

value of 100 introduces only a negligible error. Reference to Figures 3, 4, and 5 and corresponding data given in the tables clearly illustrate this point.

### Summary

Thirteen compounds have been intercompared with respect to their antioxidant activity in concentrations of 0.01, 0.05, and 0.10% in edible cottonseed oil, the same oil hydrogenated to shortening consistency, and in lard which is essentially free of naturally occurring antioxidants. None of the compounds exhibited significant antioxidant activity in the cottonseed oils, when used in a concentration of 0.01%, but they were effective in stabilizing lard under these conditions. Propyl gallate was the most effective of the compounds tested for the vegetable fats.

Examination of the data for lard indicates that the comparison of antioxidants in this and other sub-

strates essentially devoid of natural inhibitors may yield more realistic results when compared at a peroxide level of 100 milliequivalents per kilogram of substrate.

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## Buckwheat Leaf Meal Fat. II. Composition of the Fatty Acids

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A PREVIOUS paper (5) describes the preparation of buckwheat leaf meal fat, reports its physical and chemical characteristics, and gives an account of the identification of the constituents in the unsaponifiable matter and the water-soluble fraction of the saponified fat. This manuscript describes the characterization of the chief constituents in the water-insoluble fraction of the saponified fat.

*Purification of the Water-Insoluble Fatty Acids.* According to Official Methods (1), the value for insoluble acids includes the unsaponifiable matter. The quantity of unsaponifiable matter is inconsequential in most fats and oils that contain these constituents in low concentration, but since buckwheat fat contains a high percentage (14.9%) of this material, the value of 64.9% previously reported (5) for the insoluble acids did not include the unsaponifiable matter.

The insoluble acids (free of unsaponifiable matter) contain a quantity of material not of fatty acid character. Exhaustive extraction of a 221.8-g. sample of the insoluble acids with petroleum ether (boiling range 63-70°C.) gave 158.6 g. (71.5%) of soluble material and 63.2 g. (28.5%) of insoluble material. On the basis of the original fat the petroleum-ether soluble material (fatty acids) was 46.6%, and the insoluble material was 18.5%.

To free the purified fatty acids of a small amount of coloring matter, an 89.4-g. sample of the soluble material was dissolved in petroleum ether and treated with 40.0 g. of Norit. To determine whether appreciable quantities of individual acids were preferentially adsorbed by Norit, untreated and Norit-treated samples were submitted to spectrophotometric analyses (2, 3) for polyunsaturated acids and to various chemical analyses for analytical characteristics. Table I shows the results of these analyses.

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TABLE I  
Spectrophotometric and Analytical Characteristics of Purified Mixed Fatty Acids of Buckwheat Leaf Meal Fat

	Pigment-contaminated fatty acids	Pigment-free fatty acids
Peroxide value (milliequivalents/kilo).....	24.2	25.9
Iodine value (Wils).....	154.8	163.3
Neutralization equivalent.....	296.0	285.7
Hydroxyl value (%).....		0.1
Saturated acid content (%) <sup>a</sup> .....	21.8	22.0
Saturated acids by difference (%).....	17.2	19.7
Neutralization equivalent, saturated acids from Bertram analysis <sup>b</sup> .....	295.0	282.2
Iodine value, saturated acids from Bertram analysis.....		0.4
Oleic acid, calculated from iodine value and spectrophotometric analyses (%).....	28.2	18.7
Linoleic acid (%).....	18.2	20.9
Linolenic acid (%).....	32.5	37.5
Preformed conjugated dienoic acids (%).....	3.5	3.0
Ratio linolenic acid/linoleic acid.....	1.797	1.794

<sup>a</sup>Bertram method as modified by G. S. Jamieson, "Vegetable Oils and Fats," A. C. S. Monograph No. 58, 2nd Edition, 414-415 (1943).

<sup>b</sup>A single determination of neutralization equivalent was made on the saturated acids obtained from the Bertram analysis.

Both samples showed some spectroscopic evidence of oxidation by their appreciable diene absorption before isomerism and their tetraenoic absorption on heating in the absence of alkali (10). They did not appear to have reached a high state of oxidation however, and the differences in the degrees of oxidation of the samples were minor. The peroxide values of the samples substantiated the spectrophotometric findings. The linolenic/linoleic acid ratio alone indicates that Norit exerts little fractionating effect on the fatty acids. Calculations made from spectrophotometric analyses and iodine values suggest however that oleic acid may be preferentially absorbed by Norit.

Purification of the fatty acids may remove some substance which offers interference in the linolenic acid determination. Any analytical error in this determination would be multiplied in the calculation of oleic acid. In view of the uncertainty concerning

the preferential adsorption of oleic acid, the values for the unsaturated acids contained on the pigment-contaminated fraction were considered more representative, and these values were used to calculate the unsaturated acid composition of the original fat. Also polyunsaturated acids have been calculated as percentages of linoleic and linolenic acid, the commonly occurring nonconjugated diene and triene unsaturated acids, but it should be emphasized that acids of any chain length having equivalent degrees of unsaturation would yield spectra similar to these.

*Examination of the Mixed Fatty Acids.* An attempt was made to characterize the buckwheat fatty acids by converting the purified acids to methyl esters and submitting them to distillation at 2 mm. Hg. pressure through a 13-mm. by 36-in. precision-spaced wire-packed (8) adiabatic fractionating column. Each of the 22 fractions separated was examined by chemical analysis for saponification equivalent, for unsaturation by hydrogenation, and spectrophotometrically for polyunsaturated acids.

Although the samples were protected by storage under a nitrogen atmosphere, the spectrophotometric analysis for polyunsaturated acids showed that these fractions had autoxidized to degrees ranging from mild to advanced so that no completely satisfactory analysis was possible. Fraction 14, the largest, 10.58 g. from a pot charge of 119.4 g., showed the least autoxidation; and fraction 21, 4.91 g., showed the most autoxidation. Only data for these two fractions (which are representative) are shown in Table II.

