and higher molecular weight free alcohols present sometimes cause emulsification which makes the separation of layers difficult. Methanol, to the extent of 5-10% by volume, will also prevent emulsification at this stage. Acidification with a mineral acid will cause sharp separation of the liquid layers, but the product obtained upon distillation will contain whatever fatty acids were present in the original oil together with fatty acids formed by saponification of any unreduced glyceride during the hydrolysis step.

The iodine values of the alcohols were determined with Wijs reagent. A reaction time of about two hours was used in this determination.

Ultraviolet Analyses. A Cary recording spectrophotometer was used to determine the ultraviolet absorption of the unsaturated alcohols dissolved in absolute ethanol. Absorption bands characteristic of two to six conjugated double bonds were detected. Five and six conjugated bond types were present in only trace amounts. The percentage transmissions were read at 233, 281, 270, 320, and 307 millimicrons as recommended by Bradley and Richardson (2). The average wavelengths at which maximum absorption actually occurred were at 233, 279, 269, 316, and 301 millimicrons. The amount of conjugation was estimated by calculation from the ratio of the specific extinction of the sample to the specific extinction of the pure conjugated C-18 acids as given by Bradley and Richardson. No attempt was made to correct for background absorption of the carboxyl group or for the effect of the background absorption of the triene or tetraene on the diene or triene, respectively (3). Since no pure alcohols with conjugated bonds were available for use as reference standards, the specific extinctions of the conjugated C-18 acids were used. Therefore the results can be considered to be semi-quantitative only. Interference due to trace amounts of xylene would not be appreciable (9).

Hydrogenation. The menhaden alcohol and 2-3% Raney nickel catalyst were placed in a three-liter, three-neck flask equipped with an air-driven stirrer, a nitrogen inlet, a hydrogen inlet, and an outlet connected to a wet-test meter. The flask was immersed in a water bath. Absorption of hydrogen was sufficiently rapid for partial hydrogenation purposes over the temperature range from 25-60°C. After the apparatus had been flushed with nitrogen the hydrogen was passed into the flask slowly through a calibrated rotameter while the contents were being stirred rapidly enough to fill the flask with a fine spray. In this manner it was possible to feed a predetermined amount of hydrogen and to stop the hydrogenation at any point to give a product with the desired amount of residual unsaturation.

Summary

Menhaden oil, a low cost fatty acid glyceride containing a high percentage of polyunsaturated material, has been reduced by means of sodium with 86-88% yields of alcohols having a correspondingly high degree of unsaturation. It has been shown that about one-half of the polyolefinic unsaturation isomerized during the sodium reduction to conjugated double bonded structures. The higher unsaturated alcohols were selectively hydrogenated to give a colorless product which was substantially odorless and which had an average of one double bond per molecule.

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Preparation and Utilization of Cottonseed Meal Glue for Plywood[1]

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THE utilization of cottonseed meal or cake in the preparation of plywood glues has been reported in the patent literature (1,7-12,14,16-18). These patents are concerned primarily with glue formulation and do not give processing data for the preparation of plywood using cottonseed meal glue or shear strength data for the glue joints. Other publications on the viscosity characteristics of cottonseed protein dispersions have indicated that the viscosity of the dispersions tend to decrease as the dispersions are aged (2, 6). These articles indicate the unique viscosity properties of cottonseed protein as compared to other vegetable proteins whose dispersions usually increase in viscosity as they are aged. Consequently the possibility of developing a cottonseed meal glue with a long "working life," i.e., a dispersion having low viscosity for several hours, seemed likely.

The purpose of this report is to present data on the formulation of cottonseed meal glue, processing information for the preparation of plywood using the glue, and shear strengths of the glue joints.

