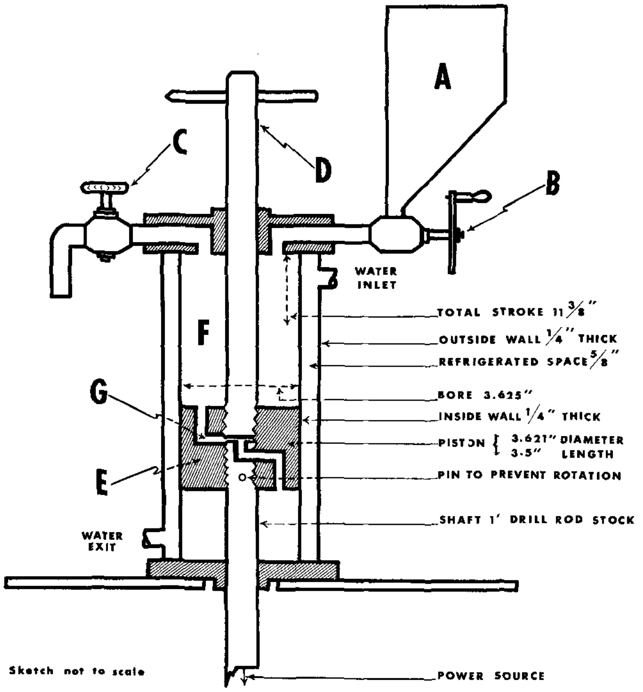

FIG. 2. Sectional view of pilot plant plasticizer—Armour and Company.

inlet oil temperature, 160° F.; cooling-water temperature, 34° F.; sample weight, 1,300 g.; time of plasticizing, 4 min.; and tempering, 48 hrs. at 83° F. Baking tests made on these samples are shown in Table V.

It is quite apparent that the performance of products plasticized through the pilot plant unit compares favorably with those obtained with plant-Votated products.

Some tests described in Table VI were made with our conventional high-ratio shortenings, comparing their performance with identical products plasticized through a plant Votator. Plasticizing conditions were the same as used on the shortening described in Table VI.

TABLE V

Performance and Plasticity Data

Sample	Air	A.S.T.M. penetration 70°F.	Lb. cake volume pilot plant plasticized [a]	Lb. cake volume plant plasticized [a]
	(% by vol.)			
A	12.2	156	256	255
B	13.1	162	260	262
C	12.4	165	262	254
D	13.0	160	278	268
E	13.0	158	250	254
F	12.2	168	265	258

[a] Armour method: Units reported are in ml./100 g. of cake.

All results are given in ml. per 100 g. Both employ the Armour Method. It should be quite obvious that margarine can easily be prepared in the unit by adding all of the ingredients through container A. Should the unit be used extensively for margarine work, internal construction of stainless steel would be recommended.

TABLE VI

Performance—High Ratio Type Shortening

Sample	Pilot plant plasticized		Plant plasticized	
	Icing volume	Layer cake volume	Icing volume	Layer cake volume
1	126	286	126	287
2	120	290	124	296
3	128	291	126	292
4	135	288	139	293
5	130	288	133	286
6	133	274	131	278

Summarizing, a pilot-plant plasticizer has been designed and built which will plasticize a 1,300-g. sample in four minutes, giving a product very similar in performance and consistency to a plant-plasticized product. The unit is quite useful for the preparation of samples for sales service as well as for research purposes.

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[Received April 20, 1959]

The Preparation and Properties of Some Urethane Foams from Castor Oil and Elaidinized Castor Oil[1]

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THE PREPARATION and properties of a series of semirigid to soft urethane foams made from formulations containing 50, 60, 70, and 80% of castor oil have been previously reported (6). The present study is concerned with the effect of variation in the degree of crosslinking on properties of castor oil urethane foams and with a comparison of foams prepared from elaidinized castor oil with analogous foams prepared from untreated castor oil.

