On the Alkalinity of Casein glue.

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抄 錄

カセイン膠のアルカリ度に就いて

市販カセイン膠の成分と膠着力を求めたり次にカセイン膠の膠着力と可溶性アルカリ度との關係を知りカセイン膠のアルカリ度は變數にして、カセインと結合してカセネートを成生する以外膠着材面をアルカリ化する役目を有し其のアルカリ化面成生の適當なる時に膠着力強大なりとす、又カセイン膠の變質はアルカリ度を減少し、「ナトリウム、タングステン」塩化ナトリウム、硼砂、「ナトリウム、ハイポサルファイト」及其他少量の塩類の混合は其の減退を阻止する能はず油は比較的有効なりとす。

Compositions of the Commercial Casein Glues.

The casein glues are generally adopted for the gluing of timber. They contain casein 40—55%, calcium salt, and sometimes a small quantity of natrium salt. The composition is shown in Table I.

The methods of analysis. There are no recognized methods of analysis for casein glue, so that I have adopted the methods, with some modification, which have served as the basis for the specificaitons for the purchase of casein used by Bureau of Aircraft Production. (Browne. J. Ind. Eng. chem. 11, (1919) 1019).

They were proposed at first by Höpfner and Burmeister (chem. Ztg. 36, (1912) 1053) and were modified somewhat for the work at the Forest Products Laboratory of the U.S. Forest Service at Madison, Misconsin.

TABLE I. Compositions of Commercial glues.

Species		Fineness %	Moisture %	Ash moisture-free %	Alkalinity moisture, casein, fat-free	Fat moisture-free %	Nitrogen moisture-free %	Casein (N×6.38) moisture-free %	Inorganic matters in ash. Large quantity	Small quantity
Pactol No. I.	United Chemical Corp. 39, Victoria Street London. S.W.I.	69.5	9.78	29.6	133	0.208	8.79	55.0	Ca. Na.	Fe. Al. Mg. K.
Certus	Merkel Co. Hamburg Germany	44.2	11.6	33.5	121	0.515	6.93	44.2	Ca. Na.	Fe. Al. Mg. K.
Napco	The Monite Water Proof Glue Co. Menneapolis Minnesota, U.S.A.	51.7	10.7	40.6	185	0.506	6.52	41.6	Ca. Na. Mg. Fe.	
Lactocol	Lactocol Ltd. 1, Central House Wembley. Hiel. N.W.	40.3	13.7	31.8	106	0.385	7.03	44.8	Ca. Na.	K. Mg.
Casco	The Casein Manufacturing Co. Park Row Building 15, Park Ros. N.Y.	54.1	12.1	19.9	86	0.437	8.11	51.7	Ca. Na.	Mg.K.Fe. Al.
Colle. R.G.	Le caseum Francais 11, Rue de Charenton, Paris	53.8	7.33	39.4	202	0.696	7.41		Ca. Na. Al.	Fe. Mg.
Caseum	Caseum Francais 30, Bis Avenue Victor-Hugo Aubervillers, France.	62.9	14.3	40.5	189	0.906	6.94		Ca. Na.	Fe. Al. Mg.

Fineness. The portion passing through the Tyler standard 100 mesh shieves (opening 0.147 m/m) is weighed and reported as percent passing 100 mesh.

Moisture. This is most accurately determined weighing out a 3. gs. sample in a glass-stoppered weighing bottle, heating to constant weight in a vacuum oven at 70° to 80° c, cooling in a disicator, and weighing. The calculation is reported as percentage for moisture-free sample.

Ash. A 3, gs. sample is accurately weighed out in a small crucible and carefully charred over the low flame of a Bunsen burner. When completely carbonized, it is placed in an electric muffle furnace and heated at a dullred heat (not order 600° c) until the ash is white, or at least slightly gray and weight is constant. The results are reported on a moisture-free basis.

Fat. G. T. Bray and F. Major have discussed the various methods of determining fat in casein and obtained the best result (J. Soc. chem. Ind. 42, 106—107). I adopted this method for determining fat in casein glue, with some modification, as follows: the casein glue is extracted with ether and the ethereal solution dried over calcium chloride. The solvent is distilled off and the residue dried at 100°C to constant weight. Then the residue is extracted with gasoline which is in turn removed and the residue dried as before. The resulting weight of gasoline soluble matter is reported as moisture-free fat content.

Nitrogen. A 2 gs. sample is introduced into a Kjeldahl's flask and 10 gs. of sodium sulphate, 20 c.c. of concentrated sulphuric acid and a small crystal of copper sulphate are then interoduced. The flask is then adjusted obliquely over a gas flame and the contents boiled briskly until the liquid, which first darkens in colour, becomes clear and colorless. When the decomposition is complete (1/2—1 hour), the flask is left to cool and the contents then diluted with 200 c.c. of water. The flask is now attached to the distilling apparatus. A 0.5 g. of granulated zinc and 200 c.c. of caustic soda solution (1 : 1) are introduced into the flask. The liquid is then boiled briskly until no more ammonia is evolved. The ammonia gas is caught by 30 c.c. of sulphuric acid (N/2) and the excess acid is back titrated. The results are reported on a moisture-free basis.