Experimental

Cottonseed Meals. The hexane-extracted meal was prepared by removing the oil from flaked cottonseed meats by means of commercial hexane as described in a previous publication (15). The hydraulic-pressed and screw-pressed meals were prepared by express-

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TABLE I

Analyses of Meals[a]

Material	Protein[b] %	Lipids %	N Solubility[c] % Total N
Hexane-extracted meal	56.1	1.53	80
Hydraulic-pressed meals			
No. 1	44.6	6.05	20.2
No. 2	45.1	5.91	39.0
Screw-pressed meals			
No. 1	45.8	3.82	42.7
No. 2	46.3	5.02	50.4

[a] Calculated on a moisture-free basis.
[b] Protein equals nitrogen content × 6.25.
[c] Solubility determined by suspending 2.5 grams of meal in 100 ml. of 0.5 M NaCl for 3 hours at 25°C.

ing the oil from cottonseed meats in the conventional manner (4). The temperatures and pressures used in expressing the oil were carefully controlled to yield meals containing protein with high solubility. The analyses of the meals are given in Table I.

Method of Testing. Birch plywood panels, straight grained, 3-ply, 3/16 in., 12 by 4 in. with the center veneer cross-laid, were prepared by spreading the glue on the veneer by means of a typical plywood glue spreader, assembling, and cold and/or hot pressing the glued veneer. Closed assembly time was approximately 10 minutes. Test pieces, 3/16 in., 3¼ by 1 in., cross-slotted to give a center section of 1 square inch, were cut from the panels. The tensile shear strengths of the test pieces were determined as specified in A.S.T.M. Designation D805-45T (3, 5) under dry (conditioned at 75°F. and 32% relative humidity for 6 days) and wet (immersed in water for 48 hours at 77°F. prior to testing) conditions. Shear strengths reported are averages of at least 20 values. Experiments were done in duplicate.

Wood failure was evaluated by visual observation. Any failure in the wood was reported, and the percentage of the total number of pieces tested showing wood failure was calculated.

The viscosities of the glue mixes were measured with a torsional wire viscometer (13) at a temperature of 77°F. The viscometer was calibrated by means of standard viscosity oils provided by the National Bureau of Standards.

The amount of glue spread per 1,000 square feet of glue line was determined by weighing the amount of spread per 96 square inches of glue line and calculating the spread for 1,000 square feet of glue line.

Results and Discussion

Preparation of cottonseed meal glue consists essentially of dispersing the protein contained in the meal in an aqueous alkali solution and adding other chemicals to improve the tack, spreading characteristics, and water-resistance of the glue. The procedure used for the preparation of all glue formulations reported is, as follows: cottonseed meal, which had been ground to pass a 200-mesh screen, was suspended in water in a ratio of 4 parts of meal to 3 parts of water. The mixture was stirred for about 15 minutes to produce a uniform paste. Prior to the addition of other reagents, the chemicals were also mixed with water; then they were added to the meal-water paste. Following the reaction to produce the glue, additional water was mixed with the product to yield a dispersion having the desired solids content. Then the glue was thoroughly blended for about one hour to give a smooth and uniform dispersion.

TABLE II

Effect of Processing Conditions on the Shear Strengths of Cottonseed Meal Glue Joints[a]

Test No.	Hot pressing conditions			Shear strength[b]	
	Time, min.	Pressure, p.s.i.	Temperature, °F.	Dry, wood failure (lbs./sq. in.,%	Wet, wood failure (lbs./sq. in.,%
1[c]	....	.....	.....	239–28	88–0
2[d]	....	.....	.....	245–33	130–0
3	10	150	181	250–30	107–0
4	20	150	181	266–36	109–0
5	30	150	181	240–23	115–0
6	10	200	181	253–43	127–0
7	10	150	201	285–40	130–10
8	20	150	201	205–26	128–0
9	30	150	201	198–23	123–0
10	10	200	201	230–13	165–13
11	10	150	237	238–6	155–0
12	20	150	237	300–36	153–15
13	30	150	237	270–20	148–27
14	10	200	237	412–70	215–43
15	20	200	237	241–10	136–0
16	2	200	237	255–5	.....
17	4	200	237	274–15	.....
18	6	200	237	278–25	146–10
19	8	200	237	284–20	133–20

