Patented July 1, 1930 1,768,823

UNITED STATES PATENT OFFICE

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TREATMENT OF WOOD PULP AND PRODUCT

No Drawing. Application filed June 13, 1929, Serial No. 370,726, and in Canada December 1, 1921.

This invention relates to improvements in the bleaching and purification of fibrous materials and especially of chemical pulp derived from wood and similar fibrous materials including jute, bamboo, cotton linters and the like.

More particularly the invention relates to the art of bleaching or purifying fibrous materials in which the bleaching material is added to the fibrous material in successive portions; and particularly to such a process in which a reactive chlorine-containing compound is used in the first stage of the bleaching treatment and soluble compounds are removed from the fibrous material between two successive bleaching or purifying treatments.

This application is a continuation in part of our co-pending applications, and particularly of our U. S. application Serial No. 449,245, filed March 2, 1921; our U. S. application Serial No. 544,322, filed March 16th, 1922. This application is in part a continuation of our co-pending applications Serial Nos. 449,245, filed March 2, 1921; 481,146 and 481,147 filed June 28, 1921; 261,696, filed March 14, 1928; 261,697, filed March 14, 1928; and 544,322, filed March 16, 1922, Serial No. 261,698, filed March 14, 1928.

In heretofore known methods of bleaching chemical pulp derived from wood with chlorine or chlorine-containing compounds, the bleaching agent, such for example, as a hypochlorite or bleaching powder, has been used upon the cellulosic material in a single stage. In the treatment of unbleached wood pulp, particularly where the cooking treatment has not removed all non-fibrous matter, as in the case of so-called kraft pulp produced from pines, the treatment by heretofore known bleaching processes is either insufficient to produce a good and strong white pulp or it may be so drastic that the cellulosic fibres are weakened and oxidized to a commercially prohibitive extent with a consequent reduction of the yield and quality of the product. In order to bleach such pulp to a high white in a single stage with the usual bleaching powder liquor, the action of the bleaching agent upon the fibres may be sufficiently severe to injure the fibres, with production of oxidation products, e. g. oxycellulose, or with more or less profound modification of part of the cellulose of the fibres, e. g., with resulting increase in the proportion of beta and gamma cellulose to alpha cellulose, etc.

The present invention includes an improved bleaching process which is carried out in two or more stages, in which the pulp is subjected in the first stage to the action of a reactive chlorine-containing compound, with or without other reactive bleaching agents, a portion only of the total amount of bleaching or purifying material usually being furnished to the fibrous material in the first stage of the complete process, and in a subsequent stage the bleaching or purifying of the fibrous material is continued by treatment thereof with an alkaline liquor, e. g., a solution to which sodium peroxide, and/or sodium perborate, has been supplied.

This process is particularly advantageous for treating and more specifically for bleaching those resistant cellulosic fibrous materials which bear a non-fibrous organic content of a nature such that treatment thereof with free chlorine renders only a part thereof readily soluble in water and leaves a relatively insoluble part thereof with the fibres, which may, however, be readily bleached by a suitable subsequent treatment, such as an alkaline bleaching treatment with liquor supplied with sodium peroxide, sodium perborate, or sodium or postassium permanganate.

The particularly advantageous results obtainable by the process of the present invention seems to be due at least in part to the use of an alkaline liquor for the treatment of partially-bleached fibrous material resulting from the first stage of the bleaching treatment. At any rate, we have found that important advantages are attained when the pulp, after the preliminary bleaching, is treated with a solution containing an alkali, e. g., sodium hydroxide. Therefore we prefer to use alkaline reagents capable of supplying alkaline compounds, e. g., sodium

hydroxide, in the liquor used in the final stage of the bleaching or purifying process. We have found that very good results are obtainable when sodium peroxide or/and sodium perborate is supplied to the liquor used for treating the partially bleached fibrous material. Sodium peroxide is especially desirable owing to the fact that it is capable of supplying sodium hydroxide and an oxidizing compound to the liquor.

While our invention is in no way to be limited to such theory, it seems probable that the treatment with strongly alkaline solutions converts into soluble compounds normally insoluble material formed by the preliminary bleaching treatment; and, particularly in the case of pulp produced by digestion with cooking liquors which do not contain large amounts of strong alkali, this treatment may also solubilize compounds formed or left on the fibers by the digesting treatment.

According to the present invention, we avoid certain of the objections to bleaching chemical wood pulps with the usual chlorine-containing compounds and we are enabled to produce a high white cellulose product of good strength, thus making it suitable for many purposes for which cellulose bleached by former methods has been found less satisfactory. According to the present invention, we may employ in the bleaching operation a solution containing a reactive chlorine-containing compound either alone or in the presence of other suitable compounds. We have found that if such agents or reagents are added in successive stages that an economy in the amount of bleaching reagents may be effected and a superior grade or quality of bleached pulp may be obtained, particularly when the partially bleached fibrous material resulting from the first stage is separated from the resulting bleach residues, etc.

The first stage can be carried out by adding a portion of the bleaching material, for example, a solution of bleaching powder or any other suitable alkaline hypochlorite, and permitting it to exert its bleaching action upon the fibrous material, such as chemical wood pulp, then removing from the partially bleached fibrous material, soluble compounds resulting from this bleaching operation, by dewatering and/or washing, or otherwise. Another portion of the same or another kind of bleaching agent may be used on this fibrous material in a subsequent stage. Thus the partially bleached fibrous material may be treated with a liquor supplied with sodium peroxide, sodium perborate, etc.

When only a small or moderate amount of bleaching material is used in such first or preliminary partial bleaching treatment, there appear to be produced compounds which are water-soluble and may be colorless and some of which are not fully oxidized. These compounds can be substantially removed from the fibrous material by the washing or dewatering operation, or otherwise, so that a reduced amount will be present with the fibrous material during the subsequent treatment.