Increasing the degree of crosslinking in urethane foams from castor oil should improve water resistance and shrinkage properties besides enhancing strength and hardness. The extent of crosslinking in castor oil urethane foams can be adjusted in the prepolymer preparation by varying the duration and temperature of reaction to permit formation of more allophanic ester groups. A series of foams was made and tested from prepolymers prepared this way from castor oil in which increased amounts of crosslinks were ap-

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[1] Presented at the 50th Annual Meeting of the American Oil Chemists' Society, New Orleans, La., April 20–22, 1959.

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parently present as evidenced by greatly increased prepolymer viscosities.

In the previous work three urethane foams were made from formulations containing hydrogenated, elaidinized, or partially epoxidized castor oil for comparison with a similar foam from castor oil. Foam from a formulation containing 60% of elaidinized castor oil, one of the simpler modified oils, was indicated in these preliminary tests to have improved water resistance and shrinkage characteristics. Thus comparison of a series of foams prepared from formulations containing 50, 60, 70, and 80% of elaidinized castor oil with the analogous series obtained from castor oil should be informative.

Experimental

Preliminary to the preparation of these foams several series of tests were made to determine optimum catalyst concentration, pH, and water content of the catalyst-water mixture used in making the foams. In the previous work the foaming procedure employed a commercial catalyst preparation of buffered 2-diethylaminoethanol. This particular preparation was later found to differ from its assumed composition and to be difficult to adjust in pH. Therefore in these and subsequent tests the catalyst-water mixtures were prepared from reagent grade 2-diethylaminoethanol (Eastman) and the desired amount of water and were adjustable in pH with concentrated hydrochloric acid. These preliminary studies were made with a prepolymer prepared in the customary manner from a formulation of 60% of castor oil and 40% of an 80/20 tolylene di-isocyanate (80% of 2,4- and 20% of 2,6-isomers). Results from these tests permitted selection of optimum conditions used in preparation of the foams in the two series outlined above.

Optimum Foaming Conditions. Since in the earlier work the 2-diethylaminoethanol was used at a level of 1.9 g./100 g. of prepolymer a series of foaming tests was made in which the catalyst concentration was varied from one-half to twice this amount. The data in Table I show that the 1.9 g. of catalyst level resulted in a foam of reasonable foaming time, density, and area shrinkage. Also it was observed that the height of this foam was some 15% greater than that obtained with the lower 0.95 g. level. Therefore the 1.9 g./100 g. of prepolymer level was considered about the optimum catalyst concentration to use and would be desirable for comparison with previously reported results.

In a second series of foaming tests the catalyst concentration was held at the 1.9 g./100 g. of prepolymer level, and the catalyst mixture was adjusted from a pH of 12–13 down to 9.0. It will be observed from Table II that the catalyst mixtures below a pH of about 10.1 produced the better results and that actually those about pH of 9.8 appeared optimum.

TABLE I
Effect of Catalyst Concentration on Foam Characteristics

Catalyst concentration[a]	Foaming time	Foam density	Foam shrinkage	
			Area	Linear
	min.	*lbs./cu. ft.*	%	%
0.95	60+	2.7	3	13
1.90	29	2.8	10	19
2.85	13	2.1	19	17
3.80	8	2.1	17	8

[a] Grams of DEAE (2-diethylaminoethanol) per 100 g. of prepolymer. The catalyst as added contained the amount of water required for the calculated residual isocyanate content of the prepolymer.

TABLE II
Effect of pH of Catalyst-Water Mixture on Foam Characteristics

Catalyst-water mixture		Foaming time	Foam density	Foam shrinkage	
Composition[a]	pH			Area	Linear
		min.	*lbs./cu. ft.*	%	%
Commercial DEAE catalyst+H_2O[b]	10.6	30–40	2.8	11	20
DEAE+H_2O[b]	12–13	10	5.2	39	47
DEAE+HCl+H_2O[c]	10.1	18	2.9	10	20
DEAE+HCl+H_2O[c]	9.84	20	2.6	2	1
DEAE+HCl+H_2O[c]	9.7	41	3.0	0.1	5
DEAE+HCl+H_2O[c]	9.0	240+	4.0	nil	nil

[a] DEAE concentration of 1.9 g./100 g. of prepolymer.
[b] Amount required for the calculated residual isocyanate content of prepolymer.
[c] Amount required for the determined residual isocyanate content of the prepolymer.

