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METHOD OF IMPREGNATING AND LAMINATING FIBROUS MATERIALS WITH LIGNIN

William G. Van Beckum and Arnulf K. Esterer, Longview, Wash., assignors to Weyerhaeuser Timber Company, Longview, Wash., a corporation of Washington

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This invention relates to a method for impregnating fibers and fibrous products with lignin to thereby provide a strengthening and bonding agent for said products. The invention also includes the thermopressed products bonded and strengthened by such methods.

The advantages of lignin as a bonding and strengthening agent for fibrous materials are well known. Lignin is itself the natural binding agent used by nature for cellulosic fibers. Obviously, such lignin as it occurs in nature must be substantially insoluble in water, else the wood would disintegrate. Similarly, lignin free acids, isolated from raw wood without substantial degradation, are insoluble in water.

Among the sources for the water-insoluble lignin free acids for use in this invention may be sound wood from which the lignin is obtained by mild extraction methods using alkaline reagents, as disclosed in the invention of Clark C. Heritage and William G. Van Beckum for Lignin Products, application Serial No. 711,790, filed November 22, 1946, now abandoned, or in the invention by the same inventors for Processing of Lignocellulose Material, application Serial No. 33,278, filed June 16, 1948, now Patent No. 2,541,058; or the lignin for use in the invention may be certain naturally occurring raw materials of high lignin content, such as the cubical decay described and disclosed by Clark C. Heritage in application Serial No. 128,239, filed November 18, 1949, for Decayed Wood as a Binding Agent, in which the lignin content of the decay material may run as high as 70%; or such as the cork and parenchyma tissue components of Douglas fir bark and other coniferous tree barks which average from 60% to 65% lignin content.

The problem which presents itself in connection with the use of lignin as a bonding or strengthening agent for fibrous materials is how to bring about its intimate dispersion in the fiber. While some metal salts of lignin are water-soluble, they provide no answer to the problem; first, because they are not thermoplastic and, therefore, have no bonding and strengthening properties; and secondly, because, if heated to the point of decomposition, they leave an objectionable residue of a metal oxide or other compound. Water-insoluble salts of lignin would not be usable for the same reasons, even if a suitable solvent were provided.

Applicants have ingeniously discovered that the lignin may be introduced into the fiber or fibrous materials by use of the aqueous solution

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of the ammonium salts of the lignin acids. Upon evaporation and drying, the water of solution is removed, leaving the ammonium lignate. Upon further heating, as during the thermopressing operation, the ammonium lignate decomposes into ammonia and the water insoluble lignin free acid form, thereby providing an intimate dispersion of the lignin free acid in and on the fiber. Under heat and pressure, the fibers are caused to coalesce and bond together by means of the thermoplastc lignin in the free acid form.

It is, therefore, an object of the present invention to provide a method for the impregnation or saturation of fibers and fibrous materials with lignin acid. It is an ultimate object to provide thermopressed products prepared from fibrous materials impregnated with an intimate dispersion of lignin. It is an incidental object of the invention to provide a non-metallic aqueous solution of lignin. Other objects and advantages of the invention will appear through the specification.

In accordance with the invention, those lignins obtained from lignocellulose materials without substantial degradation, which form water soluble ammonium salts, may be introduced into fibrous materials such as wood fiber, cotton fiber, paper and fiber board, as the aqueous solution of the ammonium salt, which salt is then decomposed to the water-insoluble acid form under heat and pressure to produce various articles of manufacture possessing such properties as high strength, water resistance, and smooth, hard and pleasing surfaces. The products may, as in the application to paper, take the form of laminates, or bulk fiber may be employed to form articles of non-laminous construction. While the invention is illustrated herein as applied to cellulosic or lignocellulosic fibrous materials, it is to be understood that it is useful for any fibrous materials which may be bonded with lignin and which are compatible with an alkaline reagent.