We have found that chemical pulps obtained, for example, by the soda, sulfite and sulfate processes, so-called, are not only given a white color, but retain their white color much better and longer when bleached according to the process of the present invention than when bleached by chlorine or a hypochlorite in a single-stage, i. e. according to the common methods of bleaching. The advantage of increased permanence of whiteness of the bleached pulp is a characteristic advantage of the present invention, as compared to pulps bleached by bleaching powder liquor in the customary single-stage method of bleaching.

The invention will be further illustrated by the following more detailed description of certain applications thereof, but it will be understood that the invention is not limited thereto.

The improved process of the present invention is of more or less general application. It is particularly advantageous for bleaching chemical pulp from wood that is difficult to bleach to a high white by a single stage treatment with ordinary bleaching powder or calcium hypochlorite liquor, without commercially objectionable injury to the fibers. The process is of special value as applied to chemical pulp produced by cooking wood with alkaline cooking liquors, such as pulp made by the so-called soda process or the so-called sulfate process or modifications thereof. It is also of special value for the bleaching of chemical pulp produced according to our improved processes, set forth in our prior companion applications, Serial No. 434,720, filed January 3, 1921, No. 481,146 and No. 481,147, filed June 28, 1921 and our U. S. Patent #1,651,665, in which wood is cooked with a cooking liquor made up essentially of normal sodium sulfite, or of a mixture of reagents such as caustic soda, sodium sulfide, and/or sodium thiosulfate, and sodium sulfite in varying proportions, with the caustic soda either absent or present in regulated amount such that the fibers are not seriously injured during the cooking operation. When certain woods, such as pines, are cooked with a cooking liquor so as to produce strong chemical pulp, the reaction of the cooking liquor upon the wood, with resulting conversion of a considerable portion of the wood into soluble compounds, sometimes leaves the unbleached fibrous material in such a condition that a considerable amount of reagent,

such as bleaching powder, is necessary to bleach them effectively, while an elevated temperature may also be necessary. The use of a strong alkaline hypochlorite solution upon such material at an elevated temperature may injure the fibers to an objectionable degree, e. g., above 100° C.

Pulp may be prepared from jack-pine or loblolly-pine, or pines of a similar character, by cooking the pine wood chips with a cooking liquor containing a preponderating amount of caustic soda and a lesser amount of sodium sulfide, for example, 15 parts by weight of caustic soda and 5 parts by weight of sodium sulfide per 100 parts by weight of wood (figured on bone-dry basis) at a temperature corresponding to saturated steam pressure of 110 lbs., for a period of 6 hours. The resulting pulp may be freed from the residual liquor and washed in the usual way. It may be then diluted with sufficient cool water to enable it to be readily handled (e. g., containing 1 to 5 parts of fibres in 100 parts of the diluted material) and thereafter this thin or flowable pulp may be treated with chlorine by adding a hypochlorite solution (e. g., bleaching powder) and liberating chlorine or hypochlorous acid therefrom by means of added mineral acid, such as hydrochloric acid or sulfuric acid. A moderate amount of chlorine may be thus used, for example, 5 to 10 pounds (more or less) of bleaching powder per 100 pounds of pulp (air-dry basis) together with sufficient mineral acid to give a suitable acid reaction. Instead of producing chlorine or hypochlorous acid in this way, chlorine gas can be directly introduced into the mixture of fibers and water and absorbed by the pulp. This chlorine treatment can be carried out at ordinary atmospheric temperature and requires but a few minutes for its completion, care being taken to uniformly treat the pulp and utilize the chlorine in an economical manner.

After this preliminary acid bleaching treatment, excess liquor is advantageously removed, for example, by means of a suitable pulp-thickening device, and the pulp is preferably washed to remove a considerable part of such dissolved organic matter as may be contained therein. The pulp is then subjected to a further bleaching operation, which is advantageously carried out in the presence of an alkaline liquor. For example, the bleaching liquor for the latter bleaching treatment may be supplied with a suitable alkaline hypochlorite, such as bleaching powder, or/and it may be supplied with sodium peroxide, sodium perborate, etc. The amount of bleaching material required for completing the bleaching treatment can usually be materially decreased from that commonly used, i. e. when a single stage bleaching treatment with bleaching powder liquor is employed. The amount of bleaching material supplied to the fibrous material in such second stage may, for example, be the equivalent of 10 pounds (more or less) of bleaching powder per 100 pounds of pulp (air-dry basis) and the bleaching can be promoted by heating the admixed pulp and bleaching liquor to a moderate degree. The temperature during such treatment should not be allowed to exceed the boiling point of the liquor at atmospheric pressure. When the bleaching operation is thus completed, the pulp may be washed to free it from the residual solution. It is then ready for further use as a bleached pulp.

The bleaching of such pine pulp in the manner above described has been found to provide a good strong white pulp which holds its color satisfactorily even upon prolonged exposure to air. When the pulp is made with a cooking liquor, such as a cooking liquor containing a preponderating amount of normal sodium sulfite with or without a moderate amount of other suitable digesting agent, which is without seriously objectionable action upon the fibres, the resulting pulp will contain strong fibres which may be thus bleached to a satisfactory white color, without undue injury.

An active chlorine-containing reagent which is capable of oxidizing some organic constituents and of chlorinating some organic constituents may readily be formed in place when a mixture of unbleached chemical pulp derived from wood, water and alkaline hypochlorite solution is treated with a suitable mineral acid, e. g. dilute hydrochloric acid, so as to decompose the alkaline hypochlorite and render the liquor in the mixture acid to litmus.

