is carried out, it is observed that the air in the tube 35, which is completely submerged, is quickly removed; whereas the tubes 36 and 37, which partially extend above the surface of the liquid, lose

their air content more slowly. In fact, the exposed tubes do not become completely filled with water even after protracted boiling.

Figure #5 illustrates one form of this experiment in which a closed glass tube partially filled with water and with air above the water level is employed. Immersed in the water within the tube is a glass rod, 38, to which are attached some capillary tubes, 39 and 40; all of which are closed at one end. Half of the tubes 39 are inverted; the other half 40 having their open ends pointing upward toward the air space. Even after repeated heating to temperatures appreciably above 100° C. followed by intermediate coolings, air fails to leave these tubes. Thus, even though the open ends of these tubes would appear to offer an opportunity for the free escape of air through the water to the space above, actually the capillaries contain most of their original air content because the pressure in the closed space above the water increases at approximately the same rate as that inside the tubes.

Wood chips comprise a network of similar microscopic and submicroscopic capillary tubes largely filled with air which it is desired to remove. From the foregoing description of the experiments illustrated in Figures #4 and #5, it is clear that the air in the capillaries and pores of the wood can not leave the chips as long as the digester is sealed. It is only by providing adequate venting under such conditions as will permit the very large volume of air entrained in the wood to escape that the pores of the chips can be filled with liquid. The conditions employed in commercial practice of relief in the digestion of wood do not provide an opportunity for this complete removal of air during that period of the cycle prior to the attainment of active digesting temperatures when it is most important that the delignifying liquids shall gain free access to the innermost portions of the wood.

Partial air removal leaves residual air entrapped in the innermost interstices of each chip. Upon providing elevated temperatures for digestion, even a relatively small volume of entrapped residual air will prevent the necessary contact between the treating solution and a substantial portion of the inner structure of each chip. This inevitably results in non-uniformity of distribution of the treating fluid. Therefore, the importance of obtaining substantially complete air removal can be readily appreciated.

#### d. Direct impregnation

*Swelling.*—Since wood is known to increase to a maximum volume of approximately 20% during immersion in hot water for 10-20 minutes, it would seem that swelling of the carbohydrate-lignin complex occurs very rapidly. This maximum swelling can even occur while the interior of the wood subdivision is substantially free of moisture. When alkalis are present the maximum swelling within the time cycle mentioned is somewhat greater than when water alone is used. The failure of the alkali to uniformly penetrate the wood is at least in part attributable to the partial or complete closure of the microscopic and submicroscopic pores in the wood by the swelling of the material around these pores.

After the removal of the lignin by the treating liquors, the wood fibers possess the property of absorbing and binding relatively large quantities of water. This action results in an enormous swelling of the fibers; therefore, unless the wood subdivision is thoroughly impregnated with the

delignifying solution before the treating process is started, the fibers residing in the outermost portions of the subdivision will be at least partially delignified, absorb water, and become more highly swollen. This condition will tend to further constrict or may even close the pores and capillaries, making it extremely difficult for the delignifying solution to penetrate further into the wood.

**Absorption.**—The outermost surfaces of a wood subdivision absorb considerable quantities of chemicals from the treating solutions, particularly those of an alkaline nature, so that any solution which may penetrate the subdivision is depleted with respect to the concentration of the delignifying reagent. The significance of this depletion of reagent from the solutions by absorption is apparent when it is considered that absorption is a surface phenomenon and that the surfaces of a gram of wood have been estimated to be about 310,000 square centimeters.

**Electrical double layer formation.**—When wood is treated with solutions of delignifying chemicals, ions are absorbed on the surfaces of the capillary walls with the formation of electrical double layers. These electrical double layers may affect the penetration of cooking liquors into the wood in several ways. First, the formation of such double layers, even though their thickness does not exceed several molecular diameters, may still be sufficient to seriously decrease the effective cross-sectional areas of the very minute capillaries of the wood since the rate of flow of liquids through small capillaries is proportional to the fourth power of the radius; second, the movement of liquids in the capillaries past the electrical double layers on the walls produces a streaming potential which always has the effect of retarding the flow of solutions through the capillaries. In a similar manner the flow of solutions through the membrane produces a membrane potential having a similar retarding effect.

**Lack of permeability.**—It is possible that at least some of the membranes in the wood may be impermeable or only semipermeable to the delignifying chemicals contained in the cooking liquors; consequently, delignifying ions in solution, or at least some of them, can not penetrate beyond these impermeable membranes.

