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WATER-RESISTANT ANIMAL GLUE

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This invention relates to the preparation of water resistant animal glue.

Animal glues made from hide scraps, sinews, bones, etc. have long been used to bond wood and other structures together and have been highly useful in the construction field. The joints thus formed have been unsatisfactory in that the glue is unable to withstand moist conditions. The ordinary glue is not resistant to dampness but tends to be weakened by moisture, allowing the wood joints to separate.

Research workers in the field of glue adhesives have long sought a remedy which could be applied to animal glue for giving it greater water resistancy. Hardening agents such as formaldehyde have been tried but in most cases these have caused the glue to set within a short time so that the working life was too short for commercial utilization. There has thus existed for a long time a need for a glue which would be water resistant while at the same time remaining fluid and in condition for application over a substantial period.

An object of the present invention is to provide a process for preparing a water resistant adhesive of long working life. Another object is to provide an adhesive which remains fluid for a substantial period after the paraformaldehyde or formaldehyde-liberating compound is added thereto. A still further object is to provide a method for preparing animal glue stock solutions which may be stored for long periods and then after being combined with a formaldehyde-liberating compound, will have a working life over a substantial period. A still further object is to prepare a water resistant animal glue which effectively penetrates the pores of wood, preserves the protein of the glue against bacterial action, while at the same time remaining liquid for a substantial period after the catalyst or formaldehyde-liberating compound is added thereto. Other specific objects and advantages will appear as the specification proceeds.

In one embodiment of the invention, animal glue is reacted with carbon disulfide. The treated glue is then dissolved in water and a glue solvent is stirred into the solution. This gives a liquid glue which remains fluid at room temperatures or above.

When the adhesive is to be used in making a wood joint, etc., a formaldehydic compound which liberates formaldehyde is added and the joint may be formed either as cold press or hot set. We prefer to employ paraformaldehyde but other polymers of formaldehyde, such as alpha-polyoxymethylene, beta-polyoxymethylene, and hexamethylene tetramine which give free formaldehyde, are highly satisfactory. Paraformaldehyde, however, is found to be the most efficacious.

In the reaction between carbon disulfide and the animal glue, the carbon disulfide reacts with primary amines to give dithiocarbamates which serve to block the free amino groups and links protein molecules together into larger aggregates. The carbon disulfide may be added directly to the glue flakes or we may first hydrate the glue and then add the carbon disulfide. We

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prefer to cover the glue flakes with an excess of carbon disulfide and the reaction is suitably carried out in a closed container. The flakes, after the treatment with carbon disulfide, have a golden yellow appearance.

The carbon disulfide treated glue may be dissolved in any conventional glue solvent to give a glue solution which remains liquid at room temperature. Conventional non-gelling agents such as furfural, salt solution, chloralhydrate, calcium chloride, formamide, etc. are suitable if the glue product is to be used within a few days time. If the glue solution is to be stored for long periods prior to use, we prefer to employ a liquid, aliphatic, water-soluble halogen substituted alcohol, as for example, ethylene chlorohydrin, propylene chlorohydrin, ethylene bromohydrin, monochloroglycerol, etc. Because of its ready commercial availability we prefer to use ethylene chlorohydrin.

The glue solvent may be combined with the carbon disulfide treated glue in any suitable manner. We find that a very satisfactory procedure is to add the glue to cold water to form an aqueous suspension of treated glue and then to heat it to bring about a complete solution of the solids. We prefer then to cool the solution and stir in the glue solvent.

The amount of glue solvent employed is not critical but may be varied over a wide range. Sufficient glue solvent should be present to dissolve the glue and we prefer to use at least 75% of solvent based on the weight of the glue. Larger amounts of solvent may be employed if desired but this is not necessary. From 75% to 200% of solvent based on glue weight has been found to be suitable for this purpose.

The glue stock solution is prepared for use by adding thereto a formaldehyde-liberating compound such as paraformaldehyde. The amount of paraformaldehyde or other formaldehyde-liberating compound employed is dependent upon the degree of water-resistance and the length of working life desired by the user. We have found that from about 3 to 30% paraformaldehyde, based on glue solids, may be employed and that very satisfactory results are obtained when using about 10% paraformaldehyde.

A specific example illustrating the process may be set out as follows:

To 500 grams of flaked glue was added 50 cc. of cold water and the mixture stirred until all water was absorbed as evidenced by the flakes becoming non-sticky. The hydrated glue was then put into a closed container and covered with carbon disulfide and allowed to stand at room temperature for 12 days. It was then drained by decanting the carbon disulfide and the flakes were allowed to dry by spreading them on a tray in a room for a few days.

To 100 grams of the above treated glue was then added 200 cc. of cold water and the mixture allowed to stand for about 1 hour during which time it was stirred periodically. The mixture was heated to about 60° C. and the solids went into suspension yielding a heavy, viscous liquid. After cooling to about 40° C., 100 grams of ethylene chlorohydrin was stirred in. This gave a liquid glue which remained fluid at room temperatures and below. The pH of the solution was about 6.0 due to the enhanced acidity of carboxyl groups after the basic amino groups had been blocked.

When it was desired to use the above described glue stock solution, the solution was weighed and paraformaldehyde equal to 10% of the glue solids was added. After mixing thoroughly, the adhesive was ready for use. The glue gave a working life of about 4 hours. In other examples, a longer working life was obtained. By heating the paraformaldehyde at 100° C. for 3 days,

further polymerization was effected and the working life was extended to over 8 hours.

As a further example of the process a carbon disulfide treated glue stock solution was prepared by placing glue flakes in a closed container, and covering the glue flakes with carbon disulfide at room temperature for 12 days or longer. The flakes were drained and dried as before.

