Patented Jan. 9, 1940

2,186,369

UNITED STATES PATENT OFFICE

2,186,369

ADHESIVE

Theodore Williams Dike, Seattle, Wash., assignor to I. F. Laucks, Inc., Seattle, Wash., a corporation of Washington

No Drawing. Application February 6, 1935, Serial No. 5,275

4 Claims. (Cl. 260—30)

The present invention relates to wet glues made by dispersing dry, potentially reactive, thermo-setting phenolic resins in an aqueous medium. The invention also embraces a process of making plywood or laminated structures with this glue.

The remarkable adhesive properties, water resistance, strength, durability, and chemical inertness of phenolic resins, which are insoluble in water, have long been regarded as presenting an ideal glue-base. In spite of a relatively high material cost many attempts have consequently been made to develop phenolic resin glues, but while a certain success has been obtained no existing method has been sufficiently simple and satisfactory for general use.

In the common method of gluing laminated materials, such as plywood, insulating board, etc., a dry powder adhesive base (generally either of proteinous or starchy matter) is used which is readily dispersible to provide a smooth flowing, moderately viscous solution which can be spread by the ordinary roll type glue spreaders. For various reasons a phenolic resin glue having these properties has not been available and a number of roundabout methods of use have been tried in place of this simple, direct one. For instance sheets of tissue paper have been coated with resin to form a film glue, dry resin powder has been spread on the plies by special spreading equipment providing both a uniform distribution of the powder and means for preventing its being displaced, or the dry resin powder has been suspended in an aqueous non-solvent or gum and the wet glue, including of course a large amount of water, shipped to the user for spreading.

While most of these methods have desirable features an ordinary aqueous phenolic resin glue has been much desired, both because of its convenience and flexibility, as well as on account of inherent limitations characterizing the other methods.

For instance the film method requires an inert carrier in the paper and does not work equally well under all conditions, nor does it permit either the spread or kind of resin to be varied at will. It is also very slow acting. The dry powder method, while more flexible, requires special equipment, making it less suitable for small and intermittent production. The colloid suspension method presents serious spreading difficulties due to tendency of the suspended powder to go out of suspension before being properly distributed on the surfaces, together with the excessive transportation cost of shipping the water along with the glue to the user.

The main reason for the unavailability heretofore of a dry powder base wet phenolic resin glue is the complete insolubility of phenolic resin powders in water. For instance the colloid suspension method previously referred to, specifies an "aqueous non-solvent medium" as its essential feature. The present invention reverses this plan and depends for its success upon an aqueous solvent medium. The former method requires both special machinery and skill to prepare a stable colloidal suspension in a non-solvent aqueous medium and also the water has to be added by the glue manufacturer and shipped at great expense along with the active resin to the plant where the glue is to be used. In direct contrast to this the present method involves only simple mixing with ordinary equipment so that the user of the glue is enabled to purchase a dry powder, water-insoluble phenolic resin which, by my improved method, may be made into a spreadable glue by adding the aqueous solutions and mixing according to directions.

To the accomplishment of the foregoing and related ends, the invention, then comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

Thermo-setting phenolic resins in their initial stages when not polymerized too near the final state can be dispersed in strong solutions of the alkali metal hydroxides such as caustic soda, caustic potash and the like, and if still less polymerized will then disperse in weaker solutions. These strong alkalies are also powerful hardening agents, promoting quick setting when reactive phenolic resins of neutral or alkaline type are heated in their presence.

I find that these facts can be applied in such a manner as to provide excellent phenolic wet glues so that suitable dry powdered resins can be shipped economically to the user's plant and readily made into spreadable wet glues by a simple procedure using ordinary mixing equipment.

Suitable phenolic resins are those of the quick-setting type that are not polymerized beyond the state for instance where they are soluble in a 20% hot solution of caustic soda. Still more suitable are resins somewhat less advanced

so as to be soluble in a cold 10% solution of caustic soda or its equivalent. Acid resins may also be used with the disadvantage of excess caustic being required to neutralize the acidity before dispersion is possible.

The resins should preferably be ground neither too fine nor too coarse. A particle size of minus 40 plus 80 mesh avoids lumping due to excessive fineness and slow solution due to too large particles.

In one example of producing a dispersion of good spreadability the water requirement is approximately 2 parts by weight of water to 1 part of powdered resin. The mixing and dispersing at first appears impossible but is readily accomplished if the right method is used. About two-thirds of the water should be placed in a mixer provided with a power stirring device and then the powdered resin added and mixed with the water for a few seconds till all the resin is wet and uniformly suspended in the water. The caustic soda, or potash, should be dissolved in the remainder of the water and added gradually with continued stirring. The addition should be extended over a period of about fifteen minutes to avoid lumps. The resin gradually disperses and forms a smooth, very viscous, but free flowing, glue. Solution may be accelerated by using hot water. If desired water soluble polymerization accelerators such as hexamethylenetetramine may be added.

The glue is then spread in the usual way upon the core plies with a roller spreader and the resin coated cores passed through a drying chamber to remove the water and leave a dry reactive coating on their surfaces. A temperature of 130° F. with a strong circulation will dry the cores rapidly. Higher temperatures are to be avoided because of danger of converting the resin. Where fairly thick, dry veneer is used drying may be dispensed with entirely, a short period of time being allowed to permit the water of the glue to penetrate the wood and distribute itself more evenly.

The cores may be assembled with the face plies and pressed at once as soon as they are dry or after an interval up to several days. The conversion of the resin in the hot press will be found to be much quicker than if the same resin is used as a glue by other methods, also the bond is more deep-seated and the grip on the wood better.