The solution of lignin is prepared by dissolving the same in a selected alkaline solvent which may be evaporated, leaving a lignin salt which will decompose upon heating into a volatile constituent and the lignin free acid residue. An aqueous solution of ammonia is preferred, but quaternary ammonium compounds, such as the tetraalkyl ammonium hydroxides, and volatile amines, may also be employed. Application of heat provides more rapid solution. The lignin material should be in free acid form and be sub-

stantially pure, that is, relatively free of contamination by metal salts. If an appreciable quantity of insoluble matter remains after the treatment with ammonium hydroxide, it should preferably be filtered off. Although it is generally desired to prepare solutions of relatively high concentration, more dilute solutions may sometimes be of advantage, depending in part upon the conditions of treatment, method of impregnation, and upon the amount of lignin required for the particular fiber product. The quantity of lignin impregnated into the fiber is variable, depending upon the materials employed, the conditions of treatment, and the results desired. In general, the quantity of lignin in a mixture of lignin and fiber varies from about 10% to about 60%, based upon the dry weight of the mixture.

Impregnation of the fibrous material with the alkaline lignin solution is preferably brought about by immersing the fibrous materials in a bath of the saturant. However, other methods may be used such as spraying the fibrous material with the solution or pouring a quantity of the solution over the fibrous material. Length of time of immersion may be used to control the extent of penetration or the quantity of lignin to be introduced. The fibrous material may be either in the form of the raw divided fiber material, a preform, or a pressed product such as, by way of example, paper or a soft board of the insulating type, which is capable of absorbing the solution. The fibrous material may be unsized or sized to whatever degree best serves the purpose.

Other materials may be incorporated in the lignin solutions where variations in physical properties are desired. It has been found advantageous to add a small amount, e. g., not substantially more than about 10%, of diacetone alcohol to a solution of lignin in aqueous ammonia in order to enhance the flow properties of the lignin during hot pressing and to permit the use of lower pressures in the subsequent thermopressing operation. Ethylene glycol, glycerine and methyl Cellosolve have also been found to improve the flow of lignin and reduce the pressure required during the thermopressing operation. Such materials probably function as a plasticizer for the lignin, and any other plasticizer compatible with lignin may be effective.

Compounds containing active methylene groups, e. g., formaldehyde, hexamethylenetetramine, etc., may be added to improve strength properties and to decrease temperature and/or pressure conditions of the thermopressing operation. Resin-forming constituents such as phenols, urea and melamine, and an aldehyde, when incorporated in the saturants, provide for further strength, decreased temperature and pressure requirements, and also provide for thermosetting properties in the final pressed products. Like characteristics are provided by incorporating partially reacted thermosetting resins in the A and B stages. Such resins in quantity ranging from about 4% to about 20% by weight of the dry constituents have provided thermopressed products exhibiting remarkably high strengths and bright, smooth surfaces.

After the fiber has been impregnated with the desired material, the water of solution is driven off, either by drying in air or by the aid of heat. The fiber or fibrous article, as the case may be, is then subjected to heat and pressure in a mold. The conditions of the thermopressing operation are variable, depending upon the types of fiber and saturant and upon the results desired. Pressures ranging from about 200 to about 2000 pounds per square inch have been found very satisfactory with pressing temperatures of from about 250° F. to about 350° F. These conditions are not intended as limitations, however, for those skilled in the art will recognize that many combinations of pressure and temperature are available which may be practiced to suit the particular problem.

Illustrative of a typical application of the invention is the manufacture of a paper laminate. 300 grams of lignin free acid, insoluble in water, was suspended in 1500 ml. of water and stirred during slow addition of 100 grams concentrated ammonium hydroxide. Stirring was continued until a smooth solution was obtained. Then 166 grams of an aqueous phenol formaldehyde resin containing 60% resin solids (equal to 100 grams resin solids) was slowly added during stirring for an additional 15 minutes. Ten sheets of 130 pound ream weight paper were soaked in the solution as prepared for 16 hours, air dried for 4 hours, soaked again for 5 hours, then dried at 65% relative humidity at a temperature of 70° F. The sheets were found to have absorbed the lignin and resin to the extent that they contained 44% impregnated solids and 56% paper. The composition is, therefore, 5 parts paper, 3 parts lignin, and 1 part phenol formaldehyde resin. Nine of these sheets were pressed together at 200 pounds per square inch and 325° F. for 10 minutes, allowing for gas release after 1 minute of pressing, and then cooled in the press.

The laminated product thus prepared had a flexural strength of 15,090 pounds per square inch, tensile strength of 7,780 pounds per square inch, and an Izod impact strength of 0.79 foot-pounds per inch of notch.