[a] Glue composition: hexane-extracted meal, 100 parts; NaOH, 4 parts; Na_2SiO_4, 15 parts; CS_2-CCl_4, 3 parts; $Ca(OH)_2$, 15 parts; H_2O, 335 parts; pH 12. Glue viscosity: 640-650 poises at one hour. Glue spread: 19 pounds of glue (dry basis) per 1,000 sq. ft. of glue line. Cold pressing conditions: assembled plywood pressed at 77°F. and 150 p.s.i. for 1,440 min. prior to hot pressing, except where otherwise noted.
[b] Average of 20 values determined for 3-ply test pieces by tensile shear tester at dry (conditioned at 75°F. and 32% relative humidity for 6 days) and wet (immersed in water for 48 hours at 77°F. prior to testing) conditions.
[c] Cold pressed only at 77°F. and 150 p.s.i. for 1,440 min.
[d] Cold pressed only at 77°F. and 200 p.s.i. for 1,440 min.

Effect of Processing Conditions. The data in Table II show the effect of processing conditions on the shear strengths of cottonseed meal glue joints. It is clear that cold pressing of the panels followed by hot pressing significantly increases the wet shear strength of the glue joint (compare tests 1 to 3-15). It may also be concluded from the data presented in Table II that wet shear strength may also be increased by changing the total pressure applied to the panels during cold pressing; however the wood failure values were not affected. Compare Tests No. 1 and 2. Comparisons of Tests No. 7 and 10 to 15 show that Test No. 14, prepared by cold pressing at 77°F. and 150 p.s.i. for 1,440 minutes followed by hot pressing at 237°F. and 200 p.s.i. for 10 minutes, yielded a panel having good test values. At lower temperatures and longer times of hot pressing, at lower temperatures and lower pressures of hot pressing, and at the same conditions of pressing as Test No. 14 but for longer times of hot pressing, panels having lower test values were received. In general, the higher the temperature of hot pressing of the panels at an optimum time of pressing produced a glue joint having satisfactory wet shear strength and wet wood failure values. The higher temperature of hot pressing for a short period of time gave a glue joint having the maximum dry shear strength and dry wood failure values.

Effect of Urea Solvent. The effect of dispersing the protein contained in the meal in aqueous urea solution followed by addition of formaldehyde on the shear strengths of cottonseed meal glue joints is shown in Table III. These data show that cottonseed meal glue, having only a slightly alkaline reaction, can be made and used to prepare glue joints with satisfactory shear strength and wood failure values. These data are of special significance for certain plywood glue users who require a glue, that has a low pH, to minimize discoloration of the veneer.

TABLE III

Effect of Urea Solvent for Cottonseed Meal and Processing Conditions on the Shear Strengths of Glue Joints [a]

Glue composition	Solids, %	Viscosity, (1 hour) poises	Spread, lbs./1,000 sq. ft. glue line, dry wt.	pH	Pressing conditions		Shear strength [b]	
					Cold, p.s.i.	Hot, p.s.i.	Dry, wood failure (lbs./sq. in., %)	Wet, wood failure (lbs./sq. in., %)
No. 1	53	202	18	7.5	150	150	282–50	153–30
100 grams hexane-extracted meal, 100 grams urea, 100 grams water, 270 ml. 37% HCHO	53	202	18	7.5	none	150	284–45	150–15
	53	202	18	7.5	150	none	153–20	89–0
No. 2	43	218	18	7.8	150	150	287–45	149–10
50 grams hexane-extracted meal, 100 grams urea, 100 grams water, 270 ml. 37% HCHO	43	218	18	7.8	150	200	292-45	159–35
	43	218	18	7.8	200	200	300–60	166–30
No. 3								
75 grams hexane-extracted meal, 150 grams urea, 100 grams water, 400 ml. 37% HCHO	44	225	14	7.8	200	200	266–20	140–15
	63		19	8.1	200	200	298–45	163–20
Urea-formaldehyde glue, equal parts	45	.....	19	8.1	200	200	264–20	127–0

[a] Meal, urea, and water reacted prior to addition of formaldehyde. [b] See Footnote b, Table II. The pressing conditions were cold pressing at 77°F. for 1,440 minutes at the pressures indicated followed by hot pressing at 237°F. for 5 minutes at the pressures indicated unless otherwise noted.