We have found that it is advantageous, when employing bleaching liquors capable of oxidizing non-fibrous organic matter associated with fibrous material derived from wood, for example, chemical pulp, to so conduct the first or preliminary bleaching stage that all or substantially all of the oxidizing power of the bleaching agent or agents added in regulated amount (less than sufficient for the entire amount of oxidation to be effected) is utilized before the resulting liquor and its dissolved constituents are removed from the resulting fibrous material, and further, so that such liquor when removed from such partially bleached material (fibrous), contains organic matter which is capable of reacting with oxygen derived from a permanganate such as potassium permanganate. For example, by treating such unbleached chemical pulp with chlorine alone, or with a hypochlorite alone, or with a manganate or permanganate alone, or with various of these reagents used simultaneously or in conjunction or

in any other manner, but with the amount of such reagent or reagents employed in the first stage or preliminary bleaching treatment being less, such as for example, one-half, more or less, than the entire amount of bleaching agent or agents needed for the desired total degree of bleaching, and consuming all or substantially all of such reagent or reagents (supplied in the first stage) in reaction or reactions with organic matter thereof, the resulting liquor will in most cases, if not all, contain some organic matter which is capable of reacting with oxygen from a dissolved oxidizing agent such as potassium permanganate. By removing such a liquor from the partially bleached fibrous material, and particularly if the fibrous material is washed before the second treatment, such oxidizable organic matter is removed from the fibrous material before the second or subsequent addition of bleaching agent or agents is made thereto. Thus we have made it possible to reduce the amount of bleaching agent or agents required for the complete bleaching process.

The improved process of the present invention makes it possible to economize in the amount of steam required for the bleaching operation, as well as enabling a reduction to be effected in the amount of bleaching reagent required, and permits the production of superior bleached products in case of chemical pulps, for example such chemical pulp as can be obtained by digesting pine chips with a sodium sulfite digesting liquor until the encrusting matter is solubilized to such an extent as to permit of converting the residue of the chips into chemical pulp by the usual blowing of the digester contents into a blow pit. Such chemical pulp can be subjected to a subsequent treatment by means of a liquor supplied with sodium hydroxide so as to remove some of the resinous or pitchy ingredients, etc., which have not been completely removed by the digesting treatment. Such pulp-making and treating operation is more fully described in our former application, Serial No. 481,147, filed June 28, 1921. When the pulp-making and pulp-treating operation of such former application is combined with the bleaching and refining or purifying treatment of the present invention, bleached pulp of high white, characterized by fibres of relatively great strength as compared with pulp from pine produced and bleached by the heretofore known methods, may be readily obtained. Such pulps are new and distinct commercial products. In particular, such pulps may have a relatively large amount of alpha cellulose, such as around 90% or even more, and the bleached fibres are relatively very durable and resistant to mechanical action such as beating, etc. Such bleached pulps substantially retain their whiteness when exposed to air.

The preliminary treatment of the pulp with chlorine can be effected by introducing free chlorine or chlorinated water or an acid hypochlorite solution into a thin pulp, or by producing such compound therein. The resulting pulp may then be delivered to a thickening device, which is advantageously of acid-resistant construction, although the liquor may be rendered non-acid after the chlorine has been substantially fully used up and before it reaches the thickening device. Soda or lime may be used for fixing any remaining free acid. The chlorine acts upon unbleached pulp very rapidly even at ordinary temperatures so that its required work (and any subsequent treatment with soda or lime) can be finished before the chlorine-treated pulp has reached the thickener. The thickening may, for example, be done in a Belmar bleacher (so-called) equipped with a suitable drum-washer, or in other suitable thickening device. By subjecting the pulp to a preliminary chlorine or acid hypochlorite treatment in this way, a special bleaching operation may be avoided, in so far as the thickening and the removal of the residual acid or non-acid bleach liquor takes place at the same time. The preliminary bleaching treatment and liquor removal appear to alter or remove certain resistant organic matter present so that the subsequent bleaching, for example, with chloride of lime liquor, can be carried out at a moderate temperature, thereby permitting a saving in steam for heating, while giving an improved bleached pulp which has not been subjected to the injurious action of a stronger alkaline bleach liquor at high temperatures, e. g., substantially higher than 100° C. The bleached pulp accordingly may have an improved color as well as improved properties in other respects, and the bleached pulp obtained, e. g., from pines, is usually very different from such pulps bleached by the usual single-stage bleaching method with bleaching powder liquor.

According to another application of the invention, the preliminary bleaching operation can be carried out by adding to and admixing with the pulp chloride of lime solution or sodium hypochlorite solution in amount sufficient to bleach a substantial amount of the pulp but advantageously less than enough for complete bleaching, and thereafter adding and admixing a limited and regulated amount of acid sufficient to give the pulp a mildly acid reaction and to liberate chlorine or hypochlorous acid, and, after the first bleaching treatment, a predetermined amount of alkali (such as lime or soda) can be added in amount sufficient to give the pulp a mildly alkaline reaction,

and also adding enough additional bleaching material, such as sodium peroxide, sodium perborate and/or an alkaline hypochlorite, to complete the bleaching operation, and then moderately heating the pulp and liquor during the latter bleaching treatment but maintaining the liquor throughout such treatment at temperatures not exceeding its boiling point at atmospheric pressure.

We consider it more advantageous, however, to subject the pulp to a dewatering and washing operation after the first-stage bleaching treatment and before the subsequent alkaline bleaching treatment, in order to remove certain objectionable matters from the pulp before adding the bleaching liquor for the second bleaching treatment.

Pulp which is difficult to bleach with an alkaline hypochlorite in a single stage (e. g., a solution of bleaching powder) can nevertheless be readily bleached by the improved multiple-stage treatment of the present invention. For example, we have found that kraft pulp, produced from a spruce or pine by the sulfate process (so-called) and which was difficult to bleach to a high white in the ordinary manner with bleaching powder liquor, could be readily bleached to a strong white pulp by the present process. We have also found that pulp from Canada jack-pine, Minnesota jack-pine, Virginia loblolly pine, yellow pine, etc., (produced by means of a cooking liquor comprising a limited amount of caustic soda and lesser amounts of sodium sulfide and sodium sulfite) could be readily bleached by our new method to a high white strong pulp by means of a moderate amount of reactive chlorine-containing bleaching agent.

