

UNITED STATES PATENT OFFICE

2,442,897

PROCESS FOR RESINIFYING LIGNO-CELLULOSIC MATERIALS WITH UREA-FORMALDEHYDE

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2 Claims. (Cl. 260—17.3)

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described and claimed, if patented, may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment to me of any royalty thereon.

This application is a division of my copending application for patent, Serial No. 462,191, filed October 15, 1942, which is in turn a division of my application for patent, Serial No. 383,798, filed March 17, 1941, upon which Patent No. 2,313,953 issued on March 16, 1943.

My invention relates to processes for plasticizing and resinifying wood and other ligno-cellulosic materials, and to products made from said materials.

For brevity and clarity whenever the word "wood" is used in this specification and the claims, it is understood that I include in its definition a ligno-cellulosic complex. It is further understood that such ligno-cellulosic materials may include the natural constituents of trees and plants in varying proportions. I have in mind particularly trees and plants of all kinds.

A principal object of my invention is to produce solid compressed wood of great density and strength.

A further object of my invention is to produce molded articles from comminuted wood.

A further object of my invention is to produce plywood and laminated compressed wood of great density and strength.

A further object of my invention is to produce wood which can be readily formed when hot and wet.

A further object of my invention is to produce wood which can be readily formed when hot and dry.

A further object of my invention is to produce a material which is thermosetting, which has very low hygroscopic properties; and which has permanence of size and shape.

Other objects of my invention include the production of molded articles from solid wood, from laminated wood, and from plywood.

My invention, in its various modifications, is based upon the facts that aqueous solutions of urea and thiourea, separately or in mixture, have

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a marked softening effect upon wood, and that urea and/or thiourea can be combined with various chemicals, such as the aldehydes, to form thermo-setting resins.

I am aware that urea and other chemicals have been used in the chemical seasoning of wood. However, the purposes, methods employed, and results secured are all entirely different from my invention. In chemical seasoning it is essential that only the surface layers of the wood to be dried be impregnated with the chemical, whereas in my invention the entire volume of the wood should be impregnated. In chemical seasoning, the vapor-pressure characteristics of the aqueous solutions of the chemical and the anti-shrink properties of the dry chemical within the wood are of paramount importance; whereas, in my invention the ability of the aqueous solution of the chemicals to soften the wood and the ability of said solution to condense and polymerize into a thermo-setting resin are most essential properties. In chemical seasoning it is desired to maintain the green size and form of the wood insofar as possible; whereas in my invention an important object is to modify the original form.

I have pointed out in Patent No. 2,298,017 that urea, NH_2CONH_2 , and thiourea, NH_2CSNH_2 , separately or in combination, have a marked softening effect upon wood at elevated temperatures, and that this effect may be applied to produce new and useful results. The discovered effects vary widely in intensity among the various ligneous and cellulosic materials of differing origins; therefore, successful application of my invention will depend in large measure upon the proper selection of materials, and successful utilization of any given material will likewise depend upon the proper selection of a suitable treating or conversion method. In general, the effects are most intense in the case of ligneous materials.

I have discovered that wood which has been treated and softened by soaking in an aqueous solution of urea and/or thiourea can be resinified and given superior new properties by soaking it, preferably before drying, in a water solution of furfuryl alcohol ($\text{C}_4\text{H}_7\text{OCH}_2\text{OH}$) or of an aldehyde, in the presence of a catalyst.

I have also discovered that it is possible to secure a preliminary softening and a final resinification of the wood by the use of a single aqueous

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treating solution consisting of urea and/or thiourea, together with an aldehyde and/or suitable other chemicals such, for instance, as furfuryl alcohol, in the presence of suitable buffers and catalysts.

Among the aldehydes which may be used are formaldehyde (HCHO), furfural (C₄H₃OCHO), and acetaldehyde (CH₃CHO). The ratio of aldehyde to urea and/or thiourea may range, on an atomic weight basis, from a maximum of 1 to 1 to a minimum of 1 to 10. If maximum water resistance be desired this ratio should not be larger than 1 to 1.5.