Alkalinity. A 0.5 g. sample is mixed with 30-50 c.c. of distilled water in 250 c.c. flask, shaken well, and the solution titrated at once with N/10 HCL solution, using 0.5 c.c. of alcoholic phenolphthalin solution (1 g. per 100 c.c.) as indicator.

TABLE II. The compositions of Casein glues. (Mark "0" shows the component which is contained in the glue.)

	U.S. 1506201	U.S. 1506202	U.S. 1506203	Brit. 187200	Air Board Specif.	U.S. 1291369	U.S. 1310706	Revue des Produits chemiques		Crosspletsch's Adhesive	Jeromin's Caseinadhesive		Halls' Casein glue		Water Proof glue	Liquid Casein glue	Powdered Casein glue	Casein and Borax glue		Solid Casein adhesive	Casein glue for card board Boxes	
Casein	% 50-75	% 50-75	% 50-75	% 70	part 100	100 part	part 100	0	part 150	0	0	lbs. 25 } 50	part 50-60	0	Albumen	part 10	part 15-20	0	0	0	part 45	0
$Ca(OH)_2$	10-20	6-12	–	ca.2	18	12~22	18	–	–	–	0	(lime water) 75	–	–	0	0	–	0	–	–	–	–
CaO	–	–	10-20	–	–	–	–	–	–	–	–	lime 2.5	20-30	–	–	–	–	–	–	0	–	–
Na-phosphate	5-15	–	–	–	–	–	–	–	–	–	–	–	20	–	–	–	–	–	–	–	–	–
Na-hyposulphite	2-8	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
$CaCL_2$	2-5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Castor oil	1-4	–	–	–	–	–	–	–	–	0	–	–	–	–	–	–	–	–	–	–	–	–
Kerosene	2-7	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Dextrin	–	2-8	2-8	–	–	–	–	–	–	0	–	–	–	–	–	–	–	–	–	–	–	0
Starch	–	3-12	–	–	–	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
MgO	–	10-20	–	–	–	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
NaOH	–	2-8	–	–	11.0	–	11.0	–	–	–	–	–	–	–	0	0	–	–	–	–	–	–
NaF	–	–	2-10	–	3.0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
NaCl	–	–	1-5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Oil	–	–	1-4	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Resin	–	–	1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Na-silicate	–	–	–	27.3	–	70	–	–	–	–	0	–	–	–	–	–	–	–	–	–	–	–
Camphor	–	–	–	0.1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Na-tungstate	–	–	–	0.25	–	–	–	–	75	–	–	–	–	–	–	0	–	–	–	–	–	–
Paraffin oil	–	–	–	–	1.5	–	1.5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Water	–	–	–	–	–	130~280, 90	–	12	–	–	–	25	–	–	–	6, % 80	–	–	100 } 0	–	64	–
Borax	–	–	–	–	–	–	–	1	–	–	–	–	–	–	–	–	1-4	0	6 }	–	1	–
Linseed oil	–	–	–	–	–	–	–	–	–	0	–	–	–	–	–	0	–	–	–	–	–	–
Alum	–	–	–	–	–	–	–	–	–	0	–	–	–	–	–	–	–	–	–	–	–	–
Sugar-candy	–	–	–	–	–	–	–	–	–	0	–	–	–	–	–	–	–	–	–	–	–	–
Water glass	–	–	–	–	–	–	–	–	–	0	–	17.5	–	–	–	–	–	0	–	–	–	–
Na-sulphite	–	–	–	–	–	–	–	–	–	–	–	–	10	–	–	–	–	–	–	–	–	–
Ammonia	–	–	–	–	–	–	–	–	–	–	–	–	–	0	–	few 0	–	–	–	–	1	–
Formaldehyde	–	–	–	–	–	–	–	–	–	–	–	–	–	0	–	–	–	–	–	–	–	–
KOH	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	–	–	–	–	–	–	–
Na_2CO_3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	–	2-8	–	–	–	–	–
K_2CO_3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	–	–	–	–	–	–	–
Borate of Na or K	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	–	–	–	–	–	–	–
Carbolic acid	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	–	–	–	–	–	–
Thymol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	or 0	–	–	–	–	–	–
$CaCO_3$	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	–	–	–	–
Ca-tannate	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	–	–
$MgCl_2$	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0
Na_3PO_4	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
K-Silicate	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Rosin	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Wood ashes	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Sea sand	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Quartz-sand	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Tannin	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Saw-dust	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Sand	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Brick-dust	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Trioxymethylene	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Gum-arabic	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

