Patented Dec. 23, 1941 2,266,736

UNITED STATES PATENT OFFICE

2,266,736

GLUE AND GLUE BASE

Lawrence Bradshaw, Bainbridge, N. Y.

No Drawing. Application March 13, 1937, Serial No. 130,795

7 Claims. (Cl. 106—146)

This invention relates to quick setting casein glues especially suitable for rapid gluing operations.

Casein glues have been used to a large extent for gluing wood and especially for making such products as plywood. They are sharply distinguishable from the animal glues, such as hide glue and fish glue, and from the common dextrine glues, in that the casein glues have a distinct resistance to water which is particularly desirable where the glued members may be subsequently subjected to moisture. Casein glues of the types hereinafter described may be used cold, whereas some other glues such as hide glue must be used while hot. A further characteristic of casein glues is their relatively slow setting or seizing as compared with certain other glues, which is advantageous for some uses, but which heretofore has limited the field of usefulness. By this I mean that a casein glue, after being spread upon a surface, does not generally develop a sufficiently adherent tackiness to securely hold the members to be glued together until the glue coating has dried, this often requiring considerable time. In using the term "setting" and "setting time," I refer to the length of time required for a glue to develop a sufficient amount of adherence after spreading, to enable the glue to grip and hold together the surfaces of the members glued.

In high-speed gluing operations, it is practically essential to use a quick-setting glue. Hide glues, applied hot, which have a relatively short setting time, have been largely used for this purpose. I have discovered how to reduce the setting time of casein glues without substantially impairing other desirable qualities thereof, thus making possible the economical use of casein glues in a new field where their distinctive properties can be used to good advantage. Paper containers, such as food containers, using one or more layers of paper glued together, can be improved by using caseing glues because the casein glue, among other desirable properties, has no objectionable odour, affords a strong bond, lends rigidity to the article, and is much more water-resistant than the hide or dextrine glues. The class of low-lime casein glues, in view of their strength and long life, are preferable for making such containers. By the term "life" is meant the period after the glue is mixed with water during which it is spreadable and usable. It is, therefore, an object of my invention to provide a quick-setting (quick-seizing or quick-gripping) casein glue, which is particularly suitable for rapid gluing operations. Another object of my invention is the provision of a glue containing milk-casein as the principal ingredient, which glue has a relatively long life and which contains an agent adapted to markedly reduce the time of setting. It is a further object of my invention to provide a method of rapidly gluing together various materials, such as paper, using the foregoing quick-setting casein glues. These new casein glues are very well suited for several present day operations of making paper containers, including paper drinking cups and food containers and the like. One method of forming such containers involves spirally winding one or more strips of paper about a cylindrical mandrel to produce a tube. The strip is wound very rapidly and the glue is applied to the paper as it is being wound. Such tubing is then cut into lengths and these lengths are provided with base members to form the container.

Another method for making containers involves the production of a laminated tubular structure of paper having a polygonal cross-section (often with the corners rounded off). To produce such tubing a similar winding operation is performed, but the paper is wound directly upon itself, instead of being wound spirally. This is known as "convolute winding." The tubing is subsequently cut to length and provided with tops and/or bottoms of metal or other material to make the finished containers. Laminated paper tubing made by these methods is usually cut and handled before the glue has thoroughly dried and it is therefore desirable to use a glue which has a quick gripping action and does not allow the paper to unwind or unravel on the mandrel or after the tubing is removed from the mandrel. Containers are also made by the side seam method, especially where the container is to be tapered for nesting with other similar containers in a convenient manner for packing and shipping. In accordance wtih this type of processing, paper is fashioned about a mandrel in over-lapping relation and glued together where it over-laps. Bottom members are then glued in place to complete the container. These side seam containers may be made of a single layer of paper or of multiple layers of paper glued together, when additional strength is desired, and in this method also a rapid gripping action of the glue is desired.

I have discovered that by adding a compound of zinc to a casein glue, the time of setting or seizing of such a glue may be very substantially decreased. In fact, the setting of the glue may be so accelerated as to make it eminently suit-

able for the high-speed production of paper containers by the above mentioned methods. Casein glues may be thus readily adjusted to many uses for which they were not suited before my invention.

The casein glues to which my invention relates are glues containing milk-casein as the principal ingredient together with a relatively small proportion of lime and one or more alkaline solubilizing agents to produce the desired fluidity when mixed with water.

As alkaline solubilizing agents one or more of the well known materials including trisodium phosphate, sodium carbonate, borax, sodium sulphite, caustic soda, and the like may be used. These agents may be employed in varying quantities and serve to dissolve the casein, when the glue is mixed with water, as is well understood in the art.

