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BLOOD GLUE

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This invention relates to a blood glue and, more particularly, to a process for insolubilizing animal blood to make a glue base, a blood glue base made from said process, and the resulting glue product.

Animal blood is known to have adhesive properties desirable for gluing wood materials as, for example, the laminations in plywood. Animal blood is coagulable by heating, the degree of coagulation being the result of a time-temperature relationship. Whole blood normally contains about 21% blood solids which comprise fibron and salts and a mixture of proteins primarily hemoglobin, globulin and albumen. In whole blood the solids are divided as follows: Approximately 14% hemoglobin, 3% globulin, 3% is albumen and 1% fibrin and salts. Heat coagulation of the protein constituents of blood takes place above about 120° F. up to the boiling point of the blood solution.

In general it can be stated that coagulation results more rapidly at higher temperatures than at low temperatures. Diluted solutions of whole blood, i.e., solutions having less than about 21% blood solids, coagulate at a different rate than in the case with whole blood. Coagulation is evidenced by the blood liquid becoming progressively thicker until the material gels to a semi-solid or solid state. During coagulation the blood solids in the solution become progressively less soluble in the water to such an extent that protracted heating of whole blood, at coagulation temperatures, results in the blood solids becoming totally insoluble in water. The degree or extent to which blood has been coagulated can be shown or determined by measuring the solubility of the coagulum in various solvents.

It has been found that the denaturation of blood by heat coagulation provides a satisfactory glue base so long as it is carried on only to such an extent that the blood material retains substantial dispersibility in cold, dilute, aqueous alkali metal hydroxide solutions, for example sodium hydroxide solution at temperatures less than about 100° F. No standard tests are known to us for measuring the dispersibility of a blood glue base in alkali. However, substantial dispersibility or solubility of blood material in aqueous alkaline medium, as defined herein, is obtained when the blood passes the following test procedure. In accordance with this test, a sample containing 10 grams of coagulated blood is placed in 100 cc. of 0.2% sodium hydroxide solution having a temperature of from 60° F. to 80° F. The resulting mixture is stirred for one hour and thereafter permitted to stand for 15 hours. At the end of this time, the mixture is again stirred and is then filtered. For the present purposes at least 1% of the blood should be determined to be dispersed or dissolved in the filtrate.

The viscosity of coagulated blood varies in direct proportion to the extent or degree to which the blood has been coagulated, or conversely to the degree to which the solubility of the protein constituent has been reduced. Diluted blood solutions will evidence lower viscosity after coagulation than viscosities attained with coagulated whole blood, even though the degree of coagulation or the reduction in solubility is the same in both instances.

For the purposes of this invention we employ the word "coagulum" as meaning a blood solution in which there has been a reduction in the solubility of the protein constituents by heating.

This invention is concerned with the partial coagulation of an aqueous blood solution at a blood solids content normal for whole animal blood or reduced therebelow, to produce a blood coagulum. This processing is followed by drying the coagulum as in a spray dryer while applying controlled heat to blood particles suspended in the drier atmosphere, for the purposes of further insolubilizing the blood protein while simultaneously forming a dried blood powder. This dried powder may be further insolubilized by additional heating as in an oven. The end product is a blood glue base powder having little or no solubility in aqueous medium at room temperatures, but having substantial solubility in dilute aqueous alkaline medium.

This invention is also concerned with the treatment of the insolubilized dried blood powder with alkaline conditioning chemicals in cold water dispersions to form a glue mix. The invention is additionally concerned with the provision of desirable adhesive properties in such a glue mix through the treatment of the same with synthetic thermosetting phenolic resin to provide an alternative form of glue mix.

The more important objects of this invention are to provide a simple and practical method for processing blood for glue base purposes using conventional equipment; a blood base glue which is readily adaptable for storage in dry form and has a long storage life; a glue base adaptable to compounding by methods capable of being practiced simply and directly in a plywood mill; a blood glue mix having superior spreading properties over a wide range of viscosities and which is characterized by having fine consistency, not being curdy or grainy, and which is suitable for use at relatively low spreading rates in conventional glue spreaders; and a blood glue having desirable water resistance characteristics.

Other objects include providing a blood glue mix having desirable time-viscosity characteristics; a low gelation tendency upon standing; useful with synthetic thermosetting resins; and capable of forming bonds in laminated panels having high water resistance when either cold or hot pressed.