	Casein solution	U.S. 821620	Eng. Patent 24662	Glue Powder	French Patent 370940	Germ. Patent 270200	Lehner's Casein putties	Lehner's Casein putties		Casein Putty	Casein cement	Casein cement for glass	Casein cement for Metals	Casein & water-glass cement	Washable cement	Wenk's Casein cement	Pitch Barm	Casein Stopping	Casein cement for stone	Insoluble casein		
Casein	part 1	0	lbs. 300-500	0	part 100	0	part 100	part 12	0	part 200	part 1	part 100	part 8	part 10	ounce 18	0	0	part 1.5	0	0	part 47	part 5
$Ca(OH)_2$	–	–	–	0	–	–	25	50	–	–	–	20 (Skin-milked cheese)	–	–	–	0	–	water soluble casein	0	–	29.5	–
CaO	–	–	–	–	–	Alkali	–	–	–	40	–	–	–	–	9	–	–	–	–	–	–	1
Na-phosphate	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Na-hyposulphite	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
$CaCL_2$	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Castor oil	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Kerosene	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Dextrin	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Starch	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
MgO	–	–	–	–	–	–	–	–	0 (Calcined)	–	–	–	–	–	–	–	–	2 (calcined)	–	–	–	–
NaOH	–	0	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0	–	–	–	–	–
NaF	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
NaCl	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Oil	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Resin	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Na-silicate	–	–	–	–	80	–	–	–	Alkali Silicate	–	–	–	–	–	–	–	–	–	–	–	15.5	–
Camphor	–	–	–	–	–	–	–	–	–	1	–	–	–	–	–	–	–	–	–	–	–	–
Na-tungstate	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Paraffin oil	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Water	1-3	–	–	–	600	–	200	–	–	–	–	50	–	–	pints 7	–	–	–	–	–	–	–
Borax	–	–	10	0 (or Na-silicate)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Linseed oil	–	–	–	–	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Alum	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Sugar-candy	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Water glass	–	–	–	–	–	–	–	–	–	–	3	–	–	60	–	–	–	–	–	–	–	–
Na-sulphite	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Ammonia	–	–	–	–	–	–	–	–	–	–	–	–	–	–	pints 0.5	–	–	–	–	–	–	–
Formaldehyde	–	0 or	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
KOH	–	0	–	–	–	–	–	–	–	–	–	–	–	–	–	or 0	–	–	–	–	–	–
Na_2CO_3	–	–	–	–	12	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
K_2CO_3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Borate of Na or K	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Carbolic acid	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Thymol	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
$CaCO_3$	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	8	–	–	–	–
Ca-tannate	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	1% of gallic-acid, cutch, quercitannic acid.	–	–	–	–	–	–
$MgCl_2$	–	–	–	–	100	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Na_3PO_4	0.1-0.12	–	–	–	or 80 (Na-silicate)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
K-Silicate	–	–	–	–		–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Rosin	–	–	–	–	–	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Wood ashes	–	–	–	–	–	–	20	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Sea sand	–	–	–	–	–	–	–	50	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Quartz-sand	–	–	–	–	–	–	–	–	–	–	–	–	10	–	–	–	–	–	–	–	–	–
Tannin	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Saw-dust	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	2	–	–	–	–
Sand	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	} 0	–	–	–
Brick-dust	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	}	–	–	–
Trioxymethylene	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	–	–
Gum-arabic	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	8.0	–

The number of cubic centimeters of N/10 acid used up by one gram of moisture, fat, casein-free casein glue is called the " total alkalinity " of the sample.

A 1.0 g. sample is mixed with 200 c.c. of destilled water and are shaken at constant temperature 25°c for 3 hours and filtrated through filter paper.

A 10 c.c. of filtrate is titrated with N/10 HCL solution as above. The number of cubic centimeters of N/10 acid used up by one gram of moisture, fat, casein-free casein glue is called the " soluble alkalinity " of the sample.

Basic salts in casein glues.

The various kinds of basic salts are mixed in commercial casein glues; the calcium salt is the main basic salt in casein glue, and magnesium oxide, sodium hydroxyde, potassium or sodium silicate, borax, sodium carbonate, water glass etc. are sometimes mixed. Table II shows the compositions of casein glues which are reported in books or literature.

The relation of joining pressure to joining power.

Animal glues increase the joining power very rapidly with increase in joining pressure up to about 200 lbs. per sq. in. Beyond this point the strength continues to increase gradually to 1000 lbs. per sq. in., and it is evident that if maximum strength is desired a high pressure showed be used-certainly not less than 200 lbs. to the sq. in. (R. H. Bogne. Chem. and Met. Eng. (1920) 197.)

Casein glues do not decrease strength as rapidly as animal glues in the case of low pressure, and do not increase strength rapidly with increase in joining pressure. But the joining power of casein glue increases gradually with increase in joining pressure up to about 15 kg/cm^{-2}, it coincides with animal glue. It appears that the joining pressure which must be above 15 kg/cm^{-2} depends more on the wood than on the glue.

The joining powers of commercial casein glues.