In the third series of preliminary tests conducted, the quantity of water present in the catalyst-water foaming mixture was varied between 100 and 120% of the theoretical requirement (based upon chemical analysis) (4), while adjusting the pH between 9.8 and 9.9 and holding the amine content at the 1.9 g. level. The results from this series, given in Table III, indicate that optimum foaming characteristics resulted with 10% of additional water in the catalyst-water mixture. Accordingly subsequent foam preparations were made with a catalyst-water mixture containing 1.9 g. of 2-diethylaminoethanol per 100 g. of prepolymer and 10% excess water over that required for the analyzed residual isocyanate and were adjusted with concentrated hydrochloric acid to a pH in the 9.8 to 9.9 range.

TABLE III
Effect of Water Content in Formulation on Foam Characteristics

Catalyst-water mixture[a]		Foaming time	Foam density	Foam shrinkage	
Excess water[b]	pH			Area	Linear
%		*min.*	*lbs./cu. ft.*	%	%
0	9.84	20	2.6	2.2	0.7
5	9.87	20	2.6	1.5	2.1
10	9.87	20	2.5	0.3	0.7
20	9.89	21	2.4	1.0	1.7

[a] Contained 1.9 g. DEAE/100 g. of prepolymer.
[b] Above that required for the determined residual isocyanate in the prepolymer.

Prepolymers. Prepolymers for the preparation of the urethane foams were made by the procedure previously described (6). Materials used were a commercial grade of dry castor oil, a laboratory-elaidinized castor oil (2) containing about 70% of its double bonds in the *trans* configuration, and a commercial grade of 80/20 tolylene di-isocyanate. For the series of foams with increasing degrees of crosslinking, temperatures chosen for prepolymer preparation were 110°, 130°, and 150°C., respectively, while for the series from elaidinized castor oil 110°C. was used for the prepolymer of 60% oil content, and 130°C. for that of 50% oil content. All prepolymers were heated at their respective reaction temperatures for 1 hr. except the prepolymer containing 50% of elaidinized castor oil, which was heated for 4 hrs. Properties and analyses of the oils and prepolymers are tabulated in Table IV. Methods of the American Oil Chemists' Society (1) were used in the determinations except that percentage of hydroxyl was determined by a modification of the method of West *et al.* (5), using a 3/1 ratio of pyridine/acetic anhydride, nitrogen by a macro Kjeldahl procedure, unreacted isocyanate by the method of Tazuma *et al.* (4), and viscosities by the use of Gardner Bubble Viscometer tubes.

TABLE IV
Properties of Castor Oils and Prepolymers

Tests	Castor oil			Elaidinized castor oil [a]			
Oils							
Viscosity, cps. at 50°C.	130			210			
Melting point, °C.	....			34–45			
Moisture (Karl-Fischer), %	0.05			0.19			
Hydroxyl, %	4.98			4.66			
Acid value	0.67			0.00			
Iodine value (Wijs)	85.2			83.2			
Saponification value	179			186			
Nitrogen, %	....			0.06			
Prepolymers							
Oil in formulation, %	60	60	60	50	60	70	80
Temperature of prep., °C.	110	130	150	130	110	110	110
Viscosity, cps. at 25°C.	15,400	34,200	140,000	15,500	23,500	......	......
Residual isocyanate, %	11.5	11.1	10.1	15.4	11.4	8.6[b]	5.7[b]

[a] Laboratory isomerized using oxides of nitrogen, analyzing about 70% *trans* double bonds by infrared.
[b] Calculated values for prepolymer and oil mixtures.