100 parts of the treated glue was then suspended in 100 parts of water and the aqueous glue suspension dissolved in 200 parts ethylene chlorohydrin to give a glue stock solution which remained fluid indefinitely at room temperatures.

When ready for use, the above glue stock solution was weighed and 5% paraformaldehyde, based on the weight of glue solids, was added with thorough mixing.

The final product not only had long working life but also it remained liquid without the application of heat and was highly effective in penetrating the pores of wood, producing an extremely sturdy bond resistant to water.

The present application is a continuation-in-part of our co-pending application Serial No. 66,394, filed December 20, 1948, for water resistant animal glue, and now abandoned.

While in the foregoing specification, we have set forth specific steps in considerable detail for the purpose of illustrating an embodiment of the invention, it will be understood that such details may be varied widely by those skilled in the art without departing from the spirit of our invention.

We claim:

1. In the preparation of a water resistant glue, the steps of treating solid, hydrated animal glue with an excess of carbon disulfide to decrease the reaction rate of the protein molecules in said glue with formaldehyde by blocking the free amino groups in said protein molecules, forming a viscous suspension of the treated glue in water, adding sufficient ethylene chlorohydrin to said suspension to keep said suspension in fluid condition at room temperature, and finally mixing with said suspension a formaldehyde-liberating material, said formaldehyde-liberating material providing about 10% by weight of formaldehyde compared to the weight of the glue solids.

2. In the preparation of a water resistant glue, the steps of treating solid, hydrated animal glue with an excess of carbon disulfide molecules in said glue with formaldehyde by blocking the free amino groups in said protein molecules, forming a viscous suspension of the treated glue in water, adding ethylene chlorohydrin to said suspension to increase the liquidity of said suspension, said ethylene chlorohydrin being added in about equal parts by weight to the glue solids, and finally mixing with said suspension paraformaldehyde in an amount equal to about 10% of the weight of the glue solids therein.

3. In the preparation of a water resistant glue, the steps of treating animal glue with carbon disulfide to decrease the reaction rate of the protein molecule in said glue with formaldehyde, forming an aqueous suspension of the treated glue, dissolving said suspension in a non-gelling glue solvent, and adding thereto a formaldehyde-liberating material, said formaldehyde-liberating material providing from 3 to 30% by weight of formaldehyde compared to the weight of the glue solids.

4. In the preparation of a water resistant glue, the steps of treating animal glue with an excess of carbon disulfide to decrease the reaction rate of the protein molecules in said glue with formaldehyde, forming an aqueous suspension of the treated glue, dissolving said suspension in ethylene chlorohydrin, and adding thereto

a formaldehyde-liberating material, said formaldehyde-liberating material providing from 3 to 30% by weight of formaldehyde compared to the weight of the glue solids.

5. In the preparation of a water resistant glue, the steps of treating animal glue with an excess of carbon disulfide to decrease the reaction rate of the protein molecules in said glue with formaldehyde, forming an aqueous suspension of the treated glue, adding ethylene chlorohydrin to said suspension, the amount of said ethylene chlorohydrin used being at least 75% by weight of the animal glue present, and adding thereto a formaldehyde-liberating material, said formaldehyde-liberating material providing from 3 to 30% by weight of formaldehyde compared to the weight of the glue solids.

6. In the preparation of a water resistant glue, the steps of treating solid, hydrated animal glue with an excess of carbon disulfide to decrease the reaction rate of the protein molecules in said glue with formaldehyde by blocking the free amino groups in said protein molecules, forming a viscous suspension of the treated glue in water, dissolving said suspension in ethylene chlorohydrin, and adding a formaldehyde-liberating material, said formaldehyde-liberating material providing about 10% by weight of formaldehyde compared to the weight of the glue solids.

7. In the preparation of a water resistant glue, the steps of treating animal glue with an excess of carbon disulfide to decrease the reaction rate of the protein molecules in said glue with formaldehyde, forming an aqueous suspension of the treated glue, adding from 75 to 200% by weight of ethylene chlorohydrin to said suspension to increase the liquidity of said suspension, and immediately before using the glue adding to said suspension about 10% by weight of paraformaldehyde compared to the weight of the glue solids in said suspension.

8. The product produced in accordance with the process of claim 3.

9. The product produced in accordance with the process of claim 7.

10. In the preparation of a glue stock solution and a water-resistant glue therefrom, the steps of treating animal glue with carbon disulfide to decrease the reaction rate of the protein molecules in said glue with formaldehyde, forming an aqueous suspension of the treated glue, adding sufficient ethylene chlorohydrin to said suspension to keep said suspension in fluid condition at room temperature, thereby producing a glue stock solution which can be stored for long periods of time, thereafter mixing a formaldehyde-liberating compound with said glue stock solution, and setting the resulting mixture to a water-resistant state.

11. In the preparation of a glue stock solution and a water-resistant glue therefrom, the steps of treating animal glue with carbon disulfide to decrease the reaction rate of the protein molecules in said glue with formaldehyde, forming an aqueous suspension of the treated glue, dissolving said suspension in a non-gelling glue solvent to form a glue stock solution which can be stored for long periods of time, thereafter mixing a formaldehyde-liberating compound with said glue stock solution, and setting the resulting mixture to a water-resistant state.

References Cited in the file of this patent

UNITED STATES PATENTS

1,506,013	Lindauer et al. _____	Aug. 26, 1924
1,814,768	Rippey et al. _____	July 14, 1931
2,089,460	Wilmanns et al. _____	Aug. 10, 1937
2,643,194	Fencil _____	June 23, 1953