TABLE IV

Comparison of Cottonseed Meal Glue With Other Water-Resistant Glues [a]

Glue mix	Solids, %	Viscosity poises	Spread, lbs./1,000 sq. ft. glue line, dry wt.	Shear strength [b]	
				Dry. wood failure (lbs./sq. in., %)	Wet, wood failure (lbs./sq. in., %)
Hexane-extracted meal [c]	29	640	19	412–70	215–43
Hydraulic-pressed meals [c]					
No. 1	40	326	34	274–18	82–5
No. 2	40	323	34	270–18	82–0
Screw-pressed meals [c]					
No. 1	40	318	36	266–10	77–0
No. 2	40	295	34	268–18	82–5
Hexane-extracted meal, urea, and formaldehyde [d]					
No. 2	43	218	18	300–60	166–30
Casein-glue mix ready for use upon addition of water [e]	33	623	22	472–83	150–35
Peanut-meal glue [f]	35	250	26	417–15	147–0

[a] Each glue mix and glue line prepared as recommended to give maximum shear strengths. [b] See Footnote b, Table II. [c] See Table I and Table II, Footnote a and Test No. 14. [d] See Table III. [e] Glue mix commercially available; cold pressed at 77°F. and 200 p.s.i., for 1,440 minutes hot pressed at 237°F., for 10 minutes at 200 p.s.i. [f] See Burnett, R. S., and Parker, E. D., Trans. Am. Soc. Mech. Eng. *68*, 751-6 (1946); cold pressed for 1,440 minutes at 77°F. and 200 p.s.i.

TABLE V

Comparison of Viscosity of Cottonseed Meal Glue With Other Water-Resistant Glues

Glue mix	Solids, %	Viscosity poises		
		1 hour	3 hours	5 hours
Hexane-extracted meal				
1. 4% Sodium hydroxide [a]	29	660	585	625
2. 4% Sodium hydroxide plus 1.25% trichloroacetic acid [a]	29	361	314	.....
3. 5% Sodium hydroxide plus 1.25% trichloroacetic acid [a]	29	.....	324	308
4. 6% Sodium hydroxide plus 1.25% trichloroacetic acid [a]	29	315	281	.....
Screw-pressed meal [a]—No. 1	40	352	412	384
Hydraulic-pressed meal [a]—No. 1	40	338	390	425
Hexane-extracted meal, urea, and formaldehyde [b]—No. 2	43	78	218	255
Casein-glue ready for use upon addition of water [c]	33	852	690	615
Peanut-meal glue [d]	32	295	373	710

[a] See Table I and Table II, Footnote a. [b] See Table III. [c] Glue mix commercially available. [d] See Table IV, Footnote f.

Comparisons of Water-Resistant Glues. Comparisons of cottonseed meal glue with other water-resistant glues are made in Tables IV and V. The glues reported in Table IV were prepared as recommended to give maximum shear strengths for the glue joints. It is seen that hexane-extracted cottonseed meal glue compares favorably with commercial casein glue and peanut meal glue, each glue mix and glue line being prepared as recommended to give maximum shear strengths. The cottonseed meal glue seems to be better than both of these glues when compared on a wet test basis, and cottonseed meal glue has a higher dry wood failure value than peanut meal glue. Lower values for shear strength and wood failure of glue joints containing hydraulic- and screw-pressed meals, as compared to hexane-extracted meal, are probably due to the fact that the proteins contained in these meals are less soluble and more denatured than the proteins contained in the hexane-extracted meal. Of economic significance, the glue spread required to give the desired results is lower for hexane-extracted meal than for the other glues reported.