Chemical pulps derived from, for instance, jack pine or loblolly pine, are impaired in strength or yield, usually both, if the cooking operation is so conducted with cooking liquor carrying a large amount of caustic soda as to produce pulps readily bleached to a high white in a single-stage bleaching operation with the usual bleaching powder liquors. The process of the present invention enables us to produce from such woods finished pulps of high white with less impairment.

It is a further advantage of the present invention that it makes possible the satisfactory bleaching of chemical pulp from wood produced by what is commonly known as the short-time or quick-cook method, that is, by carrying out the cook with cooking liquors of various degrees of strength or of concentration, pressure, temperature and time, and terminating the cook without carrying it to completion. Such pulp, produced by the short-time or quick-cook method, so-called, cannot be readily and satisfactorily bleached by ordinary bleaching methods, and usually results in a bleached product of inferior quality. We have found, however, that such pulp, which heretofore would be considered under-cooked and difficult to bleach by common bleaching methods can advantageously be bleached by the process of the present invention and brought to a good white color with materially less injury to the stock than with methods of bleaching heretofore commonly used. The present invention makes possible therefore the production of a satisfactory bleached pulp from under-cooked stock, thus avoiding the necessity in many cases of continuing the cooking operation for the normal period of time, etc. The cutting down of the time of the cooking operation makes possible a material increase in the number of digestions which can be carried out in a given apparatus, and correspondingly increases the producing capacity of the digesters over the usual practice in the art. We accordingly include and claim as a part of our invention the production and bleaching of such under-cooked pulp by treating such pulp in the manner herein described.

The latter stage of the multiple-stage bleaching process can be carried out at ordinary temperature if a somewhat increased time is permitted for the bleaching operation, especially with pulp such as poplar pulp made by the soda process and spruce pulp made by the so-called (acid) sulfite process, although it is usually better to warm the pulp and admixed liquor to a moderate degree. Bleached pulps of excellent white color can be thus obtained, with relatively decreased injury to the pulp, in that the process avoids the severe treatment with strong alkaline hypochlorite liquors at relatively high temperature such as tends to oxidize the pulp with resulting production of oxy-cellulose or to modify the pulp with resulting production of high amounts of beta and gamma cellulose, etc. The latter stage of the bleaching process can be carried out by the addition of sodium perborate, sodium peroxide or by permanganates, for example, by sodium or potassium permanganate, using either an alkaline solution or one which is made acid by the addition of a suitable acid in sufficient amount. When an alkaline permanganate solution is employed the pulp preferably should be warmed somewhat to facilitate or expedite the bleaching operation. When an acid solution is used, the bleaching takes place readily at ordinary temperatures although a moderate heating may be employed. The manganese compound deposited on the fibers can be readily removed with a solution supplied with sodium sulfite, or bisulfite, and sulfuric acid, or by a solution of sulfurous acid, and the pulp can then be freed from dissolved reagents by washing.

Instead of using chlorine or an active

chlorine-containing reagent alone in the first step, composite bleaching liquors may be employed which contain a manganate or permanganate, in addition to such active chlorine-containing reagent. For example, a liquor containing from about one-fourth part to about three parts, more or less, of sodium permanganate or its equivalent, and about one-fourth to fifteen or twenty parts of sodium hypochlorite or its chemical equivalent, such amounts of bleaching reagents being based on the air-dry weight of the pulp, such as chemical wood pulp. The particular ratios of such reagents within the limits named above may be chosen in each case according to the desired degree of bleaching and the material which is to be bleached. A portion of such liquor, ordinarily about one-half, more or less, may be added to the pulp for the first stage of the process and is left in contact with the pulp until substantially all of the bleaching reagents have been used up. The spent liquor is then separated from the pulp and the latter preferably washed to remove soluble oxidizable compounds. The remainder of the bleach liquor is then added to the fibrous material and the bleaching carried to the necessary or desired degree. The hypochlorite in such bleach liquor appears to act in a somewhat different and more advantageous manner than when used alone, while the action of the permanganate is supplemented by the action of the hypochlorite so that a lesser amount of permanganate need be used than if it were used alone. When a two-stage bleaching treatment is carried out with such composite liquors, they may be either acid or alkaline, but that used in the second stage is advantageously alkaline, particularly when the bleaching liquor in the final bleaching stage is supplied with sodium peroxide or sodium perborate.

Short leaf pine, cotton linters, black gum, red gum, tupelo gum, chestnut, white oak, black oak, red oak, hickory, birch, beech, maple, bamboo, popular, jute, spruce and balsam, have been pulped by our pulping process and the pulps thus produced have been bleached by one or more of the processes of the present invention and in each instance high white strong pulps were obtained.

It will be seen that the present invention comprises a multiple-stage bleaching process in which bleaching liquors are used containing active chlorine-containing reagents, such as hypochlorite, in which the spent liquor from the first stage is preferably and advantageously removed, as far as practicable, from the pulp before the second bleaching stage of the process is commenced. The second bleaching stage of the process may be carried out either with the same type or with a different type of bleaching liquor from that which is used in the first stage and may be carried out either at ordinary temperatures for a sufficient time or advantageously with moderate warming of the solution. The final bleaching operation can also be carried out with sodium perborate, sodium peroxide, or sodium or potassium permanganate (with or without sulfuric acid) with subsequent treatment of the pulp with sodium bisulfite and sulfuric acid, or a solution of sulfurous acid followed by a washing operation.