Shear strength is measured to determine the joining powers of casein glues, based upon the testing method of military specification for aircraft materials, that is, walnut test pieces whose joined areas are 6.25 sq. cm., are selected for joining materials.

Commercial casein glues are mixed with distilled water in proportion as in Table III. and ground in the glass-mortar until the milky adhesive substances are obtained, then test pieces are glued under 15 kg/cm^{-2} pressure for 24 hours and tested a week after removing pressure. The results are as Table IV.

TABLE III. Proportion of glue and water.

Species	Casein glue	Water
Napco	100	180–200
Casco	100	200–225
Caseum	1	1
	450	1000
Certus	1 lb	0.756 litre For soft wood
	1 lb	0.666 ,, For hard wood
Lactocol	100	150
Pactol	100	170
Colle. R.G.	100	200

TABLE IV. The joining powers of commercial casein glues.

Species	Joining power (kg/cm²)
Pactol	59 (49–67)
Certus	61 (54–66)
Napco	58 (34–69)
Casco	62 (57–68)
Caseum	57 (52–65)
Colle. R.G.	63 (52–71)
Animal glue	59 (54–64)

Apparatus for decomposition study of casein glue.

Casein glue decomposes ultimately when exposed to a damp atomosphere for a long time. For many months studies have been under way at the Forest Products Laboratory to discover the cause of this decomposition, and the conclusion has been reached that the decomposition of ordinary alkaline casein glues is not due to the action of bacteria or molds. It appears to be due entirely to chemical action of the alkali in the glue. Moisture and suitable temperature are necessary to decompose casein glue, therefore, I used as the decomposition apparatus an incubator, the temperature of which was 25–35°, and humidity about 95%. (Fig. 1.)

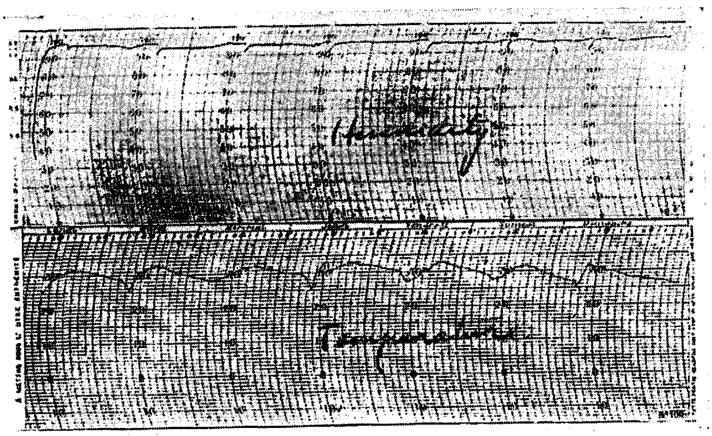

Fig. 1.

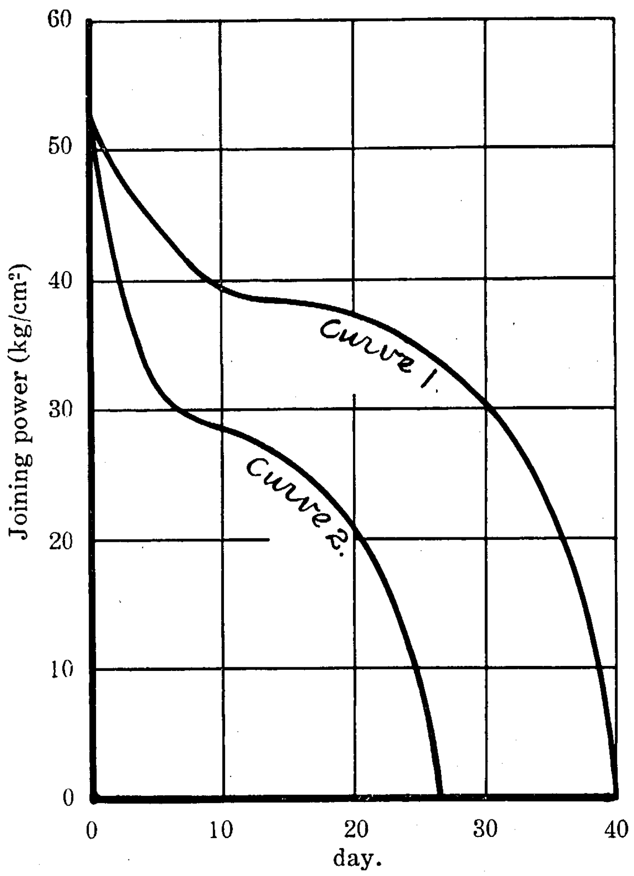

Fig. 2.
The decreasing curve of the joining power of Pactol in the incubator.

