CASEIN GLUES: THEIR MANUFACTURE, PREPARATION, AND APPLICATION

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By

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Introduction

The use of casein in the gluing of wood is reported to be a very ancient art. European craftsmen apparently understood a method of gluing with a crude casein (possibly the curd of soured milk mixed with quick lime) in the Middle Ages, and the art continued in a small way to modern times. The manufacture of casein glue as a separate industry, however, seems to have started in Switzerland or Germany in the nineteenth century. In the United States casein glues were used only to a very limited extent until about 1916 or 1917, when the need for a water-resistant glue for the construction of military aircraft suddenly aroused interest in casein glue and promptly led to its extended production and use.

For some purposes, the principal requirements of a casein glue are water and mold resistance combined with satisfactory dry strengths. For other purposes, however, it is sometimes desirable to formulate the casein glue to produce one that possesses other desirable characteristics, such as cheapness, low staining tendencies, long working life, high dry strength, or good spreading characteristics, even at some sacrifice of water resistance. The glue user has available, therefore, a variety of casein glues of different properties from which he may choose according to his needs.

Manufacture of Casein

The principal ingredient of casein glue is casein, which is the chief protein constituent of milk. When milk becomes sour, it separates into curd and whey. The curd, when washed and dried, is the casein of commerce. When made in this way, it is known as self-soured or naturally soured casein. Casein is also precipitated by mineral acids, such as hydrochloric or sulphuric, and by rennet. In preparing the glue, caseins precipitated by the different methods will require different amounts of water to produce solutions of similar viscosity (4). Satisfactory glues, however, can be

1 Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

2 The underlined figures in parentheses refer to Literature Cited at end of text.

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produced from caseins precipitated by any of these methods provided the casein is of good quality.

The starting point in the manufacture of casein is skim milk, that is, whole milk from which the fat has been removed in the form of cream (6). The following are the usual steps in the manufacturing process: (1) the precipitation of the casein; (2) washing the curd to remove the acid and other impurities; (3) pressing the damp curd, wrapped in cloth, to remove most of the water; (4) drying the curd; and (5) grinding it to a powder. The care with which these various steps are carried out determines the quality of the finished product.

It has been found that casein of the very highest grade is not essential for glue making. It does not follow, however, that a decidedly inferior casein will yield a high-grade glue; for instance, moth infection may alter the properties of casein to such an extent that water-resistant glues cannot be prepared from the infected material. A casein suitable for glue making should have a low fat and acid content, should be free from burnt or discolored particles, sour odor, larvae, maggots, and other extraneous animal matter; and it should be ground fine enough to pass through a 20-mesh sieve.

Formulation of Casein Glues

The principal ingredients of a casein glue are casein, water, hydrated lime, and sodium hydroxide. A glue can be prepared with casein, water, and hydrated lime. A properly proportioned mixture of these three substances will give a glue of high water resistance, but its working life will be very short. A glue can also be prepared of casein, water, and sodium hydroxide. When properly prepared such a glue will have excellent dry strength and a long working life, but it will not be water-resistant in the sense ordinarily applied to casein glues. By adjusting the proportions of sodium hydroxide and lime, glues of high water resistance and convenient working life may be obtained.

Glues containing sodium hydroxide, hydrated lime, and casein are suitable for wet-mix glues only. The hygroscopic properties of sodium hydroxide prevent storing a casein glue containing it without danger of decomposition. The alkali can be introduced in an indirect manner, however, so that the casein can be mixed with all the necessary ingredients, except water, in the form of a dry powder that can be handled and stored conveniently. One way to do this is to replace the sodium hydroxide with chemically equivalent amounts of calcium hydroxide and a substance that, when dissolved in water, reacts with the calcium hydroxide to form sodium hydroxide. Any convenient sodium salt of an acid whose calcium salt is relatively insoluble may be used, provided it is not hygroscopic and does not react with the lime of the casein when the mixture is kept dry. The sodium salt may be, for example, sodium oxalate, sodium tartrate, sodium citrate, sodium salicylate, sodium phosphate, sodium sulfite, sodium fluoride, sodium arsenate, sodium arsenite, or sodium stannate (9).

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To improve resistance to deterioration caused by molds or other microorganisms, preservatives such as copper salts, mercury salts, or the chlorinated phenols or their sodium salts are sometimes added to casein glues. Amounts of chlorinated phenols in the neighborhood of 5 percent of the weight of the casein will often result in marked improvement in mold resistance without seriously affecting the working properties of the casein glue.