When sodium peroxide is utilized in the final bleaching stage of the process, we prefer to add it to a liquor which is substantially free from an active chlorine-containing bleaching reagent, such as free chlorine, hypochlorous acid, or an alkaline hypochlorite. Thus we may add to the mixture of fibres and water supplied to the last bleaching stage, an amount of sodium peroxide which is chemically equivalent (in bleaching effect) to from around 3 to 15 parts (more or less) of bleaching powder (35% available chlorine basis) per 100 parts of fibres, by weight. The amount of sodium peroxide supplied to the partially bleached fibrous material will vary somewhat depending upon the amount of bleaching agent which has been utilized in producing the partially bleached material, in general the less the amount of colored organic matter present with the partially bleached fibrous material, the less the amount of sodium peroxide needed. When relatively large amounts of sodium peroxide are supplied to the water present with the partially bleached fibrous material, the sodium hydroxide formed is capable of materially assisting in the bleaching and purifying treatments inasmuch as such sodium hydroxide is capable of rendering some of the non-fibrous material sufficiently soluble so that some of the undesired compounds can be readily separated from the bleached fibres, thereby improving the quality of the pulp.

We have found that the following method of applying the process gives good results. After washing the unbleached pulp to remove substantially all the residual liquor resulting from the cooking of the wood chips, bamboo, jute, cotton linters, etc., the pulp is treated with chlorine gas while being transferred to a washing or pulp thickening device. The pulp may be subjected to chlorine gas in any suitable manner, e. g., by adding enough water to the pulp so that it may be readily handled and then pumping the thinned pulp to the top of a baffled tower (preferably acid-resistant) allowing the pulp to pass downward thru the tower and come into contact with chlorine gas introduced preferably near the bottom of the tower, as more fully set forth in our co-

pending application, Serial No. 470,961, filed May 19, 1921, upon which Patent No. 1,730,315 was issued on October 1, 1929. The major portion of the chlorine may thus be absorbed by the pulp. Any chlorine escaping from near the top of the tower may then be conducted to a tower in which milk of lime is circulated so as to absorb this portion of the chlorine which escaped from the first tower. In this manner, by regulating the flow and amount of pulp and of chlorine, the desired amount of chlorine can be absorbed by the pulp in one tower and at the same time produce a suitable amount of alkaline hypochlorite bleaching liquor suitable for the second stage of the bleaching process. Sodium hydroxide solution may be used in the second tower instead of milk of lime. The chlorine-treated pulp may be further thinned with water, if desired, and then sent to a thickener (with or without treatment with lime or soda) where the excess liquor is removed. This may then be followed by the second-stage treatment. Instead of passing the pulp through a tower, it may be treated with chlorine gas with or without thinning by agitating the pulp while the chlorine gas is being introduced, passing any escaping chlorine into milk of lime or a solution of sodium hydroxide. The treated pulp should be dewatered or washed before the second-stage treatment.

Although a number of examples given above have included an acid treatment in one of the stages of the bleaching process, the invention is in no way limited thereto and in some cases, particularly where the use of acid-resisting apparatus may be undesirable, both stages of the process may be performed with non-acid bleaching liquors, such, for example, as alkali metal or alkaline earth metal hypochlorite, or composite liquors containing hypochlorites as described above. The final bleaching treatment may be carried out with alkaline liquor supplied with sodium peroxide and/or sodium perborate with or without an alkaline hypochlorite.

The following is an example of one manner in which the bleaching operation may be performed with non-acid bleaching liquors. The well-washed and unbleached chemical pulp, e. g., spruce pulp obtained by a sulfate process or an acid-sulfite process, composed of around three to seven pounds of fiber to around 97 to 93 pounds of water, more or less, such a mixture of fibres and water constituting a thin or flowable pulp, may be treated in the first stage with a bleaching powder liquor prepared by dissolving calcium hypochlorite in cool water. Such bleaching liquor may advantageously have some calcium hydroxide in solution and even a small amount in suspension in it so as to render it moderately alkaline. The amount of bleaching material added to the pulp for the first-stage treatment may vary somewhat. Thus an amount of bleaching liquor which contains around three to fifteen parts, more or less, of bleaching powder (35% available chlorine) for each 100 parts fibers, by weight (air-dry basis), may be added to the pulp and thoroughly mixed therewith; then the mixture comprising fibres and a preponderating amount of water may be gradually heated, while it is being well agitated and circulated, by the addition of steam in regulated rate and amount, for example, such as will not overheat one portion to an objectionable temperature, and the temperature of the mixture gradually brought up in a substantially uniform manner to around 30 to 60 degrees centigrade, more or less. The treatment may be thus continued until the liquor shows by test that substantially all of its available bleach has been exhausted; then the treated pulp may be subjected to a dewatering operation by means of any suitable device, and the treated pulp may with advantage be given a washing treatment by means of water so as to remove substantially all of the bleach residues and dissolved organic matter from the pulp. Then the dewatered, and preferably washed, pulp is admixed with an additional charge of bleaching liquor of the kind described above, the amount thus added being sufficient or somewhat more than sufficient to carry the bleaching to the desired degree, the mixture of pulp and added bleaching liquors is circulated and gradually heated and thoroughly mixed, the heating being continued until a temperature of around 30° to 60° C., more or less, has been reached. When the fiber has been bleached to the desired degree, the bleach residue is removed in any suitable manner and the bleached fiber then well washed with water. The amount of bleaching liquor added for second-stage treatment may vary somewhat, depending upon the material to be bleached, the degree of whiteness desired, the amount of bleaching reagent utilized in the first-stage treatment, etc. Generally, an amount of bleaching liquor carrying from three to fifteen parts, more or less, of bleaching powder (35% available chlorine) per 100 parts of fibers by weight is sufficient for the second-stage treatment; and in general the larger the amount of bleach used in the first-stage treatment, the lower the amount required for the second-stage treatment. It is advantageous to maintain the liquor (with the pulp) mildly alkaline to litmus until removed. Instead of using hypochlorite alone for effecting the final bleaching treatment, a portion or all of such hypochlorite may be replaced with an equivalent amount of sodium peroxide or/and sodium perborate.