Additional ingredients may also be employed; for example a small quantity of a protein or proteinaceous material obtained directly or derived from a seed meal such as soybean meal, peanut meal, and the like, may be added to or used in place of a part of the milk-casein. Various other proteinaceous materials may also be used in minor proportions, so long as they do not detract from the beneficial properties of the glue imparted thereto by the milk-casein. A quantity of an urea may also be added to the glue as a solvent for the casein.

No claim as made therein broadly to glues containing the components disclosed in the last three above paragraphs, except when in conjunction with a component capable of imparting the desired quick-setting or quick-seizing property, as described.

I incorporate an alkaline earth oxide or hydroxide although preferably in a small proportion, in the glue to improve the strength. Hydrated lime may be used for this purpose. When a long-life glue is desired, the lime or other alkaline earth oxide or hydroxide, is preferably used in an amount less than about 12%. It is particularly desirable, of course, to have a glue of relatively long life which may still possess the property of quick setting or quick seizing when spread in a thin film on one or more surfaces to be glued. Various other modifying or addition agents and/or fillers may be employed as is understood in the art, including such materials as fluorides, sulphites, whiting or wood flour. The above addition and modifying agents are preferably used only in minor proportions so that the milk-casein remains the principal ingredient of the glue.

Any suitable compound of zinc may be used as an accelerator of the setting of the glue. Such compounds may be salts, either organic or inorganic, oxide, hydroxide, or compounds containing zinc in the anion, e. g. sodium zincate. These compounds of zinc have a very pronounced effect on the setting time of the glue. The accelerator compounds in accordance with my invention may be either soluble or insoluble in water although, in general, the soluble compounds can be used in lesser amounts than the insoluble compounds to impart the desired quick setting to the glue. Various zinc compounds may be mentioned as examples, although it is to be understood that the invention is not limited to the compounds specifically enumerated. The oxide or hydroxide of zinc is a very effective accelerator and is relatively inexpensive. Various inorganic salts of zinc, such as zinc borate, carbonate, halides, nitrate, phosphate, silicate, sulphate or sulphite, may be mentioned as examples. Zinc salts of organic acids are also particularly suitable since in general they are not strongly acidic and consequently have less tendency to neutralize the lime and alkaline casein solubilizing agents in the glue. The acetate, benzoate, lactate, oleate, oxalate, salicylate or stearate of zinc are examples of such organic salts. More complex organic salts may also be employed and, in fact, a particularly effective accelerator of this type is zinc diethyl-dithiocarbamate.

The proportion of the setting accelerator employed in the glue can be varied considerably. Amounts of the foregoing accelerator compounds as small as 0.1% have an appreciable effect on the time of setting of the casein glue. The quantity of the accelerator used will also necessarily vary somewhat according to the particular accelerating compound selected. A preferred range of accelerator is from about 0.1% to about 5%. Where an acidic compound is used as an accelerator, it is desirable to use either a relatively small quantity of the acidic compound or to increase the quantity of alkaline agents sufficiently to off-set the acidity of the setting accelerator. The above percentages are computed on a dry basis and represent the proportion of accelerator in the dry glue.

Various proportions of water may be mixed with the dry glue compositions in preparing the glues for use, the quantity of water depending upon the particular composition of the glue and the desired consistency of the final product. In general, the amount of water used may vary from 1 to 5 parts of water to 1 part dry glue. Some of the liquid low-lime casein glues of my invention, after mixing with water, retain their desired consistency or viscosity and remain spreadable and usable for 48 to 72 hours, or longer.

The following casein glue compositions are given by way of example as illustrative of the invention, but it is to be understood that the invention is in no way limited thereto.

Table I

	A	B	C	D
	Parts by weight	*Parts by weight*	*Parts by weight*	*Parts by weight*
Casein	85	76.5	50	80
Calcium hydroxide	5	4.5	10	6.
Trisodium phosphate	5	4.5		4.5
Sodium fluoride	5	4.5	6	1.75
Sodium sulphite				2.75
Calcium carbonate		10		
Wood flour				5.
Peanut meal			30	
Sodium carbonate			4	
Zinc oxide	2			
Zinc phosphate		2		
Zinc chromate				0.5
Zinc lactate			0.5	
	102	102	100.5	100.5

In the above examples, the addition of the zinc compounds in the amounts shown reduced the setting times of the glue compositions to which they are added, about 40–50%.

In order to show the effect of the setting accelerator compounds, I have devised a test which affords a comparison of this property for various glues. In performing this test a small amount of the dissolved glue is taken on the tip of the finger and spread uniformly over a given area on a piece of stiff paper. Then, by alternately raising the finger and touching the glue, and timing

the drying with a stop-watch, the time is determined at which the glue feels "dry" i. e. loses its tackiness so that the finger no longer adheres to it on touching. The determination may be repeated and an average taken. The time thus determined, affords a basis for comparison of the setting or seizing time of different glue mixtures. The following table indicates this time in seconds and shows the pronounced reduction in setting time effected by the addition of various accelerator compounds to a standard casein glue composition, namely to a particular commercial glue of good quality. The following results were obtained by averaging a number of readings for each glue compound. The same casein glue was used in each case, the only difference being the accelerator used.