*Separation of Saturated from Unsaturated Acids.* A 200-g. sample of the purified pigment-free fatty acids was separated into saturated and unsaturated acid fractions by crystallization from 1 liter of acetone at  $-20^{\circ}\text{C}$ . The saturated acids were further freed of unsaturated acids by recrystallization from

TABLE II  
Composition of Representative Methyl Ester Fractions  
of Mixed Fatty Acids

Fraction	Linoleic acid, %	Linolenic acid, %	Preformed diene as conjugated linoleic acid, %	Saponification equivalent	Iodine <sup>a</sup> value
14	24.1	52.1	0.81	294.2	207.6
21	10.6	53.7	14.0	286.5	185.3

<sup>a</sup> Calculated from the degree of unsaturation found by hydrogenation.

acetone (1 to 10) at  $-20^{\circ}\text{C}$ . An iodine value of 3.09 indicated relative freedom from unsaturated acids. A 24-g. sample of the saturated acids was converted to methyl esters by dissolving it in 41 ml. of absolute methanol, adding a solution containing 0.48 g. of concentrated sulfuric acid in 7 ml. of methanol, and refluxing for 5 hours. After cooling, 200 ml. of water were added, and the esters were extracted with ether and washed in the usual manner. The dried methyl esters had an iodine value of 2.90 (calculated from hydrogen uptake measurements). Assuming the only unsaturated ester present to be oleic acid, the amount of this ester was 3.23%.

*Fractionation of Saturated Acid Methyl Esters.* An 11.79-g. sample of the saturated methyl esters was distilled through a 7-mm. by 18-inch miniature, precision-spaced wire-packed adiabatic fractionating column.<sup>2</sup> Table III gives the composition of the fractions obtained.

<sup>2</sup> Distillation of a known mixture of methyl myristate, methyl palmitate, and methyl stearate showed that the column was highly efficient in their separation. In the preliminary tests flooding could not be controlled between 0.4 and 10 mm. Hg. pressure using a capillary nitrogen bleeder. It was effectively controlled however below 2.5 mm. Hg. pressure with the use of a magnetic stirrer. Small fraction cuts were taken, and their indices of refraction were read immediately, to follow methyl ester separation. Little attention was given to product or pot temperatures although these were measured and recorded by potentiometer during the fractionation. These temperatures fluctuated considerably owing to pressure drop in the column. By a manually operated needle valve, the reflux to product take-off ratio was maintained at not less than 10 to 1.

TABLE III  
Composition of the Saturated Methyl Esters<sup>a</sup> of Buckwheat Leaf Meal Fat

Fraction No.	Fraction wt., g.	$n_D^{20}$	Ester $\text{C}_{18}$ acid, %	Methyl oleate, <sup>b</sup> %	Ester $\text{C}_{18}$ acid, <sup>c</sup> %	Ester $\text{C}_{20}$ acid, <sup>c</sup> %	Ester $\text{C}_{22}$ acid, %	Ester $\text{C}_{24}$ acid, %
1.....	0.180	1.4293	100					
2.....	0.215	1.4294	100					
3.....	0.225	1.4294	100					
4.....	0.960	1.4294	100					
5.....	1.025	1.4293	100					
6.....	1.305	1.4293	100					
7.....	0.553	1.4293	100					
8.....	0.860	1.4293	100					
9.....	0.640	1.4294	100					
10.....	0.390	1.4294	100					
11.....	0.390	1.4294	100					
12.....	0.245	1.4294	100					
13.....	0.562	1.4294	100					
14.....	0.665	1.4294	100					
15.....	0.580	1.4297	100					
16.....	0.155	1.4339		26.6	73.4			
17.....	0.195	1.4355		32.1	67.9			
18.....	0.185	1.4340		20.5	79.5			
19.....	0.275	1.4339		9.9	66.2	24.0		
20.....	0.307	1.4339		13.2	47.9	38.8		
21 <sup>d</sup> .....	1.075	1.4384					100 <sup>e</sup>	
22 <sup>f</sup> .....	0.420	1.4349 <sup>g</sup>						100 <sup>h</sup>
23 <sup>i</sup> .....	0.140	1.4369						
24 <sup>j</sup> .....	0.245							
Total.....	11.792		74.6	1.78	6.13	1.57	9.12	3.56
Total, corr. <sup>k</sup> .....			78.5	.....	6.45	1.65	9.60	3.75

<sup>a</sup> Distilled at 0.90-0.40 mm. Hg. pressure.

<sup>b</sup> Calculated from hydrogen No., assuming methyl oleate to be the only unsaturated ester present.

<sup>c</sup> Calculated from hydrogen No. and saponification equivalent.

<sup>d</sup> A fraction obtained by sudden introduction of nitrogen into still pot.

<sup>e</sup> X-ray data show presence of traces of  $\text{C}_{24}$  and  $\text{C}_{28}$  acid esters.

<sup>f</sup> Column drainage.

<sup>g</sup> Reading at  $80^{\circ}\text{C}$ . Fraction was solid at  $50^{\circ}\text{C}$ .

<sup>h</sup> X-ray data show presence of a trace of  $\text{C}_{30}$  or higher acid esters.

<sup>i</sup> Fraction-cutter washings.

<sup>j</sup> Still-pot residue.

<sup>k</sup> For fractions 23 and 24 and for methyl oleate.

TABLE IV  
Analyses of Methyl Esters of Saturated Acids Prepared from Buckwheat Leaf Meal Fat

Fraction No.	Iodine value <sup>a</sup>	Saponification equivalent <sup>b</sup>	X-ray powder pattern identification of methyl esters of saturated acids with carbon content of							
			C <sub>16</sub>	C <sub>18</sub>	C <sub>20</sub>	C <sub>22</sub>	C <sub>24</sub>	C <sub>26</sub>	C <sub>28</sub>	C <sub>30</sub> or higher
16.....	22.8	301								
17.....	27.5	301								
18.....	17.6	297								
19.....	8.5	306	..... <sup>c</sup>	Major	Minor	.....	.....	.....	.....	.....
20.....	11.3	311	.....	Major	Minor	.....	.....	.....	.....	.....
21.....	∞	..... <sup>d</sup>	.....	.....	.....	.....	Trace?	Major	Trace?	.....
22.....	∞	..... <sup>d</sup>	.....	.....	.....	.....	.....	.....	Major	Trace?

<sup>a</sup> Calculated from the degree of unsaturation found by hydrogenation.

<sup>b</sup> A modified method for micro samples by C. L. Ogg and C. O. Willits of this laboratory. (Manuscript in preparation.)

<sup>c</sup>..... means none detected.

<sup>d</sup> Values not determined because the high molecular weight acids were solvent insoluble.

The indices of refraction (6) show that the first 15 fractions are pure methyl palmitate. X-ray powder patterns prepared by L. P. Witnauer (11) support this conclusion. The remaining fractions, 16 to 22, were analyzed for saponification equivalents and for unsaturation by hydrogenation values; also fractions 19 to 22 were submitted to x-ray examination. Table IV shows the results of these analyses. This information was used to calculate the composition of fractions 16 to 22 inclusive. Only 1.78% of the 3.23% methyl oleate present in the original methyl ester mixture was accounted for in the distilled fractions. The difference was probably represented by decomposition material retained in the still residue.