Foam Preparation. Foams were prepared from the above prepolymers in a manner similar to that previously described (6). Each 200-g. batch of prepolymer was mixed with 1.0 g. of a dispersing agent[4] and then the required amount of catalyst-water mixture. After a thorough, rapid agitation period of 1 min. the mixture was allowed to foam in polyethylene molds (10 cm. deep and 30 × 12 cm. in cross-section), from which the foams could be easily removed. The preparations of foam from formulations containing 70 and 80% of elaidinized castor oil were found to be somewhat more sensitive and critical in the pre-foaming standing period than in the preparation of similar foams from castor oil. Data on the preparation of the foams are included in Table V.

Testing. After standing at least three days at room temperature (*ca.* 25°C.) the foams were cut into specimens suitable for testing. The samples that were to be tested for compression and tensile strength were conditioned (at 21°C. and 65% R.H.) for at least three days before testing. Tests were made on at least four specimens from three or four separate batches of each formulation. Using the procedures already described (3, 6), the foams were tested for foaming time, density, shrinkage, tensile strength-percentage of elongation, compression-deflection, compression set, water absorption, energy absorption, and the effect on strength properties of accelerated humid aging. In addition, water vapor penetration was determined as follows: 1-in. thick cylindrical samples 1 sq. in. in cross-section were inserted into the open end of a 150-mm. × 27-mm. I. D. test tube, containing 20–25 g. of anhydrous silica gel. The tubes were weighed, placed in desiccators containing water, and held in a constant temperature cabinet at 35°C. for several days; the increase in weight was determined daily. The water vapor penetrating the foam samples was expressed in mg./day/in.^{2}/in. thickness. This test was conducted on the original samples and on the samples after the three weeks of accelerated humid aging treatment.

Results and Discussion

The foams prepared from prepolymers having increased amounts of crosslinks, or from the elaidinized castor oil, show that foaming times were only slightly less than for analogous castor oil foams previously reported. The data in Table V indicate foaming times of about 15 to 40 min. compared to 20 to 45 min. for the series from castor oil. Foam densities were in the range 1.7 to 6.7 lbs./cu. ft., substantially the same as the 1.7 to 6.4 range of the analogous castor oil

TABLE V
Properties of Foams

Oil in formulation		Characteristics						Tensile strength					
Type	Percentage	Prep. temp.	Foam time	Type	Density	Shrinkage		Original			Aged		
						Area	Linear	Ultimate elongation		100% elongation	Ultimate elongation		100% elongation
		°C.	(min.)		lbs./cu. ft.	%	%	%	p.s.i.	p.s.i.	%	p.s.i.	p.s.i.
Castor	60	110	20–22	Semirigid	2.4	1	3	51	19.3	......	63	18.8	......
Castor	60	130	21–25	Semirigid	2.5	2	4	40	16.4	......	53	17.0	......
Castor	60	150	15–16	Semirigid	3.1	1	1	23	16.7	......	34	18.2	......
Elaidinized castor	50	130	14	Semirigid	1.7	11	11	23	14.8	......	20	6.1	......
Elaidinized castor	60	110	22–27	Semirigid	2.7	1	1	44	34.7	......	48	15.9	......
Elaidinized castor	70	110	23–34	Soft	4.2	3	3	125	31.7	27.3	135	15.5	12.0
Elaidinized castor	80	110	30–40	Soft	6.7	4	2	142	8.9	7.5	157	3.7	2.9