In general this invention comprises a process of making a glue base comprising heating an aqueous blood solution, having a blood solids content based on the weight of the solution between about 10% and that which is normal for whole animal blood. The heating is conducted at temperatures between about 120° F. and the boiling point of the solution, for a time in the range between about 10 and 20 minutes and preferably between about 15 and 20 minutes, while agitating and stirring the heated mass to maintain the blood particles in finely divided condition and dispersed throughout the fluid medium. Concentrated blood solutions up to 35% blood solids may be converted into coagulum as described in which case heating at lower temperatures or for shorter times is desirable. When the blood protein has been coagulated to a desired degree, the resultant liquid blood coagulum may be cooled to below about 120° F. to arrest coagulation. The coagulum, whether cool or not, is thereafter delivered to a spray dryer and reduced to particle form, that is to a powder having a low moisture content and low solubility. In accordance with this invention the spray drying operation is conducted at elevated temperatures of about 300°–600° F., above those normal for the operation of such apparatus. Air inlet temperatures between about 350° and about 450° F. may be used but a better control of insolubilization is obtained by controlling the outlet temperatures since these are determined by the effect of evaporation which takes place in the dryer chamber. Preferably the outlet temperature of the air from the spray dryer chamber is maintained between about 180° F. and 290° F., under which circumstances the

insolubilized blood powder of this invention is produced from coagulum previously produced.

The preferable starting material of this invention is fresh whole or defibrinated blood. The blood solids to liquid ratio, on a weight basis, may be between 1 part blood solids to 5 parts liquid, and 1 part blood solids to 10 parts liquid. Dilution of animal blood normally occurs on the killing floor in slaughter houses due to the wash water used during slaughtering to cleanse the carcass and to flush the floor. Under such circumstances killing floor blood will normally have a solids content between about 12% and 15%. The blood solids content, if it be desirable, may be adjusted downwards simply by the addition of water. On occasion it has been found desirable to adjust the solids to water ratio upward. This may be accomplished in different ways as, for example, by employing vacuum concentration to remove water or by fortifying the animal blood by the addition of soluble blood powder, or by the addition of a reconstituted soluble dried blood powder in water having a high solids to water ratio, the same being added to the fresh blood to produce a desirable blood-water-to-solids relation.

In the case of fresh blood as a starting material it is usually necessary and desirable to remove the fibrin and to reduce the naturally formed clots to a fluent condition, as by thoroughly beating or whipping the blood material in a vessel.

Heat coagulation of a blood solution may be carried on in various ways. For example, heating may be performed in a jacketed vessel wherein hot water or steam is supplied to the jacket to raise the temperature of the blood material. Or it may be carried out in a chamber equipped to discharge and intermingle steam directly into the blood solution. In the latter case consideration would normally be given to the diluting effect of the steam condensate on the blood solution. Other conventional heating methods will occur to those skilled in the art.

Details of this invention are set forth in the following examples.

Example I

Blood was taken directly from the killing room floor and transferred to a perforated basket strainer. A mixer comprising propeller on a shaft was used to stir and agitate the blood while in the basket. The mixer, operating at about 1800 r.p.m., broke up the blood clots and defibrinated the blood so as to transform it into a watery, thin, fluid state. The perforated basket strainer removed hair, bits of bone, and other extraneous material from this blood. Upon leaving the strainer this blood was passed to a perforated basket centrifuge where still other foreign material and separable non-blood solids were removed. The blood was then passed to a holding tank. At this time the blood solids content was about 21% based on the total weight of the blood material normal for blood, reduced by the incorporation of some wash water normally used at the killing floor. A small amount of pine oil was added as an anti-foamer agent and preservative.

This cleaned blood material was pumped from the holding tank to a jacket insulated coagulator tank, care being taken to prevent the addition of water so as not to reduce the blood solids content. The material in the coagulator tank was subjected to agitation by immersed propeller blades on the shaft of a 1½ H.P. motor operating at 1800 r.p.m. A 10 H.P. centrifugal pump, connected to the bottom of the coagulator tank, operated to withdraw blood material from the tank bottom and to return it to the coagulator tank at its upper axis through several nozzles in a radial fashion. When adequate circulation was established, steam was supplied to the casing of the centrifugal pump and injected directly into the stream of blood moving through the pump chamber and back to the coagulator tank.