Prepared Casein Glues

There are a number of prepared casein glues on the market, complete in powder form. They are made ready for use by sifting them into water and stirring the mixture. They usually contain the essential ingredients of casein, hydrated lime, and sodium salt, to which may be added materials to reduce staining, to reduce hardness, or to impart other properties. Many of the formulas are protected by patents. Directions for mixing these glues with water are usually furnished by the manufacturer.

Wet-mix Casein Glues

Those who are prepared to mix the various ingredients at the place where the glue is to be used, may prefer to prepare a glue directly from the basic materials: casein, sodium hydroxide, and lime. Approximately the following proportions are suitable.

<table>
<thead>
<tr>
<th>Parts by weight</th>
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<tbody>
<tr>
<td>Casein</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Calcium hydroxide (hydrated lime)</td>
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<tr>
<td>Water</td>
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</table>

This glue remains usable for some 6 or 7 hours at temperatures between 70° and 75° F. It is capable of giving joints that will have good dry strength and water resistance.

Sodium silicate may be used in place of sodium hydroxide or in place of dry sodium salts, and the glue so prepared will differ from all the others. A much longer working life is obtained in a glue of an alkalinity equal to that obtained by the use of sodium hydroxide or other sodium salts. Further, there is a considerable range of lime content (above that necessary to react with the sodium silicate) within which the working life decreases as the proportion of calcium hydroxide increases.

Formula 11.—Several formulas of the latter type have been developed at the Forest Products Laboratory. The best of these is formula 11, which is covered by U. S. Patent No. 1,456,842, granted in 1923 to S. Butterman and
C. K. Cooperrider (formerly of the Forest Products Laboratory) and dedicated to the public. Formula 11 follows:

<table>
<thead>
<tr>
<th>Parts by weight</th>
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<tbody>
<tr>
<td>Casein</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Hydrated lime</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Silicate of soda</td>
</tr>
<tr>
<td>Cupric chloride</td>
</tr>
<tr>
<td>Water</td>
</tr>
</tbody>
</table>

Copper salts are effective in increasing the water resistance of the glue. This improvement is most striking in those glues that do not contain as much lime as they should. It is not always advisable to employ the maximum amount of lime, because high-lime glues almost invariably have a short life; that is, a short period during which they are workable. In such cases it may be expedient to obtain high water resistance by adding copper chloride rather than by adding the maximum amount of lime. Copper chloride does not shorten the life of a glue so much as large amounts of lime; in fact, it sometimes seems to have a tendency to lengthen the life rather than to shorten it. It seems probable that the copper acts as a preservative and affords some protection to the glue when the joints are exposed in warm, damp atmospheres where molds, fungi, and other micro-organisms are active.

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2 The proper amount of water to use depends primarily upon the quality and the ash content of casein. It can be determined by mixing trial batches. With caseins containing about 3-1/2 percent of ash, 200 parts of water by weight is usually close to the proper amount. Since the ash content affects the water-taking capacity, it will prove convenient to obtain a source of casein that is uniform in ash.

4 The formula presupposes that a high-calcium chemical lime will be used. A low grade of lime often results in the presence of small lumps of lime that remain inactive and that show as small white spots in the finished glue line. A lime lower in calcium may be used, but a proportionately larger amount will be required unless one is willing to sacrifice water resistance. It is suggested that the user try 25 parts of lime to begin with. If this does not give good results, the amount can be varied within the limits specified.

5 The density of the silicate of soda used should be about 40 degrees Baume with a silica-soda ratio of approximately 3.25:1.

6 Cupric sulphate can be substituted for cupric chloride.
Formula 4B.—Formula 11 without the cupric chloride solution represents an earlier stage of development, known as formula 4B. This formula was based on U. S. Patent No. 1,291,396, granted in 1918 to S. Butterman (formerly of the Forest Products Laboratory) and dedicated to the public. This glue has excellent working properties, and a life of from 6 to 24 hours, depending on the way in which it is made. Provided the lime content is kept near the upper limit, the water resistance is approximately equal to that of formula 11.

Mixing and Applying Casein Glues

Mixing

A satisfactory casein-glue mixer should have the following characteristics: (1) a paddle that can be rotated at different speeds, (2) a bowl and a paddle either detachable or at least arranged so that they can be cleaned conveniently, and (3) a bowl and a paddle made of a metal that will not be corroded by the alkalies in the glue, as would brass, copper, and aluminum vessels. A type of mixer that has proved satisfactory at the Forest Products Laboratory is a motor-driven dough mixer, such as is used by bakers, although various other types of mixers are in successful use.

One of the essentials of accurate mixing is to weigh all components rather than to trust to measurements by volume. Accurate weighing, of course, requires scales or balances of suitable capacity and sensitivity, maintained in good working condition.