The casein glue was put in the incubator and the test pieces glued with this decomposed casein glue from time to time to determine the decreasing of the joining power (curve 1.) On the other hand, many test pieces which were joined with the new casein glue, were put in it also, and their shear strengths measured together from time to time with the joining power of the decomposed casein glue (curve 2.) The result was as Fig. 2. The joining power decreased notably after five or six days and was lost completely after four or five weeks.

TABLE V. Hardness of commercial casein glues.

Species	Hardness	Shear Strength kg/cm^2
Pactol	25	59
Certus	30	61
Napco	41	58
Casco	41	62
Caseum	34	57
Colle R.G.	35	63

The relation between the hardness and shear strength of casein glues.

The hardness of the coagulated casein glues are determined to know how it depends on the joining power. The result concludes that the hardness of the coagulated casein glues depend on their compositions and do not correspond to the joining power. To determine the hardness, the casein glue was coagulated in the walnut piece as Fig. 4 and tested with shore's tester.

The casein glue of the same composition shows the shear strength to decrease with the decrease in its hardness. Fig. 3 shows the hardness and strength of caseum which is held in an incubator for fifteen days.

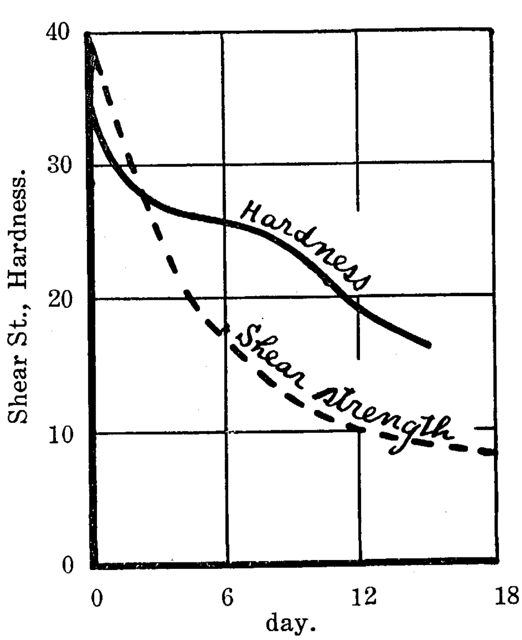

Fig. 3.
The hardness and strength of caseum.

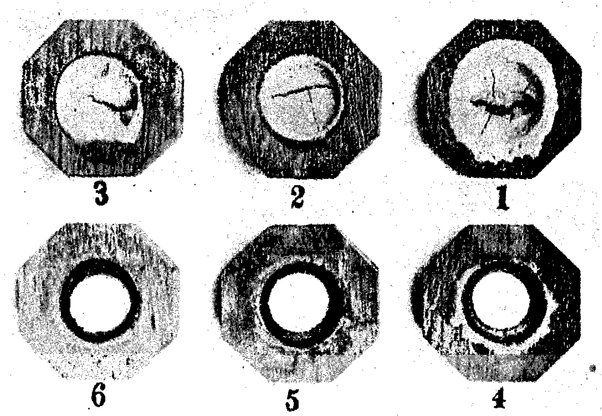

Fig. 4.

No. 1. Original. No. 2. 3 Days. No. 3. 6 Days. No. 4. 9 Days. No. 5. 12 Days. No. 6. 15 Days.

The glue which was held for six days in the incubator, glued on the wood and cracked in the direction of perpendicular to the grain, that is, we know that the gluing power on the wood is stronger than the coagulating power of caseum. But the glue which was held more than six days in the incubator, coagulated independent to the wood, that is, the coagulating power of caseum is stronger than the gluing power on the wood in this case. (Fig. 4.)

Purification of casein.

The commercial casein is treated with just enough dilute ammonia water (about 5 c.c. of strong ammonia diluted to 100 c.c.) to dissolve the casein, forming a solution neutral to litmus. The solution is diluted with distilled water and reprecipitated by dilute acetic acid. Much less acid is required for the second and subsequent precipitations than for the fast. The precipitate is washed free from acid as before and redissolved in diluted ammonia.

Reprecipitation and redissolving should be performed five or six times (Allen's commercial org. analysis. Vol. VIII P. 116 "Method of preparing casein"). The casein is washed with water, rubbed down fine with 97% alcohol, drained and washed with ether. This purified casein is used at the start of this research, and "Merc" pure casein is used in the middle of the testing.

TABLE VI. Properties of purified casein.

Moisture	Ash	Fat	Nitrogen	Acidity	
3.44	0.891	0.087	15.6	8.71	
10.00	4.0	1.0	14.25	10.5	Specification, U.S.A.
17.00	3.0	1.5	11.00	1.0 (HCl)	British specification

The method of analysis is based upon "The proximate analysis of commercial casein" (Brownc. J. Ind. Eng. chem. 11, (1919) 1099).

Variation of acidity of casein in the incubator.

A.I. Virtanen (Soc. Sci. Pennica commentations Physico-Math, I, No. 41. 1-13 (1923); Chem. Abst. Vol. 18, 2539) reported that Bacillus casei (casein bacteria) decomposed casein vigoronsly at 20°, provided the temperature of the culture was 40° for the first 24 hours of incubation.