A similar laminate prepared using one part alpha cellulose paper and one part lignin, with no phenol aldehyde resin present but pressed at a temperature of 325° F. and a pressure of 1200 pounds per square inch, had a flexural strength of 15,520 pounds per square inch and a tensile strength of 6,530 pounds per square inch. Other tests were made in which the percentage of lignin in the impregnated fiber varied from about 15% to about 60%; the percentage of cellulosic fiber varied from about 40% to about 70%; and the percentage of phenol-formaldehyde resin varied from 0% to around 15%. It will be understood that the percentage ranges for the constituents named are not critical, but may be varied extensively from the amounts specified, so long as the constituent is present in an amount sufficient to contribute its property or function to the combination. For instance, when only lignin and fiber are used, the percentages may be as low as 10% lignin and 90% fiber. Likewise, relatively small amounts of a thermosetting resin or other strengthening agent, or of a plasticizing material, may be added in combination, with the lignin and fiber being in the same ratio range as when used alone, or by substituting for a part of the fiber in the lignin-fiber ratio.

The highest strength values of any of the products tested was obtained from a laminated paper product using 4 parts of 130 pound ream weight paper, 1 part of lignin free acid, and 1 part of partially reacted phenol-formaldehyde resin. Its flexural and tensile strengths were 22,000 and 8,330 pounds per square inch, respectively. Another successful application of the invention is

in the making of canvas-base laminates. Still again, the invention has been practiced by spraying the surface of wood veneer with the solution of ammonium lignate and then preparing a laminate by hot bonding a lignin impregnated paper to the wood veneer. The surfaces in each case are attractive, smooth, hard and glossy.

Having thus described the invention and in what manner the same may be used, what is claimed is:

1. The method of making a fibrous product bonded with lignin which consists in preparing a solution of the ammonium salts of lignin acids by dissolving lignin in an aqueous solution of ammonia, subjecting a preform of the fibrous product to the wetting action of said solution of lignin, evaporating the water of solution leaving the ammonium salt of lignin intimately dispersed in situ in the fiber preform, and applying heat to decompose the ammonium salt of lignin into volatile ammonia and water insoluble lignin free acid, and applying pressure to coalesce the fibers and form a product having desired properties of flexural, tensile and impact strengths.

2. The method of impregnating fibrous material with a lignin free acid as a bonding agent, which consists of providing an aqueous solution comprising the ammonium salts of lignin acids, immersing the fibrous material in said solution, thereafter removing the water of solution, and applying heat to said fibrous material to drive off the ammonia, leaving a lignin free acid residue intimately dispersed in said fibrous material as a bonding agent, and applying pressure to coalesce the fibers and form a product having desired properties of flexural, tensile and impact strengths.

3. The method of impregnating fibrous material with a lignin free acid as a bonding agent, which consists essentially of preparing an aqueous solution of the ammonium salts of lignin acids, subjecting the fibrous material to the wetting action of said solution, evaporating the water of solution leaving the ammonium salt of lignin intimately dispersed in situ in said fibrous material, and applying heat to decompose the ammonium salt of lignin into volatile ammonia and the lignin residue, and applying pressure to cause the fibrous material to coalesce under the bonding action of the lignin residue.

4. The method of preparing a fibrous laminated product which consists essentially of preparing an aqueous solution of the ammonium salts of lignin acids, subjecting the separate fibrous laminae to the wetting action of said solution, evaporating the water of solution leaving the ammonium salt of lignin acid intimately dispersed in situ in said fibrous material, assembling said laminae in superimposed relation, and applying heat to decompose the ammonium salt of lignin into volatile ammonia and water insoluble lignin free acid, and applying pressure to cause the fibrous laminae to bond together.

5. The method of making a fibrous product bonded with lignin which consists essentially in coating and impregnating a fibrous material with substantially molecularly dispersed fusible lignin in the acid form by providing an aqueous solution of a thermally unstable salt of said fusible lignin acid and a volatile alkali-reacting substance capable of reacting with said lignin acid selected from the group consisting of an aqueous solution of ammonia and the quaternary ammonium compounds, namely, tetraalkyl ammonium hydroxides and volatile amines, subjecting said material to the wetting action of said solution, removing the solvent water to provide substantially molecular distribution of the thermally unstable salt of lignin acid on and in said material, and applying heat to the material simultaneously to decompose said salt and fuse the lignin residue as a bonding agent, and applying pressure to form a product under the bonding action of the lignin residue.

WILLIAM G. VAN BECKUM.
ARNULF K. ESTERER.

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