As the operation continued the temperature rose in the blood material until it reached approximately 152° F. This required approximately 18 minutes and produced a liquid blood coagulum of deep red color. The steam supply was thereupon discontinued but agitation in the coagulator tank was maintained to disperse the coagulated blood particles throughout the liquid medium. Under these conditions the liquid coagulum was then passed to a heat exchanger unit adapted to cool the coagulum approximately to room temperautre, about 70° F. Thereafter, the cooled blood coagulum was drawn off into a storage vessel and a small amount of pine oil was added to retard putrefaction. This blood coagulum was a very thin slurry and had a consistency approximately that of coffee cream.

Its blood solids content was slightly reduced by steam condensate produced during heating. As a result of the heating of the blood in the liquid state under the conditions described the coagulum comprised protein which was coagulated and protein which was not coagulated. The coagulated protein was evidenced by the presence of particles in the slurry. The remainder of the slurry comprised uncoagulated protein (about half of the total of the blood solids) in aqueous medium with the coagulated particles (about 50% of the total protein blood solids) dispersed therein. Upon standing and without agitation the larger particles settled out of the medium. This coagulum was temperature sensitive to a greater degree than, for example, spray dried soluble blood particles. Its blood solids content was about 16.7%.

The foregoing described coagulum was next treated in a solid basket centrifuge to remove foreign matter which appeared to be grain hulls and hair, and the cleaned coagulum was then pumped to an evaporator. By maintaining in the evaporator a shell temperature between 165° F. and 185° F. the material was concentrated to a solids content of between 19.53 and 24.4%. While it had an increased viscosity it flowed readily from the evaporator pump. It was deep red in color and its temperature during evaporation never exceeded 120° F.

The concentrated coagulum was then delivered to an 0.035-inch disc atomizer rotor of a spray drier. The rotor was axially located in the dryer chamber and revolved at 15,000 r.p.m. It comprised a disc having a peripheral upstanding slotted or perforated wall capable of receiving the concentrated coagulum and passing it outward in the form of droplets or discrete particles.

Hot air was supplied to the dryer chamber during atomization at approximately 420° F. inlet temperature. The heat transfer of the moisture in the droplets or discrete particles took place and spray dried particles of insolubilized blood in powder form were collected and removed from the lower portion of the dryer chamber. The air outlet temperature was about 200° F. during the operation.

Example II

A glue mix was compounded as outlined in the following procedure:

	Parts by weight
H_2O (at 70° F.)	260
Insolubilized blood powder, mixed thoroughly	110
Filler,[1] mixed thoroughly	27
H_2O (at 70° F.), mixed thoroughly	500
Lime (9 parts) in H_2O (18 parts), mixed thoroughly	27
Sodium silicate, mixed thoroughly	45

[1] The filler employed was a finely ground residue from the processing of corncobs and other agricultural materials to produce furfuraldehyde. The cobs are first pressure cooked with steam and dilute acid. Following removal of the furfuraldehyde therefrom, the residue is dried, ground, and marketed as a common adhesive filler for the plywood industry.

The glue mix, as described in this example, was based on insolubilized blood powder according to Example I and when completed had a viscosity of approximately 400

c.p.s. and was in a condition to readily film on standard glue spreading apparatus for transfer to plywood veneer cores.

Plywood was prepared from the foregoing glue mix, the same being spread on the veneer core at the rate of 80 lbs. of glue per 1000 sq. ft. of double glue line. The core veneers with the glue film thereon was interposed between face and back panels into a plywood assembly. The assembly was pressed for approximately 3½ minutes at a pressure of approximately 250 lbs. per square inch in a hot press in which the platens were maintained at a temperature of about 240+ F. Test specimens derived from such plywood was subjected both to a wet soak shear test and a dry shear test, according to standard procedures, in which tests it was established that the glue was adequate to meet recognized commercial standards for interior grade plywood glues.

Example III

Liquid blood having a blood-solids content of about 17.35% was heated from approximately room temperature to a temperature of about 152° F. in about 18 minutes preparatory to spray drying the same to a powder. The liquid blood coagulum was then concentrated to a solids content of about 19.53%. This coagulum was then delivered to a spray dryer in which the inlet temperature of the air to the spray dryer was varied from approximately 320° F. to 425° F. and the exit temperature of the air from the spray dryer was maintained at approximately 220° F.

Blood powder insolubilized in the manner just described was compounded into a glue mix in accordance with the formula set forth in Example II and upon being spread on veneer cores and bonded between face and back plies in the manner also described in Example II, produced satisfactory plywood gluing results.