The result was reported on the technical note of Forest Products laboratory that the decomposition of ordinary alkaline casein glues is not due to the action of bacteria or molds, and cultures of molds and bacteria could not be obtained from decomposed alkaline glues.

Did casein decompose in my apparatus? I measured the acidily of casein to determine it, and concluded that the casein did not decompose in the condition where the casein glue lost its joining power. (Fig. 5.)

Variation of alkalinity of $Ca(OH)_2$, CaO, and the mixed casein glue in the incubator.

Alkalinity of commercial casein glues are variable and stale glues have a lower alkalinity. Some commercial casein glues decrease their alkalinity to half of the first value in strage for three years. The decreasing of alkalinity of the casein glue is related distinctly to the joining power of the glue, and decreasing the alkalinity loses the joining power.

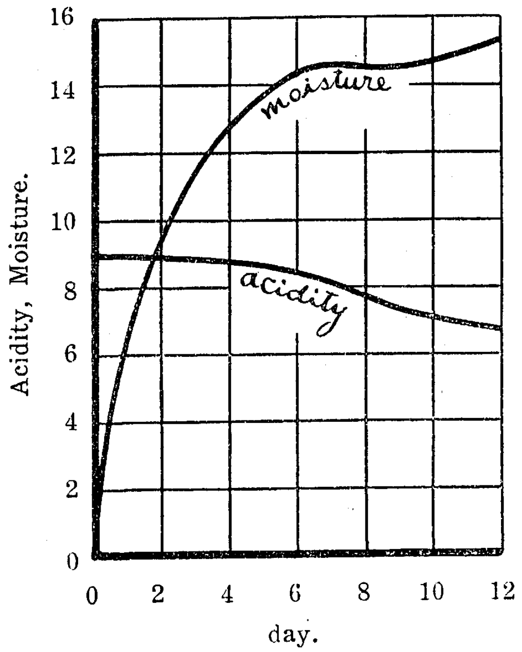

Fig. 5.

The variation of acidity and moisture of casein in the incubator.

Calcium oxide changes into calcium hydroxide and it absorbs carbon dioxide, forming calcium carbonate and water in the incubator. The alkalinity of casein glue is the difference between alkalinity of base and acidity of casein.

It appears that casein does not combine with basic salt in the measuring of alkalinity, the theoretical alkalinity of the mixed casein glue (casein 40%, $Ca(OH)_2$ 60%) is 270, and the experimental value is 262. When this casein glue is coagulated, mixed well with water and pulverized into fine powder to measure alkalinity again. This alkalinity decreases 231. Casein begins to combine with alkali, forming calcium caseinate when it is stirred sufficiently with water. Calcium caseinate does not decompose completely when alkalinity of casein glue is determined.

There are many divided opinions on the capacity of casein to combine with base. Long reported that one gram of casein combines with 9 c.c. of N/10, solution of bases, such as hydroxides or carbonates of sodium, potassium, lithium or ammonium (Jour. Am. Chem. Soc. 1907, 29, 1334) and Cohn published that one mol. sodium hydroxide combines with approximately 2100 grams casein; (Jour. Gen. Physiol. 5. 521–54; Chem. Abst. Vol. 17, 2589) and 735 grams casein not previously exposed to alkali or 535 grams casein previously saturated with base combine with one mol sodium hydroxide. Accepting 12.800 as the minimum molecular weight of casein there are approximately 18 acid groups and in addition 6 acid groups which are released in alkaline solution and casein contains 34 acid valencies (Jour. Gen. Physiol. 7. 45–79 (1924). Chem. Abst. Vol. 18. 3608).

If the decreasing of alkalinity of casein glue in combining casein with alkali is calcurated in basing of Long's combined capacity, it is about 18.

Variation of alkalinity of casein glue in vacuum chamber.

Casein glue in which 60% casein is mixed with 40% calcium oxide, is sealed in the tube of pressure 20m/m and this tube is held in the incubator for twelve days to determine its alkalinity. Alkalinity of casein glue does not decrease in this case. The decreasing of joining power of casein glue is due to the reducing of soluble alkali and the increasing of insoluble alkali in casein glue. Insoluble alkali injures the adhesive quality of casein glue, and soluble alkali recovers the joining power, therefore, the stale casein glue can be utilized again by addition of soluble alkali, though it does not obtain its original joining power.