The directions for mixing prepared casein glues are usually furnished by the manufacturer or supplier of the glue. In the absence of specific directions, trial batches, differing in glue-water ratios, may be prepared until suitable proportions are found. Several of the prepared casein glues mix well in the ratio of 2 parts of water to 1 part of dry glue (by weight). Ordinarily, the entire amount of water can be weighed into the mixer, and the glue powder then be weighed and be added gradually to the water with continuous stirring. After all the powder has been added, the stirring is continued until the mixture either becomes smooth and free from lumps or thickens into a stiff, doughlike mass. It should be noted that casein-glue formulations may either thicken into this doughlike mass, which later thins down on standing, or they may mix directly to a normal workable consistency, depending on the components used in the formulation. If the glue does not thicken but mixes, in some 15 minutes, to a smooth liquid free from lumps, it is then ready for use. If the mixture thickens to a stiff mass, however, the mixer should be stopped and the glue be allowed to stand. Mixtures of this type will usually thin down to workable consistencies in about 20 to 30 minutes. No more water should be added when the mixture thickens or it will be too thin when finally ready for use.

Wet-mix casein glues require somewhat different procedures. The casein-lime-sodium hydroxide formula can be mixed by soaking the casein in about two-thirds of the water for about 15 to 30 minutes, adding the sodium
hydroxide dissolved in about one-sixth of the water and stirring until the casein is completely dissolved, and finally adding the lime suspended in the remainder of the water and stirring until smooth.

In mixing those formulas containing sodium silicate, the casein and water are weighed into the bowl of the mixing machine and stirred sufficiently to distribute the water throughout the casein. If the casein is ground to pass through a 20-mesh screen, it should be allowed to soak for about 15 to 30 minutes before proceeding with the preparation. If the casein is more finely ground, the soaking period may be reduced. The hydrated lime is mixed with water in a separate container. With the mixer in operation, the "milk of lime" is poured into the casein-water mixture.

When casein and lime are mixed, they first form large lumps, which are balls of dry casein coated with partly dissolved casein. These break up rapidly, become smaller and smaller, and finally disappear. The solution, in the meantime, becomes somewhat thinner. A stirring device should be provided that insures thorough agitation. If a deposit of casein remains unacted upon, it may later cause lumps.

In about 1 minute after the lime and the casein have been united, it may be noticed that the glue has begun to thicken a little. The sodium silicate must be added then, or the glue will become too thick. Without regard to lumps, if they are but few, the sodium silicate should then be poured in. The glue will thicken momentarily, but the stirring should be continued until the glue is free from the lumps, which should be in not more than 15 or 20 minutes. If the glue is a little too thick, a small amount of water may then be added. If the glue is too thin, it will be necessary to start over again with a smaller proportion of water. Hence, it is important to make certain that too much water is not added originally.

The copper salt of formula 11 may be added at any one of several times during the mixing process. A convenient method, recommended for general practice, is to dissolve the copper salt and stir the solution into the moistened casein immediately before the lime is added. The solution of the copper salt may be added at the end of the mixing process, but some care will be required to avoid lumping. If so added, the solution of copper salt should be poured slowly into the glue with continuous stirring. The mixing should be continued until any lumps that may have formed are broken up and a smooth evenly colored glue is obtained. The dry copper salt may be mixed with the dry casein, but if the casein containing the copper salt is soaked for an extended period a chemical action will take place between the copper salt and the metal container.

Preservatives that are water-soluble or that can be ground to a fine powder may be added to the casein before mixing it with water. Preservatives in the form of oils may be added after the mixing is otherwise completed.
Working Life

The working life of a glue is the length of time during which it remains fluid enough to be workable. The life of a casein glue depends primarily upon (1) the amount of lime it contains, (2) the amount of water added, and (3) the temperature of the room and of the water used in preparing the glue.

The life of a casein glue varies (within limits) inversely as the amount of calcium hydroxide that is present. By reducing the amount of lime, casein glue can be formulated with an indefinitely long working life, but extension of the working life will be accomplished at the expense of the water resistance. Specifications for water-resistant casein glues (13) usually require that the glue shall set to a firm jelly.

The life of a casein glue can be lengthened by increasing the amount of water used in mixing. It is not advisable, however, to add to a glue much more water than the formula or mixing directions specify, because the water dilutes the glue and, if present in large quantities, it will seriously weaken the joints.

The setting of casein glue involves a chemical reaction that, in common with most chemical reactions, is accelerated by an increase in temperature. In hot weather, therefore, a casein glue can be expected to have a shorter working life than in cold weather.