Example IV

Another experiment involving whole blood was conducted in the manner illustrated in the above Example I. Blood powder was produced from a liquid blood starting material of about 17% solids content which had been heated in a period of 18 minutes from approximately room temperature to 149° F. to produce a blood coagulum. The drying conditions were 420° F. inlet temperature and 180° F. outlet temperature from the spray dryer. A glue mix was prepared from this powder comprising 105 parts blood powder (approximately 100 parts blood solids on dry weight bases), mixed with approximately 300 parts water at 70° F., 27 parts of the same filler as used in Example II, 500 parts water at approximately 70° F., 3 parts pine oil and 9 parts lime in 18 parts water in addition to increase the caustic concentration. There were also added 24 parts of 50% aqueous sodium hydroxide, 40 parts of phenolaldehyde resin and 40 parts sodium silicate. The glue mix had a viscosity of about 175 c.p.s.

Plywood assemblies were prepared and hot pressed as previously outlined in the above Example II, with a glue mix spread of approximately 75 pounds per 1000 square feet of double glue line. Plywood specimens were subjected to wet soak and dry shear testing in the conventional manner and demonstrated acceptable adhesive characteristics for plywood glues of commerce.

Another blood coagulum was converted into an insolubilized blood powder in accordance with Example I using a drier inlet temperature of 425° F. The blood powder was thereafter heated in an oven to a temperature of about 300° F. for a period of time of approximately 45 to 60 minutes. This post-heated and further insolubilized blood powder was prepared into a glue mix by admixing 100 parts of the powder with 300 parts of water at about 70° F., 5 parts of pine oil as a defoamer, 20 parts of 50% aqueous sodium hydroxide, 8 parts lime in 16 parts water, 40 parts sodium silicate and additional water about 200 parts by weight. Preferable post-curing temperatures are above about 170° F. up to the charring temperature of the blood powder.

This glue mix had a viscosity of about 450 cps. and when spread at the rate of 80 lbs. per 1000 square feet of double glue line on veneer core stock, followed by hot pressing at 230° F. for 3½ minutes produced satisfactory plywood.

Another glue mix base of insolubilized dried blood as described in this example was similarly compounded but also including about 35 parts of synthetic phenol-aldehyde resin and produced plywood having superior water and mold resistance and suitable plywood bonding characteristics.

Having thus described our invention, we claim:

1. The process for making a dry-glue base powder comprising: heating an aqueous blood solution to a temperature below its boiling point and above about 120° F. to partially coagulate the blood solids to form a coagulum containing insolubilized blood particles, simultaneously agitating the blood coagulum and maintaining the coagulated blood particles in finely divided condition and dispersed throughout the fluid medium, and spray-drying the coagulum to produce a water insoluble, alkali-soluble powder having a moisture content below about 30 percent while maintaining an air outlet temperature from the spray dryer between about 180–290° F. whereby to further insolubilize the blood solids.

2. The process of making a dry-glue base powder, comprising: providing an aqueous blood solution having a blood solids-to-water ratio content between about 10 and 20 percent based on the weight of the solution; agitating said blood solution and heating the same to a temperature below its boiling point and above about 120° F. to partially coagulate the blood solids therein while maintaining the coagulum fluid; and drying the coagulum to form blood solids which are water-insoluble and alkali-soluble having a moisture content below about 30 percent in a spray dryer at an air-outlet temperature from the dryer between about 180° F. to 290° F.

3. A process for making a blood powder, said process comprising the step of converting an aqueous blood solution to a liquid blood coagulum, said aqueous blood solution having a blood solids-to-water content less than about 20 percent by weight based on the weight of the solution, during said step heat coagulating the aqueous blood solution at a temperature above about 120° F. and below the boiling point of the same, during said step maintaining the coagulated blood particles in a finely divided condition and dispersed throughout the liquid blood coagulum, spray drying the liquid blood coagulum to both heat and dry the liquid blood coagulum to produce a blood powder which is water-insoluble and alkali-soluble, the temperature within the dryer after contact with the coagulum being between about 180° F. and about 290° F.