Table V presents a summary of the organic acid composition of the buckwheat leaf meal fat calculated from the data obtained in this investigation.

TABLE V  
Organic Acid Composition of Buckwheat Leaf Meal Fat

Acid	In saturated insoluble acids, %	In mixed insoluble acids, %	In the original fat, %
Saturated			
Formic <sup>a</sup> .....			0.27
Acetic <sup>a</sup> .....			Trace
Lactic <sup>a</sup> .....			0.87
Palmitic.....	78.3	17.1	7.97
Stearic.....	6.47	1.41	0.66
Arachidic.....	1.66	0.36	0.17
Behenic.....	None	None	None
Lignoceric.....	Trace	Trace	Trace
Hexacosanoic.....	9.75	2.13	0.99
Octacosanoic.....	3.87	0.83	0.39
Tricosanoic.....	Trace	Trace	Trace
Unsaturated			
Oleic.....		28.2	13.1
Linoleic.....		18.2	8.48
Linolenic.....		32.5	15.1
Preformed			
Conjugated.....		3.5	1.63
Dienoic.....			
Total.....	99.99	104.23	49.63

<sup>a</sup> Previously reported (5).

*Petroleum-Ether Insoluble Material of the Water-Insoluble Fraction.* The large quantity of petroleum-ether insoluble material found in the water-insoluble fraction (28.5% of the fraction) of the saponified fat indicates that the original fat probably contained, in addition to red pigment (5), large quantities of chlorophyll degradation products as well as the chlorophyll (2.8%) found by analysis (5).

A spectrophotometric examination of this material gave an absorption spectrum of the general shape characteristic of chlorophyll degradation products with maxima most pronounced at about 658, 498, and 410 m $\mu$ . and less pronounced at about 598 and 558.

No individual compound was identified, but there was spectral similarity to that of phylloerythrin (4).

The solubility behavior of this material resembled that of the porphyrins. The best solvent among those tried was pyridine, in which it was soluble to the extent of about 20 g. in 100 ml. of boiling solution. Formic and glacial acetic acids were also good solvents. It was moderately soluble in absolute ethanol, acetone, strong hydrochloric acid, and ammonium hydroxide solutions. It was only slightly soluble in ether, ethyl acetate, and benzene. In water and petroleum-ether it was insoluble. Where soluble, except in hydrochloric acid solution, it imparted an olive-green color to the solvent. These solutions fluoresced red when exposed to ultra-violet light. The hydrochloric acid solution was emerald green and did not fluoresce. Dilute pyridine solutions were olive green but strong ones were red.

The ash content of this petroleum-ether material was relatively low, 0.58%, and the metals present were chiefly iron and magnesium.

An attempt was made to separate and identify the porphyrins by partition chromatography according to the technique of Rimington (9). Results showed the presence of only monocarboxylic acid type compounds such as phylloerythrin.

R<sub>F</sub> value for phylloerythrin, 0.9; found, 0.89.

Values for carbon and hydrogen were in fairly close agreement with those calculated for phylloerythrin.

Anal. Calc'd for C<sub>33</sub>H<sub>54</sub>N<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O: Carbon, 71.72%; hydrogen, 6.56%. Found: Carbon, 69.28%; hydrogen, 6.82%.<sup>3</sup> Moisture: Calc'd, 3.26%; found, 3.37%.

Satisfactory values for nitrogen analysis could not be obtained either by Kjeldahl or by Dumas method.

### Summary

The composition of fatty acids of the saponified fat of buckwheat leaf meal was investigated. The mixed fatty acids amounted to 49.6% of the composition of the fat. The chief organic acids found were: linolenic, 15.1%; oleic, 13.1%; linoleic, 8.5%; and palmitic, 8.0%. Less than 1% each of such acids as formic, lactic, stearic, arachidic, hexacosanoic, and octacosanoic, and only traces of acetic, lignoceric, and tricosanoic (or higher) acids were found. The so-called "insoluble acids" of the saponified fat, less the unsaponifiable matter, contained 28.5% (18.5% based on the original fat) of material identified as red pigment and probably a mixture of chlorophyll degradation compounds, chiefly phylloerythrin.

<sup>3</sup>Averages of two determinations. Corrected for ash.

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## Polymerization of Styrene in the Presence of Fatty Acid Methyl Esters<sup>1</sup>

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IN the preceding paper on the copolymerization of vegetable oils and styrene we were unable to draw any conclusions on whether the oils copolymerize with styrene or whether the reaction products are mixtures of oils and polystyrene (4). Satisfactory separation procedures for polystyrene and triglycerides were not available, and we studied therefore the copolymerization of styrene with methyl esters of fatty acids which can be separated from polystyrene by fractionation with methanol. This gave also an opportunity to investigate the effect of structural variations and of different functional groups of methyl esters on the polymerization with styrene. The object of this paper is to present our findings.

### Experimental

**Materials.** Purified oleic acid was prepared from the Fischer U.S.P. product, using the crystallization procedure of Swern *et al.* (22). The material had an iodine value of 87.4 and contained less than 1.5% linoleic acid according to spectrophotometric analysis. The acid was used to prepare the methyl ester.

Elaidic acid was obtained from the purified oleic acid by isomerization with nitrous acid as described by Kass and Burr (10). The product had a melting point of 44°C. and an iodine value of 87.9. The acid was esterified with methanol.

Methyl ricinoleate was obtained from castor oil methyl esters by fractionation through a Vigreux column at 1 mm. Hg. (11).

Methyl 12-hydroxystearate was prepared from ricinoleate ester by hydrogenation, using Raney Nickel catalyst at 40 pounds' hydrogen pressure at 85-90°C. (6).

Methyl 12-ketostearate was obtained from the hydroxy analogue by oxidation with chromic acid in acetic acid solution (6).

Methyl 9,12-linoleate was prepared from tetrabromostearic acid by the usual debromination procedure followed by esterification of the linoleic acid with methanol.

The t,t-10,12-linoleic acid was prepared from dehydrated castor oil fatty acids according to the method of von Mikusch (13). The acid had a melting point

of 56-57°C. and was employed for the preparation of the methyl ester.