It will be found that the caustic soda has served a triple function, all three features of which contribute materially to the excellent result obtained. In the first place the caustic is the dispersing or dissolving agent for the resin which is insoluble in water alone. Second, the caustic creates a strong alkalinity which reacts with the wood so that a better and deeper seated bond is obtained, probably due to the better wetting action of the adhesive on the strongly alkaline, swollen, and partly dispersed wood fibers adjacent to the glue line. Very probably also the catalytic action of the strong alkali causes considerable condensation to take place between the resin and the alkali modified surface fibers of the wood when the assembly is hot pressed. This effect is due both to the caustic and to the method of applying the resin in dissolved state. In the third place the caustic greatly accelerates the polymerization and conversion of the resin in the press. The time in the press is much shorter than with a film glue.

The amount of caustic required is variable over a considerable range at the will of the operative according to the character of the resin used as to its solubility in caustic potash or soda and as to its natural speed of set and ability to respond to the accelerating action of the caustic.

The concentration of alkali can be varied upward from the minimum requirement to produce a good dispersion, so as to further accelerate the setting of the resin. Ordinarily a 5 to 10% solution of caustic soda is desirable. Mixtures of calcium hydrate with salts such as tri-sodium phosphate, borax, sodium carbonate, which produce caustic soda by double decomposition in water solution, may be used.

This method also permits the use of phenolic resins as adhesives which are slow setting for use by other methods, and avoids the necessity of manufacturing extremely hard, highly polymerized resins such as are necessary under other conditions. By the term phenolic resins I include resins made with phenols, cresols and the like, and formaldehyde, paraformaldehyde, furfural, acetaldehyde, etc.

By another method water-insoluble phenolic resins may be dispersed in aqueous solutions, dried by spray drying or other suitable means, and stored for use. At time of use they may be redispersed in water solution to form a spreadable phenolic resin adhesive.

Mixtures of proteinous and other adhesives dispersible in an alkaline medium may also be used and likewise the phenolic powder may be dispersed in other glues of suitable alkalinity. In this way the adhesive properties of lower cost hot press glues may be improved or the present phenolic glues may be lowered in cost of preparation and use.

This method of gluing with phenolic glues has the advantage that the kind and type of phenolic resin used may be varied, also the amount of spread, the use of special equipment for spreading is avoided, small lots of resin bonded plywood may be made at will, and the excessive burdens of water transportation and container cost as well as the spreading troubles of the colloid method are all avoided. Thus in a simple manner the advantages of dry powder base wet glues are for the first time made available to supply the growing demand for plywood bonded with phenolic resisn and, owing to the peculiar features of the method, a bond of exceptional quality is obtained having high resistance to cold water and to boiling water and high weather resistance.

I use the words dispersing or dispersion as being practically synonymous with dissolving or solution.

I regard the product which I make by dissolving the resin in the caustic soda solution for example as being in the nature of a true solution. It is quite different in its properties from what should truly be called a suspension of resin, which suspension is made for example by mixing resin in water by the use of protective colloids. These protective colloids act to keep the insoluble resin particles in a state of stable suspension, the resin particles being not dissolved but present as discrete resin particles. The same would be true of an emulsion, providing a water-insoluble, liquid phenolic resin was dispersed in an aqueous medium and kept in emulsion by means of a protective colloid. It is well known that neither suspensions nor emulsions will penetrate into the structure of wood, since the discrete colloidal particles cannot penetrate the cell walls. One disadvantage of this type of glue is that insufficient penetration is effected into the wood, thus making a superficial bond which does not get a

firm grasp on the wood surfaces. On the other hand my true solution has much better penetration and thus makes a better type of bond.

Other modes of applying the principle of the invention may be employed instead of those herein explained, change being as regards the details disclosed, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:

1. The process of making a spreadable adhesive which consists of suspending in water a partially polymerized phenol resin in a powdered form finer than forty mesh and coarser than eighty mesh, said resin being polymerized to a state where it is soluble in a cold 10% solution of caustic soda and not beyond a state where it is soluble in a hot 20% solution of caustic soda, and adding a solution of an alkali metal hydroxide of sufficient concentration to dissolve the previously water insoluble resin whereby an adhesive is formed of the dissolved resin which is capable of being polymerized by heat and pressure and which reacts with wood to form a deep seated bond.

2. The process of making a spreadable adhesive which consists of suspending in water a partially polymerized phenol resin in a powdered form finer than forty mesh and coarser than eighty mesh, said resin being polymerized to a state where it is soluble in a cold 10% solution of caustic soda and not beyond a state where it is soluble in a hot 20% solution of caustic soda, and adding a proteinous containing solution of an alkali metal hydroxide of sufficient concentration to dissolve the previously water insoluble resin, whereby an adhesive is formed of the dissolved resin which is capable of being polymerized by heat and pressure and which reacts with wood to form a deep seated bond.

3. The process of making a spreadable adhesive which consists of suspending in water a partially polymerized phenol resin in a powdered form finer than forty mesh and coarser than eighty mesh, said resin being polymerized to a state where it is soluble in a cold 10% solution of caustic soda and not beyond a state where it is soluble in a hot 20% solution of caustic soda, and adding a 5 to 10% solution of caustic soda to dissolve the previously water insoluble resin, whereby an adhesive is formed of the dissolved resin which is capable of being polymerized by heat and pressure and which reacts with wood to form a deep seated bond.

4. A spreadable adhesive formed by the process of claim 1, and consisting of a phenol resin in solution which is capable of being polymerized by heat and pressure and which will react with wood to form a deep seated bond.

THEODORE WILLIAMS DIKE.