A solution composed only of urea and/or thiourea and an aldehyde in the presence of a suitable catalyst, but without a buffer, would be unsatisfactory for the purpose intended because it would start condensing and polymerizing too soon. Therefore, for most of the purposes contemplated in my invention a catalyst and a buffer must be added. Sometimes it is expedient to use an acid catalyst and sometimes an alkaline catalyst. There is an advantage in using sodium hydroxide and enough acetic acid to form sodium acetate with some free acetic acid because sodium acetate will buffer the dilute organic acid solutions at pH values between 5.5 and 6.0. To avoid using an excessive amount of hydroxide and acid, an additional buffer is required. The most efficient buffer I have discovered is borax. Some acid salts like sodium acid phosphate seem to act as a buffer as well as a catalyst. In this case the sodium acid phosphate in the presence of weak wood acids holds the pH to about 8.

For use with molding powders, I find that buffers are not always necessary since the time required for the entire process is comparatively brief.

Five typical solution formulae are here presented:

I

Urea	grams	790
Formaldehyde (37% solution)	do	714
Water	do	485
Sodium hydroxide	do	11
Borax	do	79
Glacial acetic acid	cc	18

II

Urea	grams	790
Formaldehyde (37% solution)	do	714
Water	do	485
Sodium hydroxide	do	11
Borax	do	79
Glacial acetic acid	cc	18
Ammonia (19% solution)	cc	250

III

Urea	Grams	790
Furfural		1,279
Water		8,000
Sodium hydroxide		240
Borax		800

IV

Urea	Grams	790
Formaldehyde (37% solution)		714
Water		485
Sodium acid phosphate		20

V

Urea	Grams	790
Water		790
Furfuryl alcohol		1,185
Phosphoric acid (85%)		47

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I have discovered and demonstrated that, to secure best results, the solution formula must be modified and adjusted to suit various species and various conditions of the process. Thus, woods like oak, containing comparatively large quantities of acid, require sparing use of acid in the solution. Further, if darkening of the wood be objectionable, ammonia may not be used with oak.

The buffered urea-aldehyde solution above defined and described has outstanding advantages over other unpolymerized or partially polymerized resins. It will remain unpolymerized, at room temperatures, for weeks. It will also remain unpolymerized for days at temperatures up to 220° F. It will not completely polymerize at temperatures much below 300° F. These properties make possible the successful manipulation of the wood through the various soaking, drying, forming and compressing operations herein described and claimed.

Through proper selection of the chemicals I have been able to produce a buffered urea-aldehyde solution which permits satisfactory performance of an operating schedule involving the following steps: (a) preliminary soaking of the wood in said solution, the soaking period, everything else being the same, is relatively short when green wood is used and much longer when dry wood is used; (b) heating and softening of the soaked wood; (c) deformation, molding, and/or compression of the heated soaked wood; and (d) final condensation and polymerizing of the chemicals in said wood and drying of the finished product.

I have also been able to secure satisfactory performance of an operating schedule involving the following steps: (a) preliminary soaking of the wood in a buffered urea-aldehyde solution for various periods, depending upon size, species, and moisture content of the material; (b) drying of the soaked impregnated wood; (c) deformation, molding, and/or compression of the dry impregnated wood at elevated temperature; and (d) final condensation and polymerization of the chemicals within said wood.

The preferred operating schedule, when using two separate chemical solutions, involves the following steps: (a) preliminary soaking of the wood in an aqueous solution of urea and/or thiourea; (b) heating the soaked wood; (c) deformation, molding, and/or compression of the hot soaked wood; (d) soaking said wood in an aqueous solution of an aldehyde plus a suitable catalyst; and (e) final drying of the finished product.

It is not possible, in the present state of the art, to state with complete certainty exactly what chemical reactions take place and what physical phenomena manifest themselves in the practice of my invention but it appears now that most of the results secured support the hypothesis that the principal effective action during the preliminary soaking and heating periods is one of softening. However, it is probable, especially in the case of certain species, such as oak for instance, which contain unusually large percentages of materials which are neither cellulosic nor ligneous, that a certain amount of condensation and resinification does take place between the wood and the chemicals in the solution.

During the final resinifying steps in the various modifications of my process, the urea and/or thiourea condenses with the aldehyde and polymerizes to form a urea-aldehyde resin. In my

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process, the various chemicals in the solutions enter into the fine microscopic structure of the wood cells, with the end result that the resins which are formed completely permeate the wood structure and do not simply form a superficial coating as in various other processes in the prior art. This complete permeation practically eliminates swelling and shrinkage with changes in the humidity of the ambient atmosphere.