Blown methyl oleate was obtained by passing air through methyl oleate at a rate of 1 liter per minute at 80-85°C. until the desired peroxide value was obtained.

Methyl 9,10-epoxystearate was prepared from methyl oleate according to the method of Findley *et al.* (5).

Methyl 9,10-dihydroxystearate was obtained by hydrolysis of the epoxy ester.

Dimethyl dilinoleate was furnished by the Northern Regional Research Laboratory through the courtesy of Dr. J. C. Cowan. The ester was prepared from soybean oil and was distilled in a centrifugal molecular still.

Residual methyl dimeric ester was obtained by esterification of commercial "Dimer Acids" manufactured by Emery Industries Inc.

The styrene was a 99% commercial grade. It was distilled prior to use in an all-glass apparatus.

Eastman Kodak White Label benzoyl peroxide was used without purification.

Fischer's C. P. Xylene was shaken with fuming sulfuric acid, washed, dried over anhydrous sodium sulfate, and distilled prior to use.

**Polymerization.** In a typical experiment 10 g. of styrene and 10 g. of methyl ester were dissolved in 20 g. of xylene. The mixture was refluxed for 16 hours. Generally benzoyl peroxide, in amounts from 1 to 10% by weight based on the styrene, was added as a catalyst.

**Separation Procedures.** Unreacted styrene and solvent were removed from the reaction mixture in vacuo. The residue was then refluxed for 15 minutes with approximately 10 times its volume of methyl alcohol, and the alcohol was decanted from the insoluble residue. Extraction with methanol was repeated twice. From the combined methyl alcohol extracts a fatty ester fraction I was obtained by evaporation of the alcohol.

The methanol insoluble residue was dissolved in approximately twice its volume of benzene, and the precipitate formed by the addition of about 10 volumes of methanol for one volume of this benzene solution was separated. The benzene methanol solution was evaporated to dryness to recover fraction II. The insoluble residue, dried in vacuum, gave fraction III.

<sup>1</sup>Presented at 25th Fall Meeting, American Oil Chemists' Society, Chicago, Ill., Oct. 8-10, 1951.

TABLE I  
Results Obtained When Treating Fatty Esters With Styrene

Ester	Physical Constants of Esters			Other Constants	% Catalyst	% Styrene Reacted	Non-volatile Product	Fraction Number	Styrenation Data				Other
	Iodine Value	Saponification Value	Iodine Value						% of Ester Recovered	Iodine Value	Saponification Number		
Methyl oleate	81.4	188.5	79.3		1	86.0	Heterogeneous	I II III	76.2 10.5	187.1	187.1		
Methyl oleate	81.4	188.5	77.1		5	97.5	Heterogeneous	I II III	84.4 12.9	185.1 172.0	185.1 172.0		
Methyl oleate	81.4	188.5	74.4		10	98.7	Clear	I II III	91.0	181.9 107.7	181.9 107.7		
Methyl elaidate	83.6	189.2	81.8		1	89.7	Heterogeneous	I II III	88.5 8.6	187.2	187.2		
Methyl ricinoleate	82.5 <sup>(a)</sup>	181.2	77.3	Acetyl value = 155.7	5	99.3	Heterogeneous	I II III	92.5 6.1	170.3 156.4	170.3 156.4		
Methyl 12-hydroxystearate	.....	.....	.....	m.p. = 56.7°C.	5	97.8	Heterogeneous	I III	99.8	.....	.....	m.p. = 56.7°C.	
Methyl 12-ketostearate	.....	.....	.....	m.p. = 46.7°C.	5	89.0	Heterogeneous	I III	99.7	.....	.....	m.p. = 46.7°C.	
Methyl 9,10-dihydroxystearate	.....	170.3	.....	m.p. = 69.70°C.	5	93.2	Heterogeneous	I II III	81.9 13.2	168.1 145.4	168.1 145.4		
Methyl 9,12-linoleate	169.3	189.7	137.4		1	81.8	Heterogeneous	I III	96.2	187.1	187.1	10.6% diene conjugation	
Methyl 9,12-linoleate	169.3	189.7	132.7		5	83.5	Heterogeneous	I III	91.0	189.0	189.0	11.5% diene conjugation	
Methyl 9,12-linoleate	163.1	.....	143.9		10	97.0	Clear	I II III	76.2 16.8	180.5 172.2	180.5 172.2	5.9% diene conjugation	
Methyl t,t-10,12-linoleate	.....	190.3	.....	m.p. = 23.4°C.	1	61.8	Heterogeneous	I III	79.2	192.0	192.0	m.p. = 22.4°C.	
Methyl t,t-10,12-linoleate	.....	190.3	.....	m.p. = 23.4°C.	5	88.0	Heterogeneous	I II III	80.9 7.7	193.5 190.0	193.5 190.0	m.p. = 23.4°C.	
Blown methyl oleate	.....	234.6	53.1	P.V. = 710	None	94.5	Clear	I III	99.0	182.1	182.1		
Blown methyl oleate	.....	.....	.....	P.V. = 1556	None	95.0	Clear	I III	97.1	180.5	180.5		
Methyl 9,10-epoxystearate	.....	180.1	.....	Epoxy oxygen = 4.9	5	86.5	Clear	I IA II III	89.5 13.9	181.3 159.8	181.3 159.8		
Dimethyl dilinoleate	.....	194.2	.....		None	91.3	Clear	I IA II III	48.1 43.6	191.8 164.9	191.8 164.9		
Dimethyl dilinoleate	.....	194.2	.....		5	89.8	Clear	I IA II III	50.1 38.6	186.3 179.8	186.3 179.8		
Residual dimeric methyl esters	.....	175.1	.....		5	96.1	Clear	I IA II III	61.4 31.9	195.8 149.4	195.8 149.4		
Methyl Stearate	4.1	199.2	.....		10	97.9	Clear	I III	96.4	190.3	190.3		

<sup>(a)</sup> The 2-minute Wijs method employed—Skell & Radlove, Ind. Eng. Chem., Anal. Ed., 18, 67 (1946).