**Mechanical blocking of membranes.**—The action of delignifying reagents may produce colloidal substances which mechanically block or plug the minute capillaries of the wood.

**Chemical action.**—When wood is impregnated with delignifying solutions, a chemical reaction takes place between the reagents and various components of the wood. This reaction, of course, occurs first in the outermost portions of the wood subdivision so that the impregnating liquor, as it penetrates into the wood, is gradually depleted with respect to the concentration of the reactive chemicals in the liquor.

In the present invention, as has been described, after pretreatment with a non-delignifying electrolyte under proper conditions, a substantially uniform penetration of the delignifying solution into the wood is secured. As has been indicated, the concentration of the effective delignifying chemical is substantially uniform throughout the individual pieces of wood. The effect obtained with a dilute solution of non-delignifying electrolyte may be explained as being due to the combined influence of a number of factors which are described in the following paragraphs:

By employing the proper concentration of the

pretreating electrolyte, the membranes and capillaries of the wood are brought to their iso-electric point by the absorption on their surfaces of the ions of the pretreating electrolyte. This facilitates passage of liquids through the membranes and capillaries.

The iso-electric point for amphoteric substances such as proteins, etc. which are usually in colloidal solution is that pH or hydrogen ion concentration at which the substance apparently changes from acidic to a basic character or vice versa. This is primarily due to a surface adsorption of hydrogen ions. However, inert substances such as quartz, glass, cellulose, etc. are also capable of absorbing ions on their surfaces with the formation of electrical double layers. The statistical difference between the numbers of positive and negative charges present in this electrical double layer formation is known as the zeta potential. At the iso-electric point the number of positive and negative charges present in the electrical double layer is exactly equal and the zeta potential is consequently zero. With changing concentrations of electrolyte, the net charge on the surface changes sign as the iso-electric point is passed; consequently the iso-electric point is that point at which the net surface charge is just on the border of reversing its sign. If the electrolyte adsorbed is an acid, base or an acidic or basic salt, the iso-electric point occurs at a definite hydrogen ion concentration (pH) and is defined as such. However, neutral salts may be readily adsorbed and in such cases the iso-electric point occurs at a definite concentration of the salt, usually a very dilute concentration. The iso-electric point is commonly defined in terms of the molar concentration of the electrolyte solution from which the adsorption takes place.

Pertinent phenomena occurring at the iso-electric point are zero zeta potential and minimum or no swelling of the wood. As a result of the zero zeta potential, the resistance to the flow of liquids due to streaming and membrane potentials is reduced to a minimum. Since the effect of swelling is to reduce the cross-sectional area of capillaries in the wood through which the liquid must pass, a decrease in the amount of swelling results in improved penetration.

The adsorption of caustic soda or other delignifying reagents on the surfaces of the pores and capillaries of the wood is also reduced or prevented by pretreatment with non-delignifying electrolytes. If the adsorptive powers of the wood are satisfied by some electrolyte prior to the addition of the delignifying reagent, the concentration of such delignifying solution is not gradually decreased due to adsorption of the reagent from the solution in its passage through the pores and capillaries of the wood.

The treatment of the wood with non-delignifying electrolyte solutions is effective in obtaining more uniform distribution of the subsequently added chemicals because this treatment is given prior to the addition of the delignifying reagents. The surfaces of the pores and capillaries of the wood may be conceived to be given a protective coating of adsorbed ions before the addition of the delignifying reagents.

This "protective coating", however, has no effect on the reactions between the subsequently added delignifying reagents and the material, such as lignin, present in the wood when reactive temperatures are attained. While the adsorbed layers of non-delignifying ions are relatively

stable and are only displaced rather slowly by the addition of a solution of relatively high concentration of delignifying reagent, such displacement does, of course, ultimately take place. But, according to the present process, before this displacement has occurred, the wood has been uniformly impregnated with the desired amounts of delignifying reagents and no further movement of delignifying reagents from the solution surrounding the wood into the interior of the subdivisions is necessary. The mere addition of the same concentration of non-delignifying electrolyte to the solution of delignifying reagents would be wholly ineffective since in that case a mixture of the non-delignifying electrolyte and delignifying reagent ions, with the latter predominating, would be adsorbed. Furthermore, the concentration of ions on the surfaces of the wood would be many times that required to produce iso-electric conditions.

The preconditioning of the surfaces of the wood with very dilute non-delignifying electrolyte solutions when applied to the manufacture of wood pulp permits the production of substantially higher yields of far more uniform pulps than is possible by any of the well known delignifying systems.