4. A process for making a blood powder, said process comprising the step of converting an aqueous blood solution to a liquid blood coagulum, said aqueous blood solution having a blood solids-to-water content less than about 20 percent by weight based on the weight of the solution during said step heating the aqueous blood solution in about 18 minutes to a temperature in the range between about 120° F. and the boiling point of the same to produce coagulated blood particles, during said step maintaining the blood particles in a finely divided condition and dispersed throughout the liquid blood coagulum, spray drying the liquid blood coagulum to both heat coagulate and dry the same to blood solids having a moisture content less than about 30 percent by weight and which are water-insoluble and alkali-soluble, the temperature within the dryer after contact with the coagulum being in the range of about 180° F. and 290° F.

5. A process for making a blood powder, said process comprising removing substantially all of the fibrin from an aqueous blood solution and the step of converting the same to a liquid blood coagulum, said aqueous blood solution having a blood solids-to-water content less than about

20 percent by weight based on the weight of the solution, during said step heating the aqueous blood solution to a temperature in the range between about 120° F. and the boiling point of the same, during said step having the blood particles in a finely divided condition and dispersed throughout the liquid blood coagulum, spray drying the liquid blood coagulum to both heat and dry the same to a moisture content less than about 30 percent by weight to form said blood powder, and the temperature within the dryer after contact with the coagulum being in the range between about 180°–290° F., and subjecting the blood powder to an elevated temperature to further insolubilize the same, said powder being water-insoluble and alkali-soluble.

6. A process for making a glue-mix, said process comprising the step of converting an aqueous blood solution to a blood powder coagulum, said step comprising converting the aqueous blood solution to a liquid blood coagulum, said aqueous blood solution having a blood solids-to-water content less than about 20 percent by weight based on the weight of the solution, during said conversion of the blood solution to the liquid blood coagulum the step of heating the aqueous blood solution to a temperature of above about 120° F., and below the boiling point of the blood, during said conversion step having the blood particles in a finely divided condition and dispersed throughout the liquid blood coagulum, drying and heating the liquid blood coagulum which is water-insoluble and alkali-soluble in a spray dryer to a moisture content less than about 30 percent by weight to form blood powder coagulum, the temperature within the dryer after contact with the coagulum being above 180° F. and less than about 290° F., and improving the adhesive properties of the blood solids by mixing the blood powder with an aqueous medium and alkaline chemicals selected from the group consisting of sodium hydroxide, lime, sodium silicate, or mixtures thereof to form the glue-mix.

7. A process for making a glue-mix, said process comprising converting an aqueous blood solution to a blood powder coagulum, in said conversion the step of processing an aqueous blood solution to a liquid blood coagulum, said aqueous blood solution having a blood solids-to-water content less than about 20 percent by weight based on the weight of the solution, during said step heating the aqueous blood solution to a temperature in the range of about 120° F. and the boiling point of the same, during said step having the blood particles in a finely divided condition and dispersed throughout the liquid blood coagulum, spray drying the coagulum to both heat and dry the same to a moisture content less than about 30 percent by weight to form said blood powder coagulum, and the temperature within the dryer after contact with the coagulum being in the range between about 180–290° F., subjecting the blood powder coagulum to an elevated temperature to post-cure the same said blood powder coagulum being water-insoluble and alkali-soluble, and improving the adhesive properties of the blood solids by mixing the post-cured blood powder coagulum with an aqueous medium and alkaline chemicals selected from the group consisting of sodium hydroxide, lime, sodium silicate, or mixtures thereof to form the glue-mix.

8. A process for making a blood powder comprising heating an aqueous blood solution to a temperature below its boiling point and above about 120° F., to partially coagulate the blood solids to form a coagulum containing insolubilized blood particles, simultaneously agitating the blood coagulum, and maintaining the coagulated blood particles in finely divided condition and dispersed throughout the fluid medium, removing water from the coagulum by evaporation at a temperature far below about 120° F., and spray drying the coagulum to produce a powder having a moisture content below about 30% while maintaining an air outlet temperature from the spray dryer between about 180°–290° F., whereby to further insolubilize the blood solids, said blood solids being water-insoluble and alkali-soluble.

9. The glue mix product of the process of claim 6 which includes a phenolaldehyde resin.

References Cited in the file of this patent

UNITED STATES PATENTS

1,504,225	Fitzgerald	Aug. 12, 1924
1,732,015	Homberg et al.	Oct. 15, 1929
2,400,541	Cone	May 21, 1946
2,870,034	Sheeran	Jan. 20, 1959
2,895,928	Cone	July 21, 1959