TABLE II

Comparison of the Separation of Copolymerized Styrene and Methyl Esters With the Separation of Mixtures of Polystyrene and Esters

Ester	Type	Fraction	% of Ester Recovered	Saponification Number	Remarks
Blown methyl oleate P. V. = 710	Copolymerization conditions	I	94.8	194.9	97.7% styrene polymerized. Non-volatile—clear resin.
		II	.....	63.8	
		III	.....	22.0	
Blown methyl oleate P. V. = 710	Mixture	I	77.3	224.6	Styrene polymerized with 5% catalyst in xylene solution. 92.4% styrene polymerized. Ester added to polystyrene solution. Mixture a clear resin.
		II	24.2	129.4	
		III	.....	9.7	
Residual methyl dimeric esters	Copolymerization conditions	I	61.4	195.8	97.1% styrene polymerized. Non-volatile—clear resin.
		IA	39.1	149.4	
		II	.....	128.0	
		III	.....	13.0	
Residual methyl dimeric esters	Mixture	I	54.5	191.2	97.8% styrene polymerized (in xylene solution with 5% catalyst). Dimer ester refluxed in xylene with 5% benzyl peroxide. Solutions mixed. Residue—clear resin.
		IA	50.1	149.5	
		II	.....	99.7	
		III	.....	8.0	
Residual methyl dimeric esters	Copolymerization conditions	A*	114.5	155.2	91.1% styrene polymerized. Non-volatile—clear resin.
		B	.....	162.4	
		C	.....	113.2	
		D	.....	7.7	
Residual methyl dimeric esters	Mixture	A*	109.1	158.7	Styrene polymerized with 5% benzyl peroxide in xylene. Ester added to polystyrene solution. Non-volatile—clear resin.
		B	.....	164.0	
		C	.....	127.3	
		D	.....	7.3	
Methyl 9,10-epoxystearate	Copolymerization conditions	I	57.4	181.3	93.5% styrene polymerized. Non-volatile—clear resin.
		II	33.8	125.6	
		III	.....	7.7	
Methyl 9,10-epoxystearate	Mixture	I	85.1	177.4	Styrene polymerized with 5% catalyst in xylene. 96% styrene polymerized. Ester refluxed in xylene with 5% catalyst. Solutions mixed. Non-volatile—clear resin.
		II	.....	109.9	
		III	.....	7.9	
Methyl 9,10-epoxystearate	Mixture	I	86.8	172.8	Styrene polymerized in xylene with 5% catalyst. 94% styrene polymerized. Ester added to polystyrene solution. Non-volatile—clear resin.
		II	.....	90.5	
		III	.....	6.0	

\* Special fractionation procedure employed. Non-volatile dissolved in twice its volume of benzene. By adding 10 volumes of petroleum ether a precipitate (1) was formed. The benzene-petroleum ether solution was evaporated to dryness to yield fraction A. This fraction was extracted with petroleum ether by refluxing with 3 times its volume. The residue was labeled fraction B. Precipitate (1) was redissolved in twice its volume of benzene and reprecipitated by adding 10 volumes of petroleum ether. The soluble fraction was C; the precipitate D.

In several experiments the precipitation procedure was omitted.

In the case of methyl epoxystearate the methanol extraction of the non-volatile residue was followed by a similar extraction, using petroleum ether to give a fraction IA. The residue obtained was dissolved in benzene, and petroleum ether was employed as the precipitant.

The dimethyl dilinoleate and residual dimeric ester products were also submitted to both the methanol and petroleum ether extractions. However the residues were dissolved in approximately twice their volume of an ethyl ether acetone (50-50 by volume) mixture and precipitated with petroleum ether. Several sets of experiments were performed in which mixtures of polystyrene (prepared by refluxing styrene in xylene for 16 hours with 5% benzoyl peroxide) and the ester were prepared and submitted to the separation procedure and the fractions compared with those obtained from the copolymerized products.

#### Methods of Analysis

**Iodine Value.** The Wijs 3-minute procedure was used except where noted (9).

**Peroxide Value.** The Wheeler method was employed for determining the amount of peroxide in the esters (23).

**Acetyl Value.** The method of Helrich and Rieman was used (7).

**Epoxy Oxygen.** The procedure of Swern *et al.* was employed (21).

**Saponification Values.** The standard A.O.C.S. method was employed. In the case of polystyrene fractions the sample was dissolved in toluene before addition of the alcoholic KOH.

**Conjugation.** The degree of conjugation was measured with a Beckman Quartz Spectrophotometer, Model DU, using the A.O.C.S. Tentative Method Cd: 7-48 (12).

**Percentage of Styrene Reacted.** The amount of styrene which polymerized was calculated by means of the following equation:

$$\% \text{ styrene reacted} = 100 (R - E) / S; \text{ where}$$

R = percentage of non-volatile in reaction product,  
E = percentage of ester in reaction mixture, and  
S = percentage of styrene in reaction mixture.

The methyl esters used in this study are listed in Table I along with their analytical constants, the percentage of catalyst employed, and the percentage of the styrene which polymerized. In addition, the results of the separation of the products are given.

In Table II comparative data are presented on separations of reaction mixtures of styrene and fatty esters heated in the presence of catalyst with separations of polystyrene and fatty ester mixtures.

#### Results and Discussion

There are two schools of thought concerning the polymerization of styrene and vegetable oils as outlined in the preceding paper (4), and also references (8), (14), and (17). Homogeneity of the reaction products of oils and styrene was often given as evidence for copolymerization (1, 8, 18). Inability to separate the reaction products of styrene and fatty acids or esters was also presented as evidence for interpolymerization of these reactants (3, 16).

Another group of investigators considers "styrenated" oils as mixtures of oils and polystyrene (2, 15). Our findings lend support to the idea that no reaction

takes place between styrene and fatty acid radicals. After the removal of solvent we obtained for the most part heterogeneous, opaque mixtures which could be readily separated into relatively pure fatty esters and polystyrene as evidenced from the results presented in Table I.

Fraction I in the separation of the reaction products consists essentially of pure fatty esters. The second fraction is also a fatty ester fraction although of lesser purity. The sum of these two fractions is close to the total amount of starting esters, showing that very little if any copolymerization with styrene occurred.

On the other hand, blown methyl oleate and polymeric fatty acid esters without catalyst, and methyl epoxystearate with 5% and methyl oleate and linoleate with 10% catalyst yielded clear transparent reaction products.

These homogeneous reaction products could not be easily separated into fatty esters and polystyrene by the fractionation procedure; we used in some cases an additional fractionation step. However we experienced the same difficulties in separating mixtures of polystyrene with these esters as shown in Table II. The fractions obtained on extracting and precipitating mixtures of polystyrene and these fatty esters and the ones obtained from the esters and styrene submitted to copolymerizing conditions are so similar that neither clarity of the reaction products nor inability of separation in starting ester and polystyrene can be considered as evidence for copolymerization of epoxystearate, blown methyl oleate, and residual dimeric esters with styrene. From these findings it would appear that homogeneity depends on the mutual solubilities of polystyrene and fatty esters; the same conditions may apply for homogeneity of "styrenated" oils. In the case of oils however the conditions necessary to obtain mutual solubility are much more exacting. For example, the viscosity, the degree and type of unsaturation, and the amount of oxidation of the oil are important factors (1, 4, 8, 14, 19). The polystyrene itself, its molecular weight, and structural features would also be expected to influence mutual solubility.