The improvement over prior practices is especially marked when alkaline treating solutions are employed. Another distinguishing feature of the pulp resulting from the use of the present invention is the reduced depolymerization of the cellulose reflected in a much higher cuprammonium viscosity as distinguished from the best commercial soda and kraft products. The residual impurities in the digested pulp resulting from this invention are quite uniformly associated with the cellulose fibers. In other words, the pulps of the present invention are entirely homogeneous. This condition permits a very economical bleaching of the pulps to any desired standard of whiteness. For example, a pulp with a bleachability of 40% may be brought to the standard of whiteness ordinarily required for magazine or book paper by a carefully controlled chlorination employing chlorine gas, causticizing the chlorinated pulp, washing, and then treating with 2%-5% calcium hypochlorite with a reduction in pulp yield of not to exceed the order of 2.5%. Over-all yields of bleached pulp from 50%-52% are readily attained, which represents an increase of 20%-25% of actual bleached pulp over standard mill practices of the order of 41%.

A characteristic feature of pulp produced in accordance with the present invention is the freedom of said pulps from the products of degradation of the cellulose fibers which have been excessively treated with delignifying liquors. It has been indicated before that in connection with the ordinary digesting processes, the cellulose fibers from the outermost portions of the wood chips are severely degraded from their prolonged contact after delignification with the surrounding pool of delignifying liquors. In the present invention, by distinction, the delignification proceeds uniformly, simultaneously, and quickly through each subdivision of the entire mass of wood chips. Consequently, every part

of each fiber is delignified at any given time to substantially the same extent. Thus the delignification conditions may be terminated at any desired degree of lignin removal, with the resulting pulp product characterized by the uniform distribution of its cellulosic and non-cellulosic components. Because the treating solutions have a strong preferential action on the ligneous material, under these digesting conditions the cellulose fibers are protected and remain substantially undegraded.

It is obvious from the foregoing that the process of the invention may be used to practical and economical advantage in impregnating woody materials with other than digesting solutions. For example, solutions of dyestuffs, fireproofing compounds and other liquids may likewise be uniformly distributed through wood or woody materials.

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.

We claim:

1. A process for the delignification of wood comprising treating the wood in the form of small pieces with a heated water solution of a non-delignifying salt forming an electrolyte in the solution of a concentration low enough to be just sufficient to deposit by adsorption on the surfaces of the capillaries and membranes ions in layer formation providing protective coatings on said surfaces and facilitating the passage of an alkaline delignifying agent to the interiors of the wood pieces, subjecting said wood pieces to said electrolyte solution under time and temperature conditions effecting said adsorption of ions from the electrolyte on the interior surfaces of the wood, while avoiding delignification and maintaining the accessibility of the membranes and capillaries, then subjecting said wood pieces so impregnated with an electrolyte to soaking in an alkaline digesting liquor at a temperature below the digestion point and for a time sufficiently long to effect a complete impregnation of the wood pieces with the liquor, and then raising the temperature to digest the wood.

2. The process as set forth in claim 1 in which the electrolyte solution is at the iso-electric concentration for the wood so that the numbers of positive and negative charges present at the surface layers are substantially in equilibrium.

3. The process as set forth in claim 1 in which the wood is uniformly impregnated with a delignifying reagent at a concentration which provides an amount of such reagent in the quantity of liquor adsorbed by the wood sufficient to complete the delignification of the wood for pulping.

4. The process as set forth in claim 1 in which the electrolyte solution comprises a solution of sodium chloride of  $10^{-2}$  molar concentration.

5. The process as set forth in claim 1 in which the electrolyte solution comprises a solution of aluminum sulfate of  $10^{-5}$  molar concentration.

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FREDRICH OLSEN.

CERTIFICATE OF CORRECTION.

Patent No. 2,228,349.

January 14, 1941.

SOLDON FELDMAN, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 71-72, for "tarrate" read --tartrate--; page 6, second column, line 54, for "d. Direct impregnation" read --b. Direct impregnation--; page 7, first column, line 9, for "Absorption" read --Adsorption--; line 10, for "absorb" read --adsorb--; lines 16 and 17, for "absorption" read --adsorption--; line 23, for "absorbed" read --adsorbed--; same page, second column, line 3, for "absorption" read --adsorption--; line 15, for "absorbing" read --adsorbing--; page 8, first column, line 56-57, for "degration" read --degradation--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of May, A. D. 1941.

(Seal)

Henry Van Arsdale,  
Acting Commissioner of Patents.