In case the bleach liquor residue removed

from the bleached fibers after the second-stage treatment in any of the above examples carries a substantial or a rather large amount of unconsumed bleaching reagent, which can be determined by suitable tests, such residue can be utilized, at least in part, for a preliminary bleaching treatment of the unbleached pulp. If desired, a regulated additional amount of bleaching material may be added thereto so that the bleaching liquor for the first-stage treatment may be composed (in part) of bleach residue from the second-stage treatment and (in part) of freshly supplied bleaching material. Thus a fair or moderate excess of bleaching liquor, over that actually required for the second-stage bleaching treatment, may be added in the second-stage, and then when the color of the pulp has come up to the desired point, surplus bleach may be removed along with the liquor removed from the bleached pulp and later employed in a preliminary bleaching treatment of unbleached fibrous material. When operating in the latter manner, care should be taken to avoid heating the liquor in the second-stage to such a temperature that an objectionable amount of bleaching reagent is lost from the liquor owing to such heating treatment.

In practice, the bleached pulp and liquor, which may still contain bleaching material in substantial amount, may be treated on a rotary filter of the vacuum-type and the pulp may be washed with a regulated amount of water. The stronger liquor, with any desired amount of the washings, may then be admixed with unbleached pulp. An additional amount of bleaching material may be added to such liquor either as a solid or as a bleaching liquor, for example, such an amount as will permit bleaching the fibrous material at least to the semi-bleached condition. The bleaching material used in the first-stage should preferably be entirely utilized before the residual liquor is removed from the partially bleached fibrous material thereby produced.

In the accompanying claims we have used the term "a hypochlorite of an alkali-forming metal" as including hypochlorites of alkali metals such as sodium hypochlorite and the hypochlorites of alkaline earth metals such as calcium hypochlorite or chloride of lime or chlorinated lime, so-called. In the claims the term "an active chlorine reagent" is particularly intended to include material which is capable of furnishing chlorine in gaseous or nascent state, for example sodium hypochlorite, etc.

We claim:

1. The process of bleaching and refining fibres of chemical wood pulp, which comprises distributing throughout a mixture in which such fibres are distributed throughout a preponderating amount of water an amount of an oxidizing bleaching reagent that is sufficient to effect a partial bleaching of the fibres, and subjecting the fibres to a partial bleaching and solubilizing treatment adapted to remove less-resistant organic matter from the more-resistant fibres of the pulp by means of an alkaline liquor that is supplied with sodium peroxide, such treatment including heating the fibres and an alkaline liquor that contains an oxidizing bleaching agent to a moderate temperature but not in excess of 60 deg. C.

2. The process of producing bleached chemical pulp, which comprises treating incompletely bleached chemical pulp comprising fibres and a preponderating amount of water by means of liquor containing sodium hydroxide and an oxidizing bleaching reagent until the fibres have been substantially freed from colored organic matter and subsequently removing the resulting liquor from the bleached fibres.

3. The process of producing bleached chemical pulp, which comprises treating partially-bleached chemical wood pulp comprising fibres and a preponderating amount of water by means of liquor supplied with an alkaline reagent and an oxidizing bleaching reagent maintained alkaline and heated to a moderate temperature but not in excess of 60° C. so as to convert into soluble compounds some of the organic matter then associated with the fibres of the pulp, and subsequently removing from the pulp an alkaline liquor which contains dissolved organic matter.

4. The process for producing bleached chemical pulp obtained by a treatment which comprises pulping wood by a treatment including a digestion with a sulfite at temperatures above 100 deg. C., which includes washing the pulp, incompletely bleaching the washed pulp by means of an oxidizing bleach liquor, and completing the bleaching of the incompletely bleached pulp by means of a liquor maintained alkaline during this bleaching stage, the bleaching treatments being carried out at temperatures below 100 deg. C.

5. The process defined in claim 4, in which the liquor utilized for pulping the wood contains a sulfite of an alkali metal as an active digesting reagent.

6. The process defined in claim 4, in which the liquor utilized in the last-mentioned bleaching stage contains sodium hydroxide.

7. The process defined in claim 4, in which the liquor utilized in the last-mentioned bleaching stage is supplied with an oxidizing bleaching reagent adapted to form sodium hydroxide when added to water.

8. The process defined in claim 4, in which the first-mentioned oxidizing bleach liquor is supplied with an active chlorine-reagent.

9. The process defined in claim 4, in

which the liquor utilized for pulping the wood contains most of its digestive matter as a normal sulfite of an alkali metal.

10. The process of bleaching and refining fibres of chemical wood pulp, which comprises distributing throughout a mixture in which such fibres are distributed throughout a preponderating amount of water an amount of a hypochlorite of an alkali-forming metal that is sufficient to partially bleach the fibres, and subsequently subjecting fibrous material to a solubilizing treatment adapted to remove less-resistant organic matter from the more-resistant fibres of the pulp by means of an alkaline liquor maintained throughout such solubilizing treatment in an alkaline condition and at temperatures not substantially exceeding its boiling point at atmospheric pressure, and subsequently washing the bleached chemical pulp, sodium peroxide being supplied to the alkaline liquor that is utilized in the said solubilizing treatment.

11. The multiple-stage process for bleaching chemical pulp, which comprises distributing throughout a relatively thin or flowable pulp comprising cellulosic fibres in water a liquor which contains an amount of an oxidizing bleaching reagent adapted to partially bleach the fibres and yield a residual liquor which contains dissolved organic matter, treating the fibres therewith so as to obtain such a residual liquor, separating such a resulting liquor from the partially bleached fibres, subjecting the fibres to a bleaching treatment with an alkaline bleaching liquor supplied with an alkaline reagent in amount adapted to maintain the liquor alkaline throughout the latter bleaching treatment, such treatment including heating the bleaching liquor and fibres to a moderate temperature but not in excess of 60 deg. C., and subsequently washing the bleached fibres.