The effect of viscosity of an oil on the homogeneity of the styrenated product has been described previously, increased viscosity promoting greater compatibility (4, 8). We observed the same phenomenon. Polymeric fatty esters, being more viscous than unpolymerized esters, gave a clear product whether reacted with styrene or mixed with polystyrene.

The role of unsaturation in oils in promoting homogeneity is not apparent from our results with such esters. The unsaturated esters we investigated appear to exert little if any influence for they are almost totally immiscible with polystyrene and are recovered practically quantitatively. The unsaturation in the methyl linoleate was noticed to have partially shifted to a conjugated form. This finding is different from the results observed with triglycerides where it has been noted that increased unsaturation of the fatty acid components promotes homogeneity on styrenation (8, 14). Diene conjugation per se does not appear to increase homogeneity in the reaction of fatty esters with styrene. For example, neither 9,12-methyl linoleate nor *t,t*-10,12-methyl linoleate give homogeneous products.

We have not examined trienoic esters, but, working with linseed oil and linseed fatty acids which are rich in trienoic constituents, Petit and Fournier found no evidence for copolymerization (15). However these authors found evidence for some reaction of one mole of styrene with one mole of unsaturated fatty acid by the Diels-Alder addition. A small amount of reaction of this type could lead to homogeneity in triglycerides while it would not necessarily be sufficient to give homogeneity with monoesters. Conjugated triene unsaturation as with tung oil has been examined by Brunner and Tucker (2), who found evidence for copolymerization. It is quite possible however that in this case too a Diels-Alder reaction between styrene and fatty acid radicals contributed to homogeneity.

The influence of the concentration of catalyst on the homogeneity of "styrenated" oils has been previously demonstrated (4). We obtained similar results with the linoleate and oleate esters. Using 5% catalyst, no homogeneous product was obtained, but, by increasing the amount of benzoyl peroxide to 10%, a compatible mixture could be obtained. We have also found that a homogeneous mixture is obtained with methyl stearate if 10% benzoyl peroxide is present. Schulz showed that increasing the concentration of benzoyl peroxide in styrene will decrease the average molecular weight of the polystyrene (20). It can be expected that fatty esters and oils are more miscible with polystyrene of low average molecular weight than with polystyrene of high average molecular weight.

Blown oils (4, 14, 19) and our results on blown methyl oleate show that oxidation leads to homogeneous products with styrene. Although our results cannot rule out small amounts of these esters in the polystyrene, the fact that the saponification values in extracted residues from mixtures are as high as the ones from copolymerizing condition products would indicate that no fatty esters interpolymerized with the styrene. The effect of the hydroperoxide, one of the principal constituents of blown esters and oils, may be similar to the effect of increasing the concentration of peroxide catalyst. Since blown methyl oleate is miscible with polystyrene and the unblown ester is not, our findings do not allow any conclusions as to the presence and possible importance of such a catalytic effect of hydroperoxide groups on the styrene polymerization.

Blowing of unsaturated fatty esters gives not only hydroperoxides but also other oxygenated groups such as keto, hydroxy, and possible epoxy groups. Of these functional groups only the epoxy leads to homogeneity. This group might therefore be an additional factor in giving homogeneous products with blown oils.

Our results would indicate that little if any copolymerization takes place when styrene is polymerized in the presence of the fatty acid esters under the conditions outlined in this paper. The "styrenated" oils are possibly complex mixtures of the fatty components and polystyrene but not necessarily copolymers in the true sense. The fact that some of the homogeneous products may not be true copolymers does not necessarily detract from their utility as surface coating agents.

It would be of interest to study the effect of other catalysts, of modifiers, and of the mass and emulsion reaction techniques when polymerizing styrene in the presence of fatty acid methyl esters and to investigate the resulting products.

### Summary

Data on the products obtained on polymerizing styrene in the presence of various methyl esters of fatty acid have been presented. These data show that no copolymerization between the esters and styrene occurs and that homogeneity of some of the reaction products cannot be considered as proof for interpolymerization.

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## Modification of Vegetable Oils. XII. Plasticity of Some Aceto Derivatives of Monostearin<sup>1,2</sup>

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A RELATIVELY stable fat which solidifies to a non-greasy yet flexible solid should have many potential uses. So far as the authors are aware, a fat which is non-greasy and highly flexible at the same temperature has never been prepared heretofore. Normally non-greasiness and flexibility in fats are mutually exclusive properties. The authors have found that fats composed of certain mixtures of acetostearins are extremely flexible solids at and below room temperature. The preparation and some of the properties of these acetostearins are described here.

### Preparation of Acetostearins

Acetostearins were prepared by reacting acetic anhydride with monostearin. A temperature of 110°C. and a reaction time of one hour were used in most instances. The reactants were stirred and kept under dry hydrogen to prevent reaction of the acetic anhydride with atmospheric moisture. The reaction was interrupted as desired by adding hot water to the reaction mixture and stirring for 10 minutes to hydrolyze the unreacted acetic anhydride. After washing the reaction product with distilled water it was dried by warming it under reduced pressure and stripping with hydrogen.

Three monostearins, referred to as A, B, and C, were used to prepare the acetostearins. Monostearin A, prepared from pure stearic acid, contained 99.2% monostearin by analysis (1) and had a hydroxyl value of 306.5 according to the acetylation method of West *et al.* (2), modified by using one part of acetic anhydride to three parts of pyridine. Monostearin B was a commercial, molecularly distilled product. It had a hydroxyl value of 335.5 and

a monoglyceride content of 91.5%. The average molecular weight of the combined fatty acids in this product was 270.5, which corresponds to a 1:1 ratio of stearic and palmitic acids. Of the three monostearins only monostearin B contained free glycerol, about 2%. Monostearin C was a technical grade product made from completely hydrogenated cottonseed oil. Its hydroxyl value was 236.9, and it contained 61.0% monoglycerides of fatty acids, having an average molecular weight of 280.0.