Oil in formulation		Compression-deflection modulus						Compression set		Energy[a] absorption original	Water resistance		
Type	Percentage	Original			Aged			Original	Aged		Absorption original	Penetration	
		10%	25%	50%	10%	25%	50%					Original	Aged
		p.s.i.	p.s.i.	p.s.i.	p.s.i.	p.s.i.	p.s.i.	%	%	%	%	mg./d.	mg./d.
Castor	60	6.9	6.6	8.7	5.2	5.0	7.3	47	45	31	348	264	......
Castor	60	7.3	7.2	9.4	6.2	6.3	8.9	48	47	31	361	287	......
Castor	60	10.7	11.1	15.3	9.0	9.6	13.6	48	48	35	333	317	......
Elaidinized castor	50	4.7	5.0	6.2	5.1	5.4	7.2	50	50	27	411	264	303
Elaidinized castor	60	8.7	8.7	12.1	7.2	7.6	10.9	46	42	30	228	236	274
Elaidinized castor	70	0.49	0.52	0.87	0.31	0.40	0.68	35	21	46	196	370	458
Elaidinized castor	80	0.22	0.29	0.49	0.36	0.45	0.72	41	37	48	155	545	558

[a] Percentage of value for control foam rubber having the following properties: density, 7.2 lbs./cu. ft.; 50% compression modulus, 1.0 p.s.i.; and ultimate tensile strength, 16.6 p.s.i. at 218% elongation.

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[4] Dow Corning's DC 200 fluid of 50 centistokes viscosity was used, other equivalent dispersing agents are satisfactory.

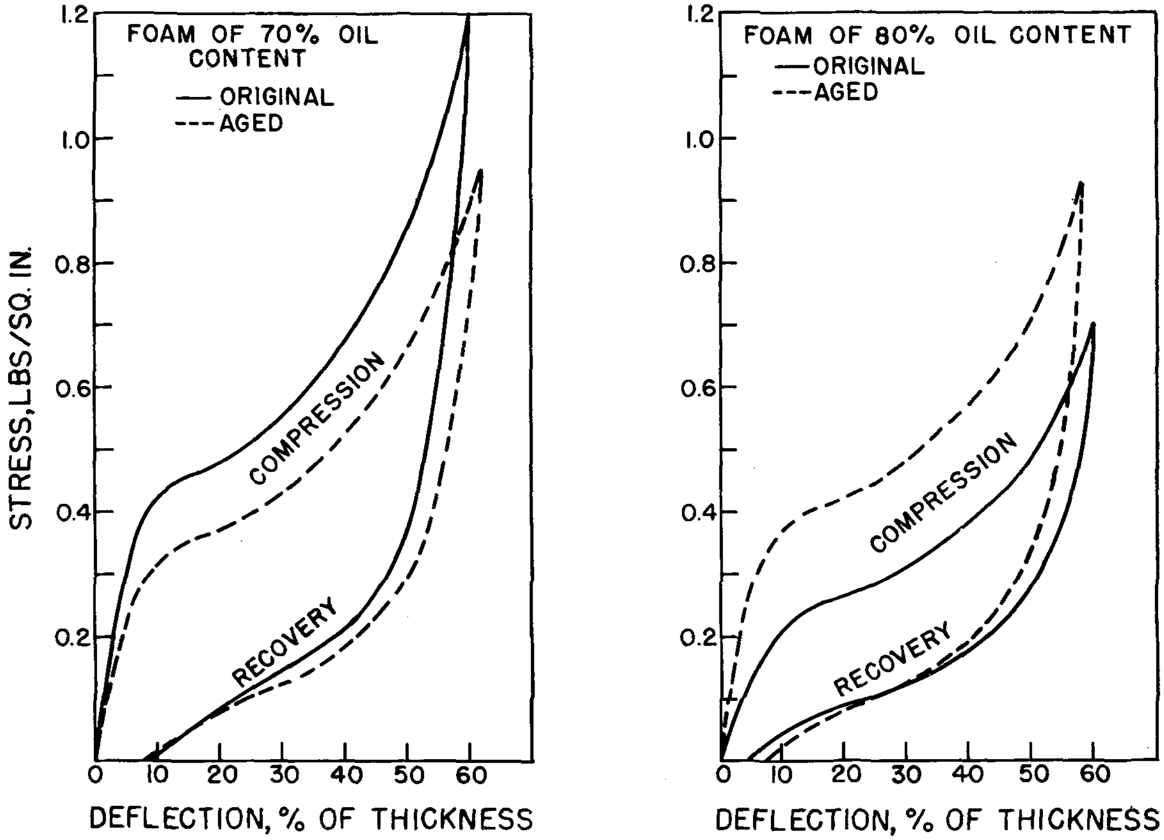

FIG. 1. Compression-recovery curves of elaidinized castor oil foams.