Spreading

Casein glue is fluid enough to be spread either by machine or by hand. It can be used on a roll spreader of the type that is used to spread vegetable glue, or it can be applied by hand with a brush or a scraper. Unnecessarily heavy spreads very seldom cause defective joints, but they do, of course, result in unnecessary waste because the excess glue is squeezed from the joint and contributes nothing to the bond. Very light spreads, however, often result in weak joints, apparently because the glue remaining in the joint is insufficient to form a continuous film of glue between the matching surfaces. Approximately 65 pounds of wet glue per 1,000 square feet of glue-joint area is often suggested as a desirable minimum.

Assembly Time

Assembly time is the interval between spreading and pressing a glue.

When casein glue is spread on wood, it does not thicken in a cool room so quickly as animal glue. The time that may elapse between the spreading of a casein glue and the pressing of the joint depends on at least four factors: (1) the moisture content of the wood, (2) the consistency of the glue, (3) the quantity of glue applied, and (4) the temperature of the wood and glue. The time will be relatively short if the wood is dry, the glue thick, the layer of glue thin, and the temperature of the wood and glue high.
In order to obtain good contact between the wooden members of a joint, the pressure should be applied while the glue is still wet. If the glue has dried too much before pressing, a poor joint will naturally be obtained, but in most cases excessive drying does not occur before 15 or 20 minutes (11).

Pressure

The pressure should be sufficient to insure complete contact between the glue film and the surfaces to be joined, but the pressure should not be so great as to crush the wood or to squeeze out too much glue. When a thick, viscous glue is used, it is difficult to squeeze it out from between the plies, or to force it into the wood, but with a thin glue it is not so difficult. If a stack of panels is assembled and put under pressure very promptly, it is easier to squeeze out the glue than if the assembly period has been long enough to allow the glue to thicken somewhat. It is probably also true that plies with exceptionally smooth surfaces would not require pressure as high as plies with rougher surfaces.

From the above considerations it can be seen that the amount of pressure to use is not independent of other factors in the gluing operation. In experiments at the Forest Products Laboratory good results have been obtained over a wide range of pressures. Under ordinary circumstances one may expect good results with a pressure of 150 to 200 pounds per square inch (11).

Duration of Pressure and Conditioning

Casein glues set quickly and within a few hours produce joints strong enough to be machined. In the gluing of spruce and woods of similar strength at a temperature of 70° F. joints as strong as the wood can be expected within 4 hours from the time the pressure has been applied. In gluing hard maple, which is stronger than spruce, tests showed that about 8 hours were required. These pressure periods are approximately the same as for the same species when glued with animal glue and somewhat shorter than required for urea-resin glues cured at 75° F. It is not necessary, however, to keep the joints under pressure all this time. If the pressure is maintained for 1/2 to 2 hours, depending on the kind of joints, and the glued members are then allowed to season before working, good results may be expected.

The above statements refer to the minimum time in which good results may be obtained. In case of emergency, it might be safe to machine wood containing casein-glue joints as early as 4 to 6 hours after pressure has been applied. Under ordinary conditions this is not desirable. The best practice is to allow glue joints to season until the moisture at the glue line has dried out or distributed itself uniformly throughout the wood. In this way sunken joints can be avoided, and the tendency of the glued block to change dimensions or shape after machining will be reduced.
The ordinary casein glues may be used for making plywood by the hot-press technique (2), in which hydraulic presses with platens usually heated with steam are used. As a rule, the water resistance of the glued joint is improved by hot-pressing, particularly if the glue is one of only moderate water resistance when cold-press methods are used. In fact, in several formulations that have been used for hot-pressing, the amount of lime appears to have been reduced below the level generally considered desirable for cold-press gluing. Since the glue contains a high proportion of water, precautions are necessary to avoid difficulties with blistering during hot-press operations. For this reason it is considered undesirable to use hot-press temperatures much in excess of 212° F. While the hot-press technique has been frequently employed with casein glues in Europe, the cold-press method of applying casein glues is most commonly used in this country.

Characteristics of Casein Glues

Dry Strength

Casein glue produces joints in most of the common species of wood that are equal to or greater than the strength of the wood itself (11). When test blocks of hard maple glued together with the grain running parallel are tested in shear (A.S.T.M. method D905-47T), a glue strength of 2,200 to more than 3,000 pounds per square inch is usually obtained, and the wood is likely to fail rather than the glue. Specifications for casein glues require joint test values of 2,800 pounds per square inch in hard maple (13).

Joints in well-made three-ply panels of 1/16-inch birch veneer often test in excess of 400 pounds per square inch, and a common specification requirement for these panels is 340 pounds per square inch.