Physical properties of the acetostearins formed by reaction of monostearin with acetic anhydride could be controlled to a considerable extent by manipulating the reaction time, temperature, and proportion of acetic anhydride employed. None of the reactions was carried to 100% completion, as evidenced by the hydroxyl value of the finished products. A plot of the hydroxyl value *vs.* reaction time at 110°C. between one hydroxyl-equivalent of monostearin B and one mole of acetic anhydride is reproduced in Figure 1. A similar curve was obtained when different proportions of acetic anhydride were reacted for one hour at 110°C.

The ratios of monostearin to acetic anhydride used in making the products subjected to elongation and bending tests were such that one equivalent of hydroxyl in the monostearin was mixed with 0.5, 1.0, and 2.0 moles of acetic anhydride, respectively. The reactions were stopped after one hour at 110°C.

Since the acetostearins were used solely for making physical measurements, no precautions were taken to assure that they were entirely free of odor and taste.

### Composition of the Products

The free fatty acid content of the acetostearins was nearly always between 1.0 and 1.5%, which is quite low in view of the fact that two of the monostearins used to prepare the products contained several tenths of a per cent of free fatty acids. Therefore it must

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<sup>2</sup> Presented at the 42nd Annual Meeting of the American Oil Chemists' Society, New Orleans, La., May 1-3, 1951.

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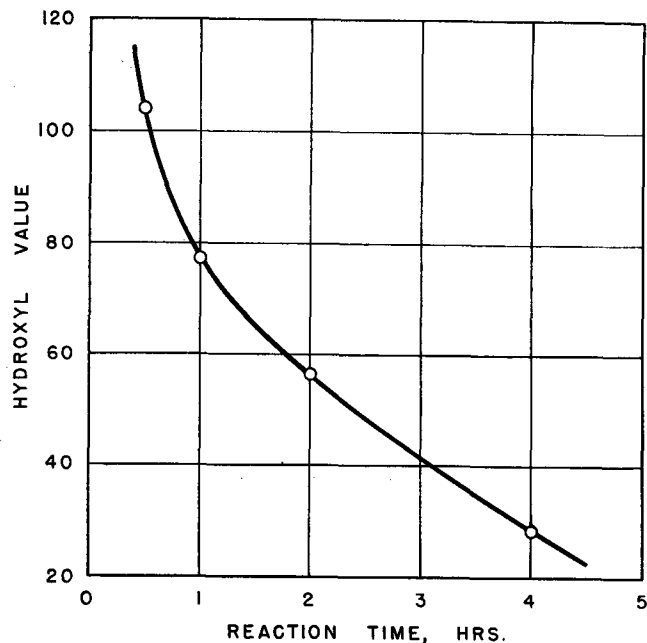


FIG. 1. Rate of reduction of hydroxyl value for one hydroxyl equivalent of monostearin B and one mole of acetic anhydride reacted at 110°C.

be concluded that reaction occurred by direct acetylation, uncomplicated by acid substitution. The short melting range of the products prepared with monostearins A and B, which in one case was less than a degree, and the fact that monostearin is relatively stable when heated to 110°C. in glacial acetic acid substantiate the validity of this conclusion.

Since the reaction consisted of uncomplicated acetylation, the approximate composition of each of the products subjected to elongation and bending tests can be calculated from the data which will be presented. For example, one product (No. 3, Table I)

TABLE I  
Elongation at Break Point and Resistance to Stretching of Acetostearins, Monostearin, and Paraffin

Product No.	Monostearin used <sup>b</sup>	Mole (CH <sub>3</sub> CO) <sub>2</sub> O/OH equivalent <sup>a</sup>	Maximum load, lbs.	Load at break, lbs.	Elongation, %
1.....	A	0.5	1.7	.....	> 800
2.....	A	1.0	0.71	.....	> 800
3.....	A	2.0	0.49	.....	> 800
4.....	B	0.5	1.6	0	467
5.....	B	1.0	0.43	0	513
6.....	B	2.0	0.32	.....	> 800
7.....	C	0.5	9.8	9.1	31
8.....	C	1.0	6.7	0.3	241
9.....	C	2.0	1.6	.....	> 800
Monostearin B.....	.....	.....	3.7	3.7	4
Paraffin.....	.....	.....	8.0	8.0	5

<sup>a</sup>Ratios are moles of acetic anhydride used per OH equivalent in the preparation of the acetostearins.

<sup>b</sup>Monostearin used in preparing the acetostearins.

which was prepared from monostearin A contained about 19% of 1-aceto-3-stearin, 80% of 1,2-diaceto-3-stearin, and 0.3% of 1-monostearin. The other acetostearin products prepared from monostearin A differed from the given composition only in the relative proportion of the different glycerides.

Mixtures resulting from the reaction between commercial and technical grade monostearins and acetic anhydride are, of course, quite complex. However for

the sake of simplicity of discussion these mixtures will be termed *acetostearins*.

### Physical Properties

**Flexibility.** The flexibilities of the acetostearins were measured by stretching test samples of each product. This was accomplished by heating the acetostearins to 60°C., pouring them into a mold at the same temperature, and solidifying them by cooling to room temperature (26°C.). After being removed from the mold, the samples were held overnight at 22°C. and tested at the same temperature.

The test samples were formed by casting the melted product in a mold consisting of three plates of 1/8-inch sheet aluminum separated by aluminum foil. The center plate, or mold proper, was cut out to form a ribbon-shaped opening. The other two plates were confining faces of the mold.

Each molded test sample measured five inches in length and 1/8 inch in thickness. The center portion of the sample was 3/4 inch in width, but one inch from each end the width increased gradually so that the ends were 1 1/4 inches wide. In making the tests, the enlarged end-sections of the sample were covered with fine sand paper and clamped in the jaws of the testing machine. The central section of the sample measuring 3 x 3/4 x 1/8 inches was subjected to stretching.

An Instron Tensile Tester was used to stretch the samples. In this machine one of the jaws is pulled away from the other at a constant rate while the machine automatically records the load or pull necessary to maintain the rate of elongation and synchronizes this value with a recording of the amount of elongation or stretch of the test sample.