12. The process according to claim 11, wherein sodium peroxide is supplied to the said alkaline bleaching liquor.

13. The process according to claim 11, wherein the said alkaline bleaching liquor contains an alkaline nonoxidizing sodium compound throughout said bleaching treatment.

14. The process according to claim 11, wherein the said alkaline bleaching liquor contains an alkaline hydroxide throughout said bleaching treatment.

15. The multiple-stage process for bleaching chemical wood pulp, which comprises distributing throughout a mixture in which cellulosic fibres are distributed throughout a preponderating amount of water, a liquor which contains an amount of an active chlorine reagent adapted to partially bleach the fibres and yield a residual liquor which contains dissolved organic matter, treating the fibres therewith so as to obtain such residual liquor, separating such a resulting liquor from the partially bleached fibres, subjecting the fibres to a bleaching treatment with an alkaline bleaching liquor supplied with an alkaline reagent in amount adapted to maintain the liquor alkaline throughout the latter bleaching treatment, such treatment including heating the bleaching liquor and fibres to a moderate temperature but not in excess of 60 deg. C., and subsequently washing the bleached fibres.

16. The multiple-stage process for bleaching chemical wood pulp, which comprises distributing throughout a mixture in which cellulosic fibres are distributed throughout a preponderating amount of water, a liquor which contains an amount of an active chlorine reagent adapted to partially bleach the fibres and yield a residual liquor which contains dissolved organic matter, treating the fibres therewith so as to obtain such residual liquor, separating such a resulting liquor from the partially bleached fibres, subjecting the fibres to a bleaching treatment with an alkaline bleaching liquor supplied with an alkaline reagent in amount adapted to maintain the liquor alkaline throughout the latter bleaching treatment and maintaining the latter liquor throughout such treatment at a temperature not exceeding its boiling point at atmospheric pressure, and subsequently washing the bleached fibres, sodium peroxide being supplied to the said alkaline bleaching liquor.

17. The multiple-stage process for bleaching chemical wood pulp, which comprises distributing throughout a mixture in which cellulosic fibres are distributed throughout a preponderating amount of water, a liquor which contains an amount of an active chlorine reagent adapted to partially bleach the fibres and yield a residual liquor which contains dissolved organic matter, treating the fibres therewith so as to obtain such residual liquor, separating such a resulting liquor from the partially bleached fibres, subjecting the fibres to a bleaching treatment with an alkaline bleaching liquor supplied with an alkaline reagent in amount adapted to maintain the liquor alkaline throughout the latter bleaching treatment and maintaining the latter liquor throughout such treatment at a temperature not exceeding its boiling point at atmospheric pressure, and subsequently washing the bleached fibres, the said alkaline bleaching liquor containing an alkaline non-oxidizing sodium compound throughout said bleaching treatment.

18. The multiple-stage process for bleaching chemical wood pulp, which comprises distributing throughout a mixture in which cellulosic fibres are distributed throughout a preponderating amount of water, a liquor

which contains an amount of a hypochlorite of an alkali-forming metal adapted to partially bleach the fibres and yield a residual liquor which contains dissolved organic matter, treating the fibres therewith so as to obtain such residual liquor, separating such a resulting liquor from the partially bleached fibres, subjecting the fibres to a bleaching treatment with an alkaline bleaching liquor supplied with an alkaline reagent that is adapted to maintain the liquor alkaline throughout the latter bleaching treatment, such treatment including heating the bleaching liquor and fibres to a moderate temperature but not in excess of 60 deg. C., and subsequently washing the bleached fibres.

19. The process according to claim 18, wherein the said alkaline bleaching liquor contains an alkaline non-oxidizing sodium compound throughout said bleaching treatment.

20. The multiple-stage process of bleaching chemical wood pulp, which comprises the following steps: (*a*) mixing the fibrous material and water sufficient to provide a thin or flowable pulp with a liquor containing a hypochlorite of an alkali-forming metal; (*b*) treating the mixture so as to react a partion of the colored organic material with bleaching material comprising a bleaching reagent supplied in step (*a*); (*c*) removing residual liquor from the partially-bleached fibrous material; (*d*) admixing with the partially-bleached fibrous material, bleaching liquor including an oxidizing bleaching agent, heating the mixture to a moderate temperature but not in excess of 60 deg. C. and treating the fibres so as to convert them into bleached chemical pulp; not more than a small to moderate amount of oxidizing bleaching agent being supplied to the fibrous material in step (*a*) and the amount of oxidizing bleaching agents applied to the fibrous materials in each of the steps (*a*) and (*d*) being materially less than that commonly used to conduct a bleaching of such wood pulp to the same degree when a single stage bleaching treatment is employed.

21. The multiple-stage process of bleaching chemical wood pulp, which comprises the following steps: (*a*) mixing the fibrous material and water sufficient to provide a thin or flowable pulp with a liquor containing a hypochlorite of an alkali-forming metal; (*b*) treating the mixture so as to react a portion of the colored organic material with bleaching material comprising a bleaching agent supplied in step (*a*); (*c*) subjecting the fibrous material and liquor to a thickening operation whereby to thicken the pulp and remove residual liquor from the partially-bleached fibrous material; (*d*) admixing with the partially-bleached fibrous material, bleaching liquor including an oxidizing bleaching agent, heating the mixture to a moderate temperature but not in excess of 60 deg. C. and treating the fibres so as to convert them into bleached chemical pulp.

22. The further improvement in claim 21, characterized by the mixture of fibres and water in step (*b*) containing at least as much as about 93 pounds of water for each 7 pounds of fibres.

23. The further improvement in claim 21, in which the total amount of available bleaching material supplied to the fibrous material is less than would be sufficient to convert the unbleached pulp into high white bleached chemical pulp in a single-stage bleaching treatment.