Water Resistance

Casein-glue joints are water resistant but not waterproof. When wet, the water-resistant casein-glue joints are stronger than wet vegetable- or animal-glue joints but not as strong as well-made phenol- or resorcinol-resin-glue joints or joints made with unextended urea-resin glues. After being soaked for 48 hours in water at room temperatures, casein-glue joints in plywood commonly show wet-test values equal to some 40 to 60 percent of their dry-test values. Casein-glue joints will withstand occasional soaking, but if repeatedly soaked and dried they will finally fail.
Mold Resistance

If casein-glue joints are exposed for prolonged periods to conditions that are favorable to the growth of molds or other micro-organisms, they will fail in time. The resistance to attack by molds can be increased by the addition of preservatives such as the chlorinated phenols, beta-naphthol, or phenyl mercury oleate (15). The copper salts in formula 11 probably act to inhibit the development of micro-organisms. Tests have been developed to evaluate the effectiveness of preservatives in casein glues (16), and these tests have been incorporated in specifications for mold-resistant casein glues (14).

While the addition of suitable preservatives increases the resistance of casein glues to micro-organisms, no casein-glue formula has been developed that is completely proof against destruction by these agents.

Casein-glue joints can be expected to prove permanently durable, therefore, only if the moisture content of the wood does not exceed about 18 to 20 percent for prolonged or repeated periods.

Hardness

There has been some complaint about the hardness of casein glues. All glues are hard to a certain degree and thus affect knives and saws. Casein glues, however, seem to be a little more objectionable than the others in this respect. No entirely satisfactory method of overcoming this difficulty is known to the Forest Products Laboratory. It will probably be helpful, when mixing glue from the raw ingredients, to discard the last few drops of the lime-water mixture. Whenever it is practical to trim panels before the glue has dried and hardened, the wear on the tools may thus be lessened. In some cases it may be found possible to use tools made of harder steel. Reducing the amount of lime in water-resistant glues is helpful, but at the same time the water resistance is lowered.

Staining

All strongly alkaline glues will stain certain species of wood. Casein glues, like other glues that are made with considerable caustic soda, will discolor the wood of oak, maple, and some other species. The discoloration appears along the glue line and on the faces of the panels where the glue or the alkali from it has penetrated.

Very thin faces will stain more quickly than faces made with thicker veneer. To leave panels under pressure for an unnecessarily long time is to encourage staining. If the panels are pressed for as short a period as is safe, and then separated on stickers and dried at once, the tendency to stain will be checked.

If the lumber is dry and the veneer well redried, the tendency to stain will be reduced. The use of dry absorbent caulbs between the faces of
adjacent panels should also help. A thin glue will penetrate further and is likely to cause staining.

If a stain has appeared, it can be removed by sponging with a solution of 1 ounce of oxalic acid in about 12 ounces of water. If this is not entirely effective, it may help to sponge the spot first with a solution of 1 ounce of sodium sulphite in 12 ounces of water, and then, while the wood is still moist, with the oxalic-acid solution. The oxalic acid should be carefully washed off after removing the stain, as its presence might interfere with subsequent wood-finishing processes. Since oxalic acid is poisonous if taken internally, it should be used with care.

Storage

Dry casein and casein glue in powder form will keep for a long time if stored under proper conditions. They should be kept in a cool, dry place because heat and moisture cause them to deteriorate. It is also advisable to store them in tight containers so that they cannot become infested with moths.

Vegetable-protein Glues

Soybean meal -- representative of a large class of substances known as vegetable proteins -- has been used considerably as a raw material for glue. It may be used alone or mixed with milk casein. Because of its relatively high content of protein matter, its gluemaking properties are more analogous to those of casein than to those of starch, from which so-called vegetable glues are made. Soybean glues of good quality are, in general, similar to casein glues in preparation, in certain properties, and in use. Soybean glues are nearly always prepared from the separate ingredients by the wet-mix process as described for casein glues. Soybean glues are cheap and have been shown to produce joints of good strength and moderate water resistance in softwood plywood, but they have not proven entirely satisfactory for gluing the stronger hardwoods. This class of glues originated on the Pacific Coast, where they have found extensive use in the plywood industry.

References

It is impossible to cover thoroughly all the points and facts that a glue user may want to know in a brief review of this kind. For more detailed information on the characteristics and technic of using casein and casein glues, the following references, some of which have been cited in this report, are suggested:

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U. S. Forest Products Laboratory
Casein glues: their manufacture, preparation, and application. 5th ed.
Madison, Wis., U. S. Forest Products Laboratory, 1961.
12 p. (F.P.L. rpt. no. 280)

Discusses manufacture, preparation, and application of casein glues.