The viscosity characteristics of the glue mixes are compared in Table V. It is seen that it is possible to adjust the viscosity of cottonseed meal glues to desired ranges by changing the concentration of alkali and by the addition of trichloroacetic acid to the glue.

Summary

The preparation of plywood glues using hydraulic-pressed, screw-pressed, and hexane-extracted cottonseed meals is described. Hexane-extracted cottonseed

meal glue compares favorably with commercial casein glue and peanut meal glue, each glue mix and glue line being prepared as recommended to give maximum shear strengths. Lower values of shear strength and wood failure of glue joints containing hydraulic- and screw-pressed meals, as compared to hexane-extracted meal, were reported.

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Lipide Content of Rice Bran

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RICE BRAN is reported to contain from 15 to 18% lipides (3, 4, 6) and to represent a minor though potential source of vegetable oil. Little information is available regarding the variations of the bran content of rough rice and of the amount of lipides in rice bran as influenced by variety and by environmental conditions under which it is grown. Consequently samples of mature rough rice of eight standard varieties from experimental plantings at Stuttgart, Ark., Crowley, La., and Beaumont, Tex., were obtained through the cooperation of the Bureau of Plant Industry, Soils, and Agricultural Engineering for investigation. The varieties were Magnolia, Bluebonnet, Blue Rose, Zenith, Caloro, Fortuna, Early Prolific, and Prelude.

Portions of 600 grams each of the rough rice samples were milled, using laboratory equipment (8), so that the three fractions, hull, bran, and polished rice, were obtained quantitatively. The hull and bran fractions were essentially free of each other. All three fractions were analyzed for moisture (7), and the bran and polished rice fractions were analyzed for lipides (1).

A small amount of endosperm was unavoidably present in each of the bran fractions as a consequence of the milling operation. Starch was determined polarimetrically (2) on the polished rice and colorimetrically (5) on the bran, and the values so obtained were used to calculate the amount of endosperm in the bran fractions. Thus the percentages of the true pericarp plus germ fractions in the rough rice were determined, assuming that the endosperm occluded in the bran fractions had the same composition as the polished rice.

Starch cells have not been found in the pericarp layer (9). The aleurone layer was occluded with the pericarp. In calculating the lipide contents of the true pericarp plus germ fractions, the lipide contents of the polished rice were taken into account.

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Results

The yields of hulls obtained on milling the rough rice samples, calculated to a moisture-free basis, ranged from 20.8 to 26.2 and averaged 23.7% while the yields of polished rice ranged from 66.8 to 73.8 and averaged 70.2%. The yield data for bran on the individual samples are given in Table I, columns 1, 5, and 9. The yields of bran ranged from 4.0 to 7.5 and averaged 6.0%, as compared to an average commercial milling yield of 8.5% (6). The variations are attributed mainly to the influence of variety and environment of production, with some caused by variations in milling. The averages indicate that the rice produced at Stuttgart gave the lowest yields of bran on milling. Rice of the Bluebonnet variety had the lowest average yield of bran (5.0%) and of Prelude the highest (7.1%).

The calculated yields of the true pericarp and germ fraction tabulated in Table I, columns 3, 7, and 11, are lower than the yields of the bran fraction. However the relative position of varieties and locations with respect to bran yield are about the same.

The lipide contents of the bran fractions on a moisture-free basis (Table I, columns 2, 6, and 10) varied from 15.3% for Prelude, produced at Stuttgart, to 23.0% for Blue Rose from the same location and averaged 19.5%.

The calculated lipide contents of the true pericarp and germ fraction (Table I, columns 4, 8, and 12) are somewhat higher than the lipide contents determined on the bran as milled from the corresponding rice samples. However the range in values is less, from 18.4% for the Prelude variety of rice produced at Crowley to 24.6% for the Bluebonnet variety from Beaumont. It appears that the variation in the lipide content of the true pericarp and germ fraction is attributable more to the influence of variety than to the environment of production.