Peanut Protein Paper Coatings

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COATED paper was introduced in about 1890. The term "coated paper" as used herein refers to any paper, board, or cardboard to which has been applied a layer of mineral matter and adhesive. The principal function of the adhesive is to bind the mineral matter so firmly to the raw stock that it will not be removed by the pull of ink during printing operations or in other similar uses. Animal glues and starch, at first used as the adhesives, have been partially displaced by casein. Soybean meal and protein, pectin, synthetic resins, alginates, gums, and other adhesives have been evaluated for use in paper coatings (1). Soybean meal and protein have been reported to meet the requirements of the industry; more than 25,000 tons of these products were used as adhesives during the past year (2).

Proteins from solvent-extracted peanut meals have a fairly high solubility and can therefore be dispersed at low pH values, having potential applications in paper coating formulations. Protein from hydraulic-pressed and screw-pressed peanut meals are not suitable since they are less soluble (3) and require a higher pH of solution to disperse the protein and dispersions so prepared weaken the raw paper stock.

Solvent-extracted peanut meal and peanut protein may soon be available in commercial quantities. The costs of isolating and processing peanut protein compare favorably with those for producing other industrial proteins (4). In view of this potential availability of industrial peanut protein an investigation was made of the conditions under which peanut protein could be used as an adhesive in paper coating formulations.

Experimental

Isolation of the protein. Oil-free peanut meal, obtained by removing the oil by means of n-hexane as described in a previous publication (5), was the source of peanut protein used in this investigation. In order to provide a basis for selecting the conditions for extracting and precipitating the protein, the optimum pH of the extracting alkali (sodium hydroxide) and the precipitating acid solutions (gaseous sulfur dioxide) were determined as a function of percentage of nitrogen dispersed. The optimum pH of the extracting solution (at which the maximum amount of nitrogen was dispersed) was 7.5, and that of the precipitating acid solution (at which the minimum amount of nitrogen was dispersed) was 4.5 (6).

The technique used in isolating peanut protein was similar to that described by Burnett (4). The conditions used in the preparations and the analyses of the peanut proteins are given in Table I. Yields of approximately 40 weight per cent protein were obtained.

Bodystock. A 50-pound coating paper raw stock having regular formation, pliability, and uniform finish was used. The raw stock gave a bodystock split with Dennison wax No. 12A.

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TABLE I

Peanut Protein Preparations

pH of extn. (NaOH)	pH of pptn. (SO_2)	Treatment of Isoelectric Curd	Temperature of Drying	Analysis of Protein	
				Nitrogen %	Ash %
7.5	4.5	None	120°F.	16.05	0.68
7.5	4.5	Water washed	120°F.	16.02	0.35
7.5	4.5	Neutralized to pH 6.5 by NaOH	120°F.	16.08	3.63

Mineral matter. Commercial samples of clay, titanium dioxide, titanium-barium oxides, and magnesium-silicon oxides were used as the mineral matter in coating formulations.

Method of testing. The adhesive strength of peanut protein in paper coating formulations was determined by a method similar to that used for control testing during actual paper coating operations utilizing the standard Dennison waxes (7, 8). Peanut protein was dispersed in water with the aid of alkali at 25°C. as follows: a weighed quantity of protein was placed in the bottom of the mixing chamber of a Waring Blendor. Water and alkali were added and the mixture blended for approximately 20 minutes to achieve complete dispersion of the protein.

Protein concentrations from 2.5 to 20% were used in the protein dispersions or colors and viscosity values for the colors of less than 10 poises at 25°C. were obtained in all formulations.