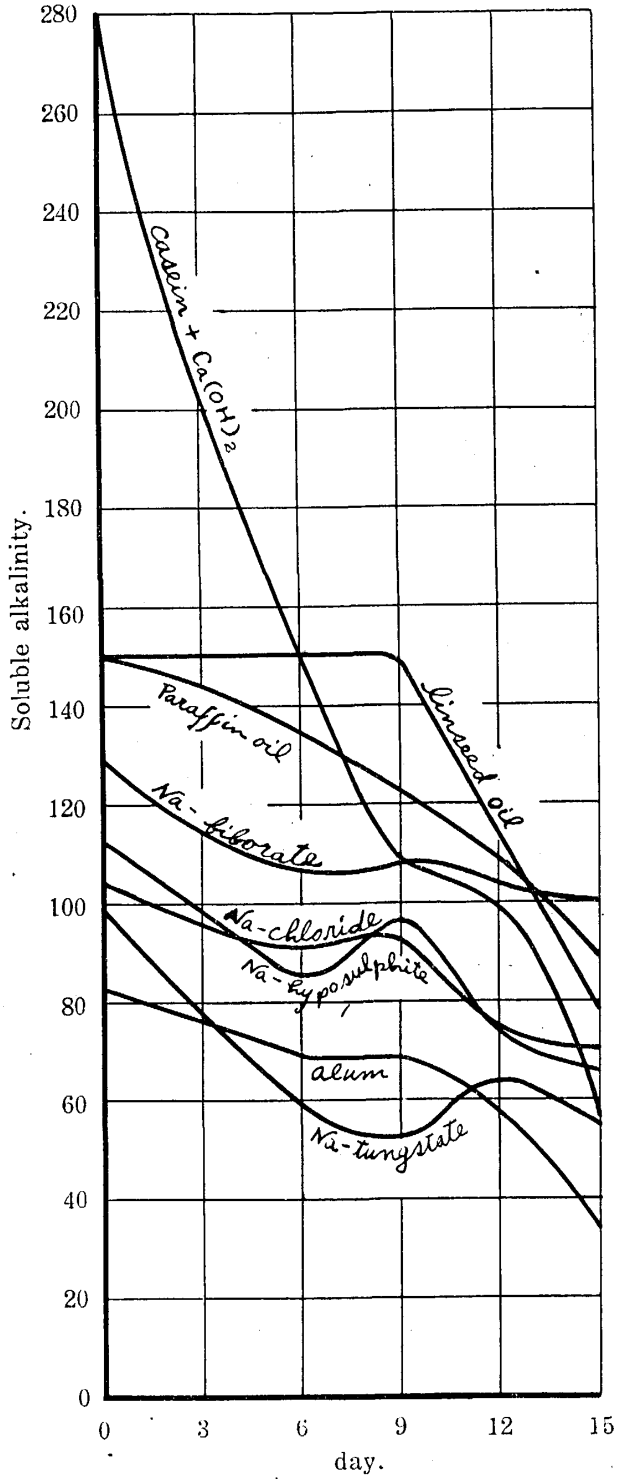

Fig. 6.

The variation of soluble alkalinity of casein glues.

Soluble alkalinity of casein glue.

It is convenient to know roughly the total alkalinity of casein glue in the decreasing of joining power, but difficult to measure it accurately. The soluble alkalinity is somewhat troublesome to measure but has an important rôle in the joining of wood and the less soluble alkalinity effects directly the joining power of casein glue. Casein glue desires to be no-reducing of soluble alkalinity for a long storking. For this purpose, 20% of alum, borax, sodium tungstate and other elements are added to the ca-casein glue (casein 50%, calcium hydroxide 30%) and the soluble alkaliniy of these mixed glues are determined.

The addition of other elements in the ca-casein glue lowers the soluble alkalinity of glue and the ca-casein glue which composition is casein 60%, calcium hydroxide 40%, has 270 soluble alkalinity and the addition of other elements 20% in this glue, (casein 50%, calcium-hydroxide 30%, other elements 20 %) reduces its value to 80–150. Oils reduce less than others in these elements and the addition of sodium tungstate, alum retards the staling of casein glue, but they lower the alkalinity of casein glue very remarkably. Soluble alkalinity is most important to produce the "alkalized surface" of timber and the addition of the elements which decrease its soluble alkalinity, therefore is insignificant. (Fig. 6.)

Hydroscopy of casein glue.

The hydroscopic property of casein glue is related to the reducing of the soluble alkalinity and depends upon the staling action. Ca-casein glue (casein 60 %, calcium hydroxide 40 %) absorps moisture gradually up to 15 %, and above this point, the rate of absorping increases in very slight degree.

When paraffin oil is added to casein glue, it retards the absorbing rate of moisture, and this glue absorps moisture gradually.

Fig. 7 shows the hydroscopic curve of the glue which is mixed with casein 62, Ca $(OH)_2$ 37, paraffin oil 1. The casein glues which are mixed with sodium hyposulphite, sodium tungstate are very hydroscopic.