24. The further improvement in claim 20, in which the total amount of available bleaching material supplied to the fibrous material is less than would be sufficient to convert the unbleached pulp into high white bleached chemical pulp in a single-stage bleaching treatment.

25. The further improvement in claim 20, in which substantially the total amount of available bleaching material supplied to the fibrous material prior to step (*c*) is consumed in the bleaching treatment prior to step (*d*).

26. The further improvement in claim 21, in which the mixture treated in step (*b*) contains at least as much as about 93 pounds of water for each 7 pounds of fibres and substantially the total amount of available bleaching material supplied to the fibrous material prior to step (*c*) is consumed in the bleaching treatment prior to step (*d*).

27. The further improvement in claim 20, in which the liquor present in step (*d*) is an alkaline liquor that is maintained alkaline until the completion of step (*d*), the entire bleaching treatment is carried out at temperatures below 100 deg. C., and the bleached pulp is washed with water after the completion of step (*d*).

28. The further improvement in claim 21, in which the liquor present in step (*d*) is an alkaline liquor that is maintained alkaline until the completion of step (*d*), the entire bleaching treatment is carried out at temperatures below 100 deg. C., and the bleached pulp is washed with water after the completion of step (*d*).

29. The multiple-stage process of bleaching chemical wood pulp, which comprises the following steps: (*a*) mixing the fibrous material with a liquor containing an oxidizing bleaching agent; (*b*) treating the mixture so as to react a portion of the colored organic material with bleaching material comprising a bleaching reagent supplied in step (*a*); (*c*) removing residual liquor from the partially-bleached fibrous material; (*d*) admixing with the partially-bleached fibrous material bleaching liquor including an oxi-

dizing bleaching agent, and treating the fibres so as to convert them into bleached chemical pulp; a small to moderate amount of oxidizing bleaching agent being supplied to the fibrous material in step (*a*) and the amount of oxidizing bleaching agents applied to the fibrous material in each of the steps (*a*) and (*d*) being materially less than that commonly used to conduct a bleaching of such wood pulp to the same degree when a single stage bleaching treatment is employed; a mixture including fibrous material and available bleaching material in step (*d*) being heated to a moderate temperature but not in excess of 60 deg. C.

30. The multiple-stage process of bleaching chemical wood pulp, which comprises the following steps: (*a*) mixing the fibrous material with a liquor containing a hypochlorite of an alkali-forming metal; (*b*) treating the mixture so as to react a portion of the colored organic material with bleaching material comprising a bleaching agent supplied in step (*a*); (*c*) subjecting the fibrous material and liquor to a thickening operation whereby to thicken the pulp and remove residual liquor from the partially-bleached fibrous material; (*d*) admixing with the partially-bleached fibrous material bleaching liquor including an oxidizing bleaching agent, and treating the fibres so as to convert them into bleached chemical pulp; a mixture including fibrous material and available bleaching material in step (*d*) being heated to a moderate temperature but not in excess of 60 deg. C.

31. The process for treating chemical pulp from wood, which comprises the following steps: (*a*) subjecting the pulp to an oxidizing bleaching treatment by means of liquor that contains a hypochlorite of an alkali-forming metal; (*b*) subjecting the pulp to the action of an alkaline bleaching liquor that is maintained alkaline throughout this step and at temperatures not substantially exceeding its boiling point at atmospheric pressure, so as to solubilize some of the normally insoluble non-alpha cellulose organic constituents then present in the pulp; (*c*) removing from the pulp between steps (*a*) and (*b*) a liquor including dissolved matter; and (*d*) washing the bleached chemical pulp obtained as a result of prior steps of the process, the process being further characterized by the use of sodium hydroxide in the alkaline liquor mentioned in step (*b*).

32. As a new product, bleached chemical wood pulp which upon prolonged exposure to air substantially retains its whiteness, such new product being obtainable by a process comprising the following steps: (*a*) a digesting treatment of wood at temperatures above 100 deg. C., by means of digesting liquor the digesting treatment being continued until most but not all of the non-cellulosic organic constituents have been dissolved in the liquor, thereby obtaining unbleached chemical pulp; (*b*) washing the unbleached chemical pulp; (*c*) partially bleaching the unbleached chemical pulp by means of bleaching liquor containing a hypochlorite of an alkali-forming metal; (*d*) removing liquor containing bleach residues from the partially-bleached chemical pulp; (*e*) bleaching the partially-bleached chemical pulp by means of a non-acid bleaching liquor containing an oxidizing bleaching agent, the pulp in admixture with a preponderating amount of liquor being heated to a moderate temperature but not in excess of 60 deg. C. while the liquor contains an oxidizing bleaching agent; (*f*) washing the bleached chemical pulp until it has been substantially freed from compounds that are readily soluble in water.

33. As a new product, bleached chemical wood pulp as described in claim 32, such new product being obtainable by the process described in claim 32, a sulfite of an alkali metal being employed as a digestant in step (*a*) of that process.

34. As a new product, bleached chemical wood pulp as described in claim 32, characterized by an alpha-cellulose content of not less than 90%.

35. As a new product, bleached chemical wood pulp as described in claim 32, such new product being obtainable by the process described in claim 32, a sulfite being employed as a digestant in step (*a*) of that process the fibres of the pulp being subjected to an alkaline solubilizing treatment between steps (*a*) and (*f*) by means of an alkaline liquor supplied with a non-oxidizing alkaline sodium compound so as to render soluble some of the less-resistant organic matter then present with the fibres, and such liquor being maintained alkaline and at temperatures not substantially higher than its boiling point throughout such solubilizing treatment, and characterized further by an alpha-cellulose content of not less than 90%.

In testimony whereof we affix our signatures.

LINN BRADLEY.
EDWARD P. McKEEFE.