A typical load-elongation curve obtained with the Instron Tensile Tester is shown in Figure 2. In this

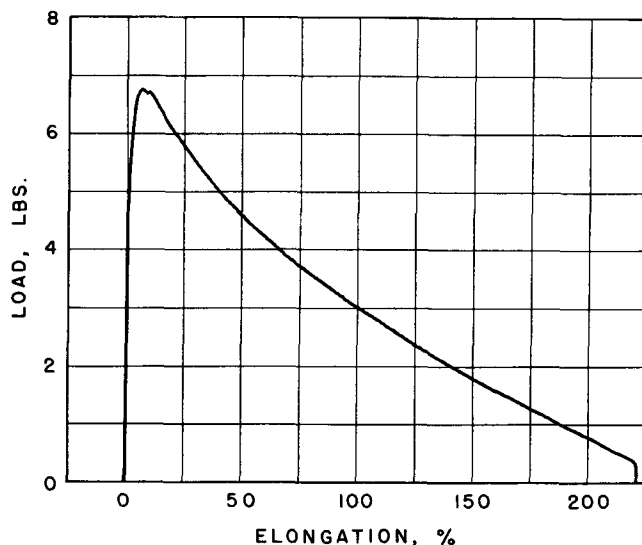


FIG. 2. Typical load elongation curve obtained by stretching a standard test piece of an acetostearin at a constant rate of one inch per minute.

test the sample was stretched at a constant rate of one inch per minute. The load increased to a maximum of 6.7 lbs. almost immediately. As the sample stretched and its effective cross-sectional area decreased, the required load decreased. When the sample had been stretched 220% of its original length, it broke. At the breaking point the cross-sectional area of the cen-

tral section of the sample was so small that the load was only 0.3 pound.

The results of the tests made by applying a stretching rate of 1.0 inch per minute are recorded in Table I. Data for tests made with monostearin B and a paraffin (m.p., 50-52°C.) are also included in the table.

Each acetostearin shown in Table I stretches far more than either monostearin B or the paraffin. More than half of the acetostearins stretched over 800%, which was the limit of the testing machine. The lowest value observed for any of the acetostearins was six times greater than was obtained with paraffin. From the data for the acetostearins prepared from monostearins B and C, it is apparent that the stretchability increased as the proportion of acetic anhydride used to prepare a given product increased.

The relative tenacity or resistance to stretching, which is indicated by the maximum load values in Table I, varied greatly, depending on the type of monostearin and proportion of acetic anhydride employed in the preparation of the products. The higher proportions of acetic anhydride gave products with the least tenacity because they acetylated greater proportions of the monostearins and transformed them into lower melting compounds.

Products made with monostearin B were not as tenacious as the corresponding products made with monostearin A, probably because the former contained monoglycerides of palmitic and possibly other fatty acids. The use of monostearin C resulted in the toughest products because it contained a large proportion of diglycerides.

The maximum loads shown in Table I are numerically equal to about 1/11 of the stress in pounds per square inch which must be applied to the molded product to start stretching at a rate of 33.3% per minute. A force of 73.7 pounds per square inch had to be applied, for example, to product No. 8 to start it stretching at a rate of 33.3% per minute.

Several of the acetostearins were subjected to stretching at rates other than one inch per minute. The results of these tests are shown in Table II.

TABLE II  
Elongation at Break Point and Resistance to Stretching of Acetostearins Under Different Rates of Elongation

Product No.	Rate of elongation, in./min.	Maximum load, lbs.	Load at break, lbs.	Elongation, %
1	1	1.7	....	> 800
	5	3.2	0	> 800
	20	4.4	0	547
2	1	0.71	....	> 800
	20	2.2	0	630
3	1	0.49	....	> 800
	20	1.6	....	> 800
4	1	1.6	0	467
	10	3.2	0	350
9	1	1.6	....	> 800
	5	3.0	0.3	613
	10	4.2	0.8	360
	20	5.4	2.2	173

From the data in Table II it can be seen that even at greatly increased rates of elongation the products flowed like liquids. A 20-fold increase in the rate of elongation resulted in about a 3-fold increase in the load or force necessary to overcome the resistance to stretching. Increased rates of elongation decreased the amount of elongation before the sample ruptured.

In order to obtain data on the flexibility of the acetostearins at a temperature other than that of the testing laboratory (22°C.) in which the Instron Tensile Tester was located, bending tests were made at 4°C. on several of the products listed in Table I. For these tests a 5 x 3/4 x 1/8-inch ribbon of acetostearin was molded on a strip of high-strength filter paper by using a molding technique similar to that described, except that a sheet of filter paper was substituted for one of the sheets of aluminum foil. The molded product was maintained at 4°C. overnight before testing.

The bending test consisted of fastening one end of the ribbon of acetostearin and filter paper to a brass cylinder one inch in diameter and rotating the cylinder at a rate of 33° per minute while pulling at the other end of the ribbon with a force of two pounds.

Paraffin and monostearin B cracked when tested in this manner. Acetostearins Nos. 7 and 8 also cracked; but products Nos. 2, 3, 4, 5, and 6 did not crack. Acetostearins Nos. 1 and 9 cracked only slightly.

The acetostearins made with monostearin B were also tested in another way, which consisted of placing strips of the products in the freezing compartment of a domestic refrigerator. The products, especially Nos. 5 and 6, remained pliable at freezing temperatures.

*Melting Range.* The melting range of a coating fat is an important physical property. This property of the acetostearins is about as important as flexibility, especially if the products are to be used as edible coatings.

The nine acetostearins listed in Table I were non-greasy solids at room temperature (26°C.), but their melting ranges, determined by the capillary tube method, differed appreciably. The melting ranges, hydroxyl values, and monoglyceride contents of the products are recorded in Table III.

TABLE III  
Melting Range, Hydroxyl Value, and Monoglyceride Content of Acetostearins

Product No.	Melting range, °C.	Hydroxyl value	Monoglyceride content, %
1.....	45.0-48.0	153	17.8
2.....	39.5-42.0	78	2.7
3.....	38.0-39.0	36	0.3
4.....	41.0-44.0	166	11.4
5.....	32.0-35.5	78	2.8
6.....	29.0-31.0	56	0.9
7.....	44.0-54.0	122	14.1
8.....	38.0-54.0	84	4.9
9.....	35.0-54.0	38	0.4

The lower temperature recorded for each product is the temperature at which melting was first observed; the higher temperature is the one at which the product was completely liquid.

Product No. 6 began melting at 29°C. and product No. 1 began melting at 45°C. All of the products except those made with monostearin C have relatively short melting ranges. The shortest melting range observed (product No. 3) was less than one degree.

When a monostearin like product B, which was composed almost entirely of monoglycerides, was converted into acetostearins, the melting points of the products were found to be roughly proportional to their hydroxyl values. From the plot of melting point vs. hydroxyl value for the products prepared with monostearin B (Figure 3) it may be seen that there