In previous experimental work I discovered that green wood may be readily impregnated with urea and/or thiourea by immersion in an aqueous solution of said chemicals. The action is principally one of diffusion and it goes forward at atmospheric temperature and pressure. It may be hastened by the use of elevated temperature, but increased pressure has only a very small accelerating effect. Dry wood can also be impregnated in this manner, but the process is much slower than with green wood. I now find that wood may be impregnated with a buffered urea-aldehyde solution quite as easily as with urea and/or thiourea alone. Other methods of impregnation may also be used in the practice of my invention.

It is recognized that certain properties of the finished products, such as hygroscopicity, fire-resistance, decay-resistance, resistance to insect attack, and weather-resistance, may be modified by the addition of various well-known chemicals—principally water-soluble chemicals—to the aqueous treating solutions. My invention contemplates the use of such chemicals added to the buffered urea-aldehyde solution.

If wood be impregnated with buffered urea-aldehyde solution and then heated, it becomes very soft and flexible, so that it may be easily bent, twisted, molded, compressed, or otherwise formed or deformed.

Subsequent drying and final heating to a temperature higher than that of the preliminary heating remove excess moisture and cause final polymerization of the resin-forming chemicals.

Likewise, wood impregnated in accordance with my invention and then dried and heated becomes quite soft and flexible, so that it may be formed or deformed, but to a lesser degree than when hot and wet.

The buffered urea-aldehyde has an advantage over other thermo-setting resin-forming chemical combinations in that it remains thermoplastic for a long time in the range of temperatures normally employed in kiln drying; and it does not become thoroughly cured until exposed to a temperature of about 300° F.

Final heating to a temperature higher than that of the preliminary heating causes final polymerization to take place.

I have discovered that wood which has been impregnated with a buffered urea-aldehyde solution possesses such a high degree of adhesiveness after proper polymerization that, under suitable conditions, sheets can be laminated and comminuted material molded without the addition of any adhesive.

My invention contemplates a method of treating, bending or otherwise forming, and resinifying wood which consists essentially of the following steps: impregnate the wood with a buffered urea-aldehyde solution; heat said wood to a temperature of about 212° F. to 220° F.; bend or otherwise form said wood; dry said wood; heat said wood to a temperature of about 300° F.

My invention also contemplates a method of treating and resinifying wood which consists es-

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entially of the following steps: impregnate said wood with a buffered urea-aldehyde solution; dry said wood; heat said wood to a temperature of about 300° F.

My invention also contemplates a method of treating, bending or otherwise forming, and resinifying wood which consists essentially of the following steps: impregnate the wood with a buffered urea-aldehyde solution; dry said wood; heat said wood to a temperature of about 212° F. to 220° F.; bend or otherwise form said wood; heat said wood to a temperature of about 300° F.

My invention also contemplates a method of treating, densifying, and resinifying wood which consists essentially of the following steps: impregnate said wood with a buffered urea-aldehyde solution; compress said wood in a suitable press; dry said compressed wood under pressure; heat said wood under pressure to a temperature of about 300° F.; release the pressure after polymerization has been completed.

My invention also contemplates a method of treating, molding, and resinifying comminuted wood which consists essentially of the following steps: impregnate said wood with a buffered urea-aldehyde solution; dry said wood at room temperature; place said wood into a suitable mold and apply pressure in a suitable press; heat said wood under pressure to a temperature of about 300° F.; release the pressure after polymerization has been completed.

My invention also contemplates a method of treating, laminating, compressing and/or molding, and resinifying sheets of wood which consists essentially of the following steps: impregnate said sheets of wood with a buffered urea-aldehyde solution; dry said sheets at room temperature; lay up the desired number of sheets one on top of another with the grain of adjacent plies oriented in the desired manner, and place the stack of sheets in a suitable press or mold; apply enough pressure to said stack to secure the desired degree of compression and/or molding, and simultaneously heat said stack under pressure to a temperature of about 300° F.; release the pressure after polymerization has been completed.

Specific illustrations of how my present invention may be practiced follow:

To produce a boat rib:

Soak a stick of green white oak heartwood, one inch square and 30 inches long, for a period of 10 days, at room temperature, in a buffered urea-aldehyde solution prepared as follows:

Mix together and heat to 150° F.