series. Shrinkage values showed improvement, partly because of the optimum foaming conditions used, by being reduced to a range of 1 to 4% in all cases except for the foam containing 50% of elaidinized castor oil, which however was reduced about half of the value for the equivalent castor oil foam, *i.e.*, 11 *vs.* 21%.

The tensile strengths (Table V) of the series of castor oil foams with increased crosslinking were lower than previously reported for an analogous foam of 60% castor oil content (6) and decreased slightly with increasing of crosslinking. On the other hand, the series with varied amounts of elaidinized castor oil showed tensile strengths up to 50% greater than that of the analogous series from castor oil (8.9 to 34.7 p.s.i. compared to 6.3 to 27.9 p.s.i., respectively). Aging of the foams of the series with increasing crosslinks had only slight effect on their tensile strengths. However aging of the foams of the series from elaidinized castor oil decreased their tensile strengths to less than 50% of the values obtained on the original samples.

Compressive strength tests (Table V) show increasing values as the degree of crosslinking increased in the foams prepared from castor oil, the 50% compression modulus for the foam from the 150°C. prepared prepolymer being nearly twice that of the value obtained for the 110°C. prepolymer. Aging of the foams decreased their compressive strengths only slightly. Compressive strengths of the series of foams from elaidinized castor oil compared favorably with those obtained on the series of foams from castor oil, results ranging from 0.49 to 12.1 p.s.i. as compared to 0.52 to 10.4 p.s.i. for the respective series. In general, aging of these foams only slightly affected their compressive strengths except for the foam of 80% elaidinized castor oil, which increased from 0.49 to 0.72 p.s.i. This is illustrated in the compression-recovery curves for 70 and 80% elaidinized castor oil foam samples (Figure 1). Similar curves of slightly lower values than were obtained on the original samples resulted from tests of the aged foam samples of 70% elaidinized castor oil whereas an increased compressive strength was observed in the curve of the aged foam as compared to the curve of the original foam from the 80% oil formulation. The recovery curves for both 70 and 80% aged foams follow closely those of the original samples.

Compression set values compared very well for the foams from 50, 60, and 70% oil content but were markedly different for the foams of 80% oil content. The foams from 80% of elaidinized castor oil gave higher values (41%) as compared to that obtained for a comparable castor oil foam (16%). The semirigid foams all showed little recovery in the compression set tests, with the values all falling in the 46–50% range (50% indicates no recovery). Aging of the foams decreased the compression set values only very little with no noticeable difference for some of the rigid foams, *e.g.*, foams from prepolymer containing 50% of elaidinized castor oil and the prepolymers of castor oil prepared at 130° and 150°C. Energy absorption values for the semirigid foams were 25–35% and for the soft foams 46–48% as compared to 20–30% and 47–50% for the respective values previously obtained on similar foams from castor oil.

For the foams in the series of increased crosslinks, water absorption values were substantially the same, ranging from 333 to 361% (Table V). However water vapor penetration values were indicated to increase with the degree of crosslinking (264 to 317 mg./day/in.^{2}/in. thickness). For the series of foams from elaidinized castor oil, water-absorption values markedly decreased from 411 to 155% as oil content increased to 80%. This is a like trend but lower than the 515 to 170% range obtained for the analogous foams from castor oil. Results of water-vapor penetration tests, ranging from 236 to 545 mg./day/in.^{2}/in. thickness, indicated an increasing trend as oil content increased. Aging caused a slight increase in these values. The foams from the formulation containing 60% of elaidinized castor oil were the most resistant to water-vapor penetration.