TABLE II

Effect of pH on Wax Pick

Formula	Protein-Pigment, g./100 g.	Pigment	Dispersing Agent	pH Color	pH Slip	Wax Pick
Protein Curd (Dried, Unwashed)						
1	40	Clay	NaOH	12.3	11.6	11
2	40	Clay	NaOH	11.9	11.3	9
3	40	Clay	NaOH	11.6	10.7	10
4	40	Clay	NaOH	10.6	10.1	10
5	40	Clay	NaOH	10.0	10.1	13
6	40	Clay	NaOH	9.9	9.9	8
7	30	Clay	NaOH	12.7	11.8	9
8	30	Clay	NaOH	11.3	10.3	10
9	30	Clay	NaOH	10.9	10.2	11
10	30	Clay	NaOH	10.2	10.1	7
Protein Curd (Dried, Water Washed)						
11	40	Clay	NaOH	12.0	11.8	9
12	40	Clay	NaOH	12.3	11.3	11
13	40	Clay	NaOH	11.9	10.6	12
14	40	Clay	NaOH	11.6	10.5	10
15	40	Clay	NaOH	11.9	10.4	10
16	40	Clay	NaOH	11.3	10.3	9
17	40	Clay	NaOH	10.4	9.8	9
18	40	Clay	NH_4OH	10.6	10.6	6
19	40	Clay	NH_4OH	9.9	9.9	6
20	40	Clay	NH_4OH	9.8	9.3	6

The mineral matter was uniformly mixed with the protein color to produce the coating suspension or slip which was filtered through a 200-mesh screen to remove large particles of mineral matter. The coating slips were aged 2 to 3 hours after which they were applied to the raw stock by means of a single sheet coater so adjusted to give a weight of 16 pounds of dry coating per ream of paper (25 x 40 inches, 500 sheets). The coated paper was dried at 101°C. to constant weight and then conditioned in a room kept at 25°C. ± 2° and 45-50% relative humidity. The

TABLE III

Effect of Protein-Pigment Ratio on Wax Pick

Formula	Protein-Pigment, g./100 g.	Pigment	Dispersing Agent	pH Color	pH Slip	Wax Pick
Protein Curd (Dried, Unwashed)						
21	40	TiO_2	NaOH	12.1	11.5	10
22	30	TiO_2	NaOH	12.1	11.1	10
23	20	TiO_2	NaOH	11.9	11.1	7
24	10	TiO_2	NaOH	12.0	11.1	3
25	40	TiO_2	NaOH	11.1	10.3	10
26	30	TiO_2	NaOH	12.1	10.1	10
27	20	TiO_2	NaOH	11.5	10.6	5
28	10	TiO_2	NaOH	11.5	10.3	3
29	40	TiO_2-BaO	NaOH	12.1	11.9	10
30	40	MgO-SiO_2	NaOH	12.0	11.9	5
31	30	MgO-SiO_2	NaOH	12.0	12.1	7
32	20	MgO-SiO_2	NaOH	12.1	12.0	9
33	40	TiO_2-BaO	NaOH	10.4	10.4	7
34	30	TiO_2-BaO	NaOH	11.0	10.8	7
35	20	TiO_2-BaO	NaOH	11.7	11.2	7
36	40	TiO_2-BaO	NaOH	10.7	10.4	8
37	30	TiO_2-BaO	NaOH	11.0	10.4	9
38	20	TiO_2-BaO	NaOH	11.0	10.8	9
39	10	TiO_2-BaO	NaOH	11.9	11.8	3
40	40	TiO_2-BaO	NaOH	11.4	11.1	9
41	30	TiO_2-BaO	NaOH	11.6	11.1	9
42	20	TiO_2-BaO	NaOH	11.3	10.9	7
43	10	TiO_2-BaO	NaOH	11.2	10.9	4
Protein Curd (Dried, Water Washed)						
44	40	TiO_2	NaOH	12.2	11.5	8
45	30	TiO_2	NaOH	12.0	11.3	8
46	20	TiO_2	NaOH	12.1	11.4	6
47	10	TiO_2	NaOH	11.9	11.4	4
48	40	Clay	Na_2CO_3	9.6	9.5	8
49	30	Clay	Na_2CO_3	9.4	9.2	4
50	20	Clay	Na_2CO_3	9.2	9.1	3
Neutralized Protein Curd (Dried)						
51	40	TiO_2	.....	6.3	6.3	6
52	30	TiO_2	.....	6.3	6.5	5
53	20	TiO_2	.....	6.5	6.7	4
54	10	TiO_2	.....	6.7	7.0	3

test that was used to measure the ease with which the coating was removed or picked from the bodystock was made on these uncalendered sheets.

Dennison's standard paper testing waxes, series 112A, were melted on the end and pressed firmly to the coated surface. The wax was allowed to cool thoroughly and then was removed with a steady, upward pull. The highest relative adhesive number of the wax at which no coating or bodystock pick was observed was recorded as the pick of the coated sheet. A coating with a wax pick number 5A has been considered satisfactory for most printing operations (1). More than 250 formulations were made and 10 to 20 coated sheets were tested for each paper coating formulation.