Table II

Percent of accelerator		Setting time in seconds
0	Casein glue (no accelerator)	60
0.5	Zinc acetate	30
0.5	Zinc chloride	30
2.0	Zinc diethyl-dithiocarbamate	20
2.0	Zinc hydroxide	25
2.0	Zinc oxide	30
5.0	do	25
0.5	Zinc lactate	25

While the above tables indicate a considerable lapse of time to produce hardening of the glue, the actual time required for these glues to effectively grip a surface after application varies greatly under different conditions. When the glue is used in the methods of preparing paper containers including the winding and gluing together of several layers of paper by the spiral winding method decribed above, especially when the hollow mandrel is heated, it requires only a fraction of one second for the glue to grip and secure the two layers of paper together. In the process of convolute winding, using a cold mandrel, three or four seconds may be required. This difference in gripping time thus varies in accordance with a number of factors including the rate of absorption of moisture by the material being glued, the temperature of the material being glued, and the thickness of the glue coating applied to the material. The tests represented by the foregoing tables are purposely made under conditions extending the setting time to afford a better comparison of the effect of setting accelerators. The setting times in these tables, however, are directly comparable to commercial gluing operations such as the high-speed production of paper containers. The casein glues of my invention are particularly suited for the rapid gluing of paper layers, as in laminated articles, the gluing of lapped seams, and the like, but these glues can also be used for many other purposes where a quick setting glue is desired. In addition to the above mentioned advantages of casein glues for paper containers, such as greater water-resistance and elimination of objectionable odour, casein glues have a distinct advantage over ordinary hide glue of producing a laminated paper product which has a higher intial rigidity and may be handled readily without crushing when it first comes from the gluing machine. The casein glues, as stated above can be used cold (i. e. at room temperature), whereas with the hide glue and other glues heretofore commonly used on these rapid tube-winding machines, it was necessary to provide a "hot gluepot," which was objectionable.

The terms and expressions which I have employed are used as terms of description and not of limitation, and in using such terms and expressions, I do not mean to exclude any equivalents of the features shown and described or portions thereof, since it will be understood that various modifications are possible within the scope of the invention claimed.

The term "alkaline earth oxide" used herein is intended to include the corresponding hydrated oxide (hydroxide).

I claim:

1. A dry base adapted for being mixed with water to produce a quick setting liquid cold casein glue, said base comprising milk-casein as its major ingredient, a substantial amount but less than 12% of an alkaline earth oxide, an alkaline solubilizing agent consisting of a fixed alkali compound to act as a solvent for said casein, and a compound of zinc in an amount capable of accelerating the setting properties of the liquid glue by chemical action.

2. A dry base adapted for being mixed with water to produce a liquid quick setting casein glue, said base containing milk-casein as its major ingredient, a substantial amount of hydrated lime which is less than about 12%, an alkaline solubilizing agent adapted to serve as a solvent for the casein, and about 0.1 to about 5% of a water-soluble zinc compound as a setting accelerator.

3. A dry base adapted for being mixed with water to give a liquid quick setting cold casein glue, said base comprising milk-casein as its major ingredient, an amount of hydrated lime which is substantial but less than about 12%, an alkaline solubilizing agent which, when water is added, acts as a solvent for the casein, and about 0.1 to about 5% of a compound of zinc as a setting accelerator.

4. A dry base adapted for being mixed with water to form a quick setting liquid casein glue, said base comprising milk-casein as its principal and largest ingredient lime and an alkaline solubilizing agent for said casein, and a zinc salt for accelerating the setting action of the glue.

5. A dry base which can be mixed with water to form a quick setting liquid cold casein glue, said base comprising milk-casein as its largest ingredient, less than 12% of lime, an alkaline alkali-metal salt to serve as a solubilizing agent for the casein, and about 0.1% to about 5% of a water-soluble compound of zinc as a setting accelerator.

6. A dry base adapted for being mixed with water to produce a quick setting liquid spreadable cold casein glue, said base comprising milk-casein, as its largest component, together with lime, sodium salts, urea and about 0.1% to 5% of a compound of zinc as an accelerator of the setting time of said glue.

7. A quick setting liquid glue, containing water and the reaction products of casein, hydrated lime, an alkaline salt of an alkali metal for dissolving the casein and a zinc compound selected from the group consisting of zinc hydroxide, zinc oxide, zinc salts and zincates, the casein being the largest of the solid components, the hydrated lime calculated as calcium hydroxide, being not over 12% of the sum of all the solid components and the zinc compound being between about 0.1% and 5% of the sum of all the solid components, which glue when applied in a cold state to paper, grips the paper much faster than the same glue but with the zinc compound omitted.

LAWRENCE BRADSHAW.