Water	grams	485
Borax	do	79
Urea	do	790
Sodium hydroxide	do	11
Glacial acetic acid	cc	11

Cool to room temperature. When cool add 714 grams of 37 percent formaldehyde solution.

After the soaking period, heat the stick to a temperature of from 212° F. to 220° F. This may be done conveniently by immersing said stick in a bath of boiling urea solution. Maintain said stick at this temperature for half an hour.

Remove said stick from the bath, immediately bend said stick over a previously prepared form, and clamp said stick in place on the form. In performing this operation, practices customary in ordinary steam bending may be followed.

Allow the bent rib to dry on the form. Heat said bent rib, while still on the form, to a tem-

perature of about 300° F. and maintain said temperature for an hour. This completes the process and said bent and resinified rib may be removed from the form and immediately used as soon as it is cool enough to handle.

To produce a light boat rib:

Soak a stick of green white oak heartwood ½ inch by ¾ inch in cross section and 30 inches long, for a period of five days, at room temperature, in a buffered urea-aldehyde solution. After the soaking period, dry said stick at a temperature of about 140° F. Then heat said stick to a temperature of about 212° F. Then bend said stick, while hot, over a previously prepared form and clamp said stick in place on the form. In performing this operation, practices customary in ordinary steam bending may be followed. Then heat the bent rib, while still on the form, to a temperature of about 300° F. and maintain said temperature for 40 minutes. This completes the process and said bent and resinified rib may be removed from the form and immediately used as soon as it is cool enough to handle.

To resinify a bearing block:

Soak a board of green white oak heartwood 12 inches square and one inch thick, for a period of 10 days, at room temperature, in an aqueous solution prepared as above specified.

Remove said board from said solution and allow said board to dry.

After said board has dried to a moisture content of about 10 percent, heat said board to a temperature of about 300° F. and maintain said temperature for an hour. This completes the process and the resinified board may be cooled and used immediately.

To resinify and compress a die block:

Soak a board of green white oak heartwood 12 inches square and 2 inches thick, for a period of 20 days, at room temperature, in an aqueous solution as above specified.

Remove said board from said solution and heat said board to a temperature of from 212° F. to 220° F. by immersing said board in a bath of boiling urea solution. Maintain said board at said temperature for an hour.

Remove said board from said urea solution, place said board in a suitable press and apply sufficient pressure to reduce the thickness of said board to 1¼ inches.

Dry said board under pressure.

When dry, raise the temperature of said board to about 300° F. and maintain said temperature for one hour.

Release the pressure and remove said board.

To mold an ash tray:

Soak a suitable quantity of fine green oak sawdust for a period of 15 minutes, at room temperature, in an aqueous solution prepared as above specified.

Remove said sawdust from said solution and dry said sawdust at room temperature.

When dry fill the ash tray mold with said sawdust; place said filled mold in a hot plate press and apply a pressure of 1000 pounds per square inch of mold area to said mold.

5 Raise the temperature of said mold to 300° F. and maintain said pressure and said temperature for a period of 30 minutes.

Release said pressure, open said mold and remove said molded ash tray.

10 To make a compressed plywood plate:

Soak 13 pieces of ⅛-inch green white oak veneer 12 inches square for a period of 5 hours, at room temperature, in an aqueous solution prepared as above specified.

15 Remove said veneer from said solution and dry at room temperature.

Arrange said dry veneer in a stack, with the grain of adjacent plies at right angles.

20 Place said stack in a hot plate press and apply a pressure of 2000 pounds per square inch of surface area of said stack.

Raise the temperature of said stack to 300° F. and maintain said temperature for a period of one hour.

25 Open said press and remove said plate.

Having thus described my invention, I claim:

1. A process for producing molded articles of resinified densified wood comprising soaking comminuted wood in a substantially unreacted aqueous formaldehyde urea solution containing an excess of urea, on an atomic weight basis, the solution containing suitable buffers to maintain the pH at about 8; removing the powder from the solution; drying the powder; and heating the dry powder under pressure at a temperature of about 300° F. until substantially complete resinification is effected.

2. A process for making a molding powder comprising soaking comminuted wood in a substantially unreacted aqueous formaldehyde urea solution containing an excess of urea on an atomic weight basis, the solution containing suitable buffers to maintain the pH at about 8, then removing the soaked wood and drying it.

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

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