Summary

The preparation and properties of two series of castor oil urethane foams, one from castor oil and the other from elaidinized castor oil, were investigated. The first series of foams was made from prepolymers containing 60% of castor oil prepared at increasing temperature levels to vary the degree of crosslinking in the final foams. These foams had lower tensile strengths than observed for a previously prepared foam of 60% castor oil and did not show significant differences in water resistance as crosslinking varied. They were increased nearly 100% in compressive strength with increased crosslinking and had very good shrinkage characteristics as values of only 1 to 2% were obtained.

A second series of foams was prepared from 50, 60, 70, and 80% of elaidinized castor oil to compare with foams from a similar series from castor oil. This series of foams of 50 to 80% elaidinized castor oil contents was similar in density (1.7 to 6.7 lbs./cu. ft.), had improved shrinkage characteristics (11, 1, 3, and 4%, respectively), showed increased compressive and tensile strengths (up to 12.1 p.s.i. at 50% compression modulus and 34.7 p.s.i. ultimate tensile for the 60% foam formulation), and had better water-resistance properties (411 to 155% *vs.* 515 to 170% water absorption) than the analogous foams from castor oil. In general, humid aging only slightly affected the values obtained for the foams and was significant in only a few instances, *e.g.,* decreased tensile in the elaidinized castor oil series.

Thus increasing crosslinks in the foam apparently did not improve water resistance but did improve shrinkage characteristics in addition to some increased strength properties, as would be anticipated. Foams from elaidinized castor oil, while similar in density and foaming characteristics to analogous foams from castor oil, exhibited less shrinkage and improved water-resistance.

Acknowledgment

The authors wish to acknowledge the assistance of J. P. Moreau for preparing and testing some of the foams, of V. P. Whitley for some of the oil analyses, and of The Baker Castor Oil Company for the castor oil used.

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[Received April 20, 1959]

Second Interim Report of the A.O.A.C.-A.O.C.S. Crude Fiber Liaison Committee

THE INITIAL INTERIM REPORT of the A.O.A.C.-A.O.C.S. Crude Fiber Liaison Committee was published in the May 1959 issue of the Journal of the A.O.A.C.(1). In this initial report the need for improvement in the precision and accuracy of the current official crude fiber method was discussed. The method itself was also discussed in detail, indicating those areas in the method where deviations or lack of operator techniques could result in loss of accuracy and precision.

In this initial report it was announced that a collaborative study comparing the official method (2, 3) with the Oklahoma State Filter Screen method (4) and a method involving the use of a Buchner Funnel (5) would be conducted by the Liaison Committee. Prior to the submitting of samples, a fourth method was submitted to the Liaison Committee by F. W. Quackenbush and E. D. Schall of Purdue University. This method utilizes a Shimer filtering funnel and, for the purposes of identification, will be referred to as the Purdue Method. The committee was intrigued by the apparent simplicity of the filtering operation using the Shimer Funnel and decided to include this method as a part of the collaborative study. Thus a total of four methods was compared.

In order to obtain complete data, that is, within-laboratory and between-laboratory precision, the A.O.C.S. statistical design was used. This requires two operators in each laboratory to run each sample by each method in duplicate on two different days. Twelve of the committee members agreed to participate, and four samples including a 50% soybean oil meal, a cottonseed meal, a dairy feed, and alfalfa meal were submitted to each laboratory. Using the design described above, each collaborator reported 16 results on each method, or a total of 64 results. More than 750 results were obtained and subjected to statistical analysis.

The methods as they were used in this collaborative study are described below. It will be noted that the collaborators were permitted some options in the choice of equipment and reagents. These are explained in the initial Interim Report.

Methods

The following reagents and apparatus were common to all methods used in the collaborative study, and in the interest of brevity only the special items will be listed under each test method.