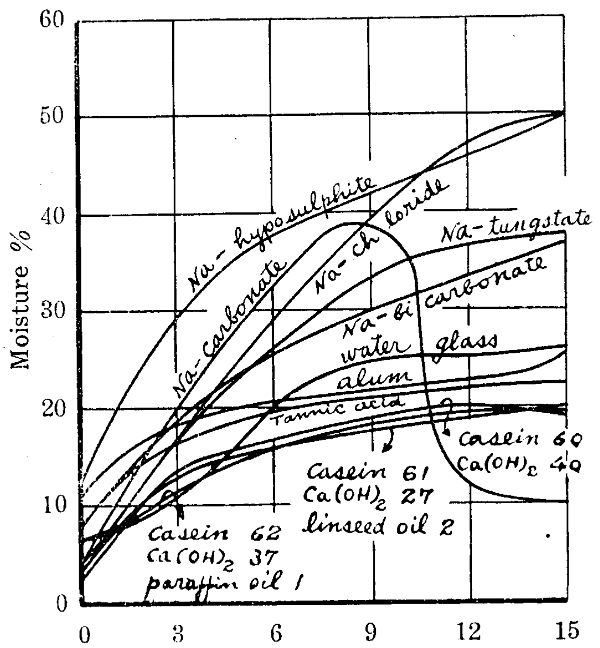

Fig. 7.
The hydroscopy of casein glues.

A little addition of oil prevents the staling and moisture absorption of casein glue. Paraffin oil and linseed oil are tested in this experiment; vegetable oil appears to be saponified somewhat and does not injure the joining power when glue is mixed with water. The shear strength of glue composed of casein 1000 gms, calcium hydroxide 16 mols, is 40 kg. per sq. cm. in addition of 8 % and is 27–65 kg. per sq. cm. in addition 16 % of linseed oil. I think, therefore, that there is no need to consider about the content of the two or three percentage of oil in casein glue.

On the alkalized surface of the timber.

The joining of glue is thought to be mechanical action, but there must be also chemical action on the casein glue. The reason that the joining power of casein glue is stronger generally than the power of animal glue, must be due to this chemical action. The explanation of this chemical reaction is still far from complete, but it appears to be true that the wood is alkalized by alkali of casein glue and produces the "alkalized surface." This alkalized surface serves as the joining mediation between caseinate and wood.

Walnut, Hinoki, Shioji are respectively treated with one normal hydrochloric acid and one normal sedium hydroxide for ten minutes, thirty minutes, one, two, and three hours at the temperature 50°C, and glued than with casein glue (casein 1000 gms, $Ca(OH)_2$ 16 mols) to determine their shear strengths. The strength of woods which are treated by acid is lower and from 45 to 60 kg. per sq. cm. The strength of woods which are treated by alkali for 10-30 minutes is very great and shows the value of 56-88 kg. per sq. cm. and longer treating, lower strength.

It is important that the alkalized surface of timber must be produced in suitable condition to be glued strongly. There is lower strength if the wood is treated severely with alkali.

We can readily explain the indistinct phenomena when an "alkalized surface" is taken into consideration. Increasing the insoluble alkali of casein glue lowers its joining power but it must be more of the producing of "alkalized surface" than of injuring itself to coagulation of casein glue, and the soluble alkalicity of casein glue predicts its joining power. Though a weak basic alkali, such as borax, alum, and magnesium oxide retards the staling of glue in storking and solubles casein in its solution, they are too weak to alkalize the timber enough. I think this is one of the reasons why they do not give the strong joining power.

Capacity of alkali in casein glue.

Casein glue must contain the alkali which alkalizes the timber, forming the alkalized surface, in addition to that combined with casein, and casein glue stales in storking, changing soluble alkali into insoluble alkali. Therefore, there must be at least the capacity of alkali which is necessary to form caseinate, alkalized surface, and may change into insoluble alkali. It is necessary that the capacity of the last alkali is as little as possible, and that other elements be added to provide the staling and to eliminate the insoluble alkali. For this purpose, the addition of a little oil is effective. It will be alone the capacity of alkali which is necessary to form a caseinate and alkalized surface if the casein glue is prepared when it will be employed.

Conclusion.

1. The joining pressure does not effect the joining power of casein glue as it does the animal glue.

1. The hardness of the coagulated casein glue depends on its composition and does not correspond to the joining power. The joining power of the same composed glue decreases with the decrease in its hardness.

1. The decreasing of joining power of casein glue is due to the reducing of soluble alkali and the increasing of insoluble alkali in casein glue.

1. Insoluble alkali injures the adhesive quality of glue and we can estimate roughly the joining power by the determination of alkalinity.

1. The addition of sodium tungstate or alum in the ca-casein glue retards the staling of glue, but lowers the soluble alkalinity and gives a lower joining power.

1. Calcium casein glue which contains sodium hyposulphite, or sodium tungstate, is very hydroscopic and a little addition of oil prevents the absorption of moisture.

1. There are both mechanical and chemical action in the gluing of the casein glue and the timber is alkalized by alkali of casein glue, producing the "alkalized surface" and the joining power of casein glue depends on the production of an alkalized surface.

1. Casein glue must contain the amount of alkali which is necessary to form the caseinate, alkalized surface, and to change into insoluble alkali in storking also.