Results and Discussion

The adhesive properties of peanut protein are dependent on several critical factors: the type of protein, pigment, and dispersing agent, pH, protein-pigment ratio, and total solids content of the slip. If the pH of the isoelectric protein curd is adjusted to a more alkaline value before drying, the neutralized protein curd may be dispersed easily at the neutralization pH by the addition of water (9, 10). If the isoelectric protein curd is dried, this protein is not as easily dispersed as the neutralized protein, and has different adhesive properties at the same pH. Date showing the effects of these variables on the wax pick tests of coated sheets are given in Tables II, III, and IV.

Effect of pH. Table II shows the effect of pH, attained by the addition of different amounts of alkali to the protein color, on the wax pick value. The pH value for the color indicates the pH of the protein dispersion prior to the addition of the pigment. After the addition of pigment there is a change in pH dependent on the type of pigment added.

The wax pick value of the coated paper was a maximum for dried, unwashed protein at pH 10.0 to 12.0 of the color and was practically constant over this pH range. This pH range corresponds to that in which higher viscosities of peanut protein dispersions have been reported (11). When a weaker alkaline dispersing agent was used a lower wax pick value was obtained.

Effect of protein-pigment ratio. The amount of adhesive per unit weight of pigment is important economically and technically. The results in Table III demonstrate the effect of varying the amount of peanut protein adhesive per unit weight of pigment in the coating slips. The wax pick value of the sheets coated with unwashed protein and titanium dioxide was practically unchanged when the protein-pigment ratio was decreased from 40 to 30 grams per 100 grams. On decreasing the protein-pigment ratio to a lower value, the wax pick value decreased. When water-washed protein was used as the adhesive the wax pick values were less and their change with decrease in the protein-pigment ratio was not as much as when unwashed protein was used. With neutralized protein as the adhesive, the wax pick value decreased proportionately as the protein-pigment ratio was decreased.

Effect of type of pigment. A comparison of formulations 2, 21, 29, and 30 (Tables II and III) shows that except for the magnesium-silicon oxide pigment the protein adhesive requirements were about the same for the different types of pigments used.

Effect of total solids content. A comparison of the data in Table IV with those in Tables II and III shows that 40% total solids in the coating slip usually gives the best wax pick test. With one exception the wax pick test decreased as the total solids content of the coating slip decreased.

Effect of type of dispersing agent. The results given in Tables II, III, and IV show that for a constant pH the type of dispersing agent affects the wax pick value of the coated sheet. Sodium hydroxide gives the highest wax pick value, and sodium carbonate, calcium oxide, and ammonium hydroxide may be listed in that decreasing order as to their utility in developing the adhesive properties of peanut protein.

Comparison of different protein binders. Comparisons of peanut protein coatings with casein and soybean protein coatings are made in Table V. Casein coatings had the highest adhesive strength with peanut protein slightly better than soybean protein. Reflectance data show that casein and soybean protein coatings were similar in degree of whiteness and peanut protein coatings were slightly darker.

These comparisons were made with a protein-pigment ratio of 15 to 100, a ratio which is commonly used in industry when casein is the adhesive.

Summary

Paper coated with peanut protein adhesive and mineral pigments gives high wax pick tests. Critical factors affecting the wax pick value are the type of protein, pigment, and dispersing agent, pH, protein-pigment ratio, and total solids content of the slip. When neutralized protein is used as the adhesive, coating slips containing 40% solids may be prepared with pH values as low as 6.3; and when these slips are applied to raw stock, the coating has wax pick values satisfactory for many printing opera-

TABLE IV

Effect of Total Solids in Slip on Wax Pick

Formula	Protein-Pigment, g./100 g.	Pigment	Dispersing Agent	pH Color	pH Slip	Per Cent Total Solids	Wax Pick
			Protein Curd (Dried, Unwashed)				
55	40	TiO_2-BaO	NaOH	11.4	11.1	45	7
56	40	TiO_2-BaO	NaOH	11.4	11.1	40	6
57	40	TiO_2-BaO	NaOH	11.6	11.2	34	9
58	40	TiO_2-BaO	NaOH	11.8	11.7	19	13
59	40	MgO-SiO_2	NaOH	10.6	10.6	45	6
60	40	MgO-SiO_2	NaOH	9.6	9.8	40	5
61	40	MgO-SiO_2	NaOH	10.0	10.0	34	6
62	40	MgO-SiO_2	NaOH	9.2	9.6	19	6
63	40	MgO-SiO_2	NaOH	8.7	9.1	15	4
64	40	MgO-SiO_2	Na_2CO_3	7.8	8.4	40	6
65	40	MgO-SiO_2	Na_2CO_3	8.1	8.3	34	6
66	40	MgO-SiO_2	Na_2CO_3	8.3	8.3	19	6
67	40	MgO-SiO_2	Na_2CO_3	8.1	8.1	15	9
68	40	Clay	NaOH	11.6	10.7	40	10
69	40	Clay	CaO	12.0	11.9	24	9
70	40	Clay	CaO	12.1	12.1	19	7
71	40	Clay	CaO	12.2	12.3	15	7
72	40	Clay	CaO	12.0	11.5	19	8
73	40	Clay	CaO	12.0	11.6	15	7
74	30	Clay	NaOH	11.3	10.1	38	10
75	30	Clay	CaO	12.2	12.3	24	7
76	30	Clay	CaO	12.2	12.5	14	4
77	30	MgO-SiO_2	NH_4OH	9.1	9.2	44	7
78	30	MgO-SiO_2	NH_4OH	9.5	9.6	38	6
79	30	MgO-SiO_2	NH_4OH	9.5	9.5	32	6
80	30	MgO-SiO_2	NH_4OH	9.4	9.3	24	7
81	30	MgO-SiO_2	NH_4OH	9.4	9.7	14	4

tions. Over a pH range of 8 to 12, coatings prepared from unwashed protein give high wax pick values, whereas those prepared with water-washed protein give slightly lower values.

TABLE 5

Comparison of Peanut Protein Paper Coatings With Other Protein Coatings

Protein	Protein-Pigment, g./100 g.	Pigment	Dispersing Agent	pH Slip	Wax Pick	Reflectance*	
						Whiteness	Yellowness
Peanut (unwashed)	15	Clay	Na_2CO_3	9.1	5	0.66	0.11
Soybean (alpha)	15	Clay	Na_2CO_3	8.7	4	0.69	0.10
Casein (H_2SO_4)	15	Clay	Na_2CO_3	8.8	7	0.69	0.11

* Using MgO Standard and Hunter Multipurpose Reflectometer.

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☆ ☆ ☆ ABSTRACTS ☆ ☆ ☆

Oils and Fats

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THE COMPONENT ACIDS AND GLYCERIDES OF NEAT'S FOOT OIL. T. P. Hilditch and R. K. Shrivastava. *J. Soc. Chem. Ind. 67*, 139(1948). The component acids of a specimen of neat's foot oil consisted of myristic 0.7, palmitic 16.9, stearic 2.7, arachidic 0.1, tetradecenoic 1.2, hexadecenoic 9.4, oleic 64.4, ocadecadienoic 2.3, octadecatrienoic 0.7, and unsaturated $C_{20\text{-}22}$ acids 1.6% (wt.). Component glycerides, studied after partial separation by low-temperature crystallization from acetone, were found to include, *inter alia*, about 35% palmitodiolein, 23% of hexadecenodiolein, 8% of polyethenoid-diolein, 7% of oleopalmitostearin, and probably not much more than 10% of triolein, with minor amounts of other mixed glycerides. The presence of fairly substantial proportions of hexadecenoic acid in neat's foot oil had not been previously noted. The specific utility of the oil as a lubricant cannot, as at one time supposed, be connected with a high content of triolein.

SOUTH AFRICAN FISH PRODUCTS. PART XXVIII. THE COMPOSITION OF THE LIVER OIL OF THE SEVEN-GILLED SHARK, *Heptranchias pectorosus*, (Garman). M. L. Karnovsky, W. S. Rapson, and (Miss) H. M. Schwartz. *J. Soc. Chem. Ind. 67*, 144(1948). The composition of the unsaponifiable fraction, and of the fatty acid fraction of the liver oil of *Heptranchias pectorosus* has been determined. Since α-glyceryl ethers of the unsaponifiable fraction have been quantitatively determined and their relationship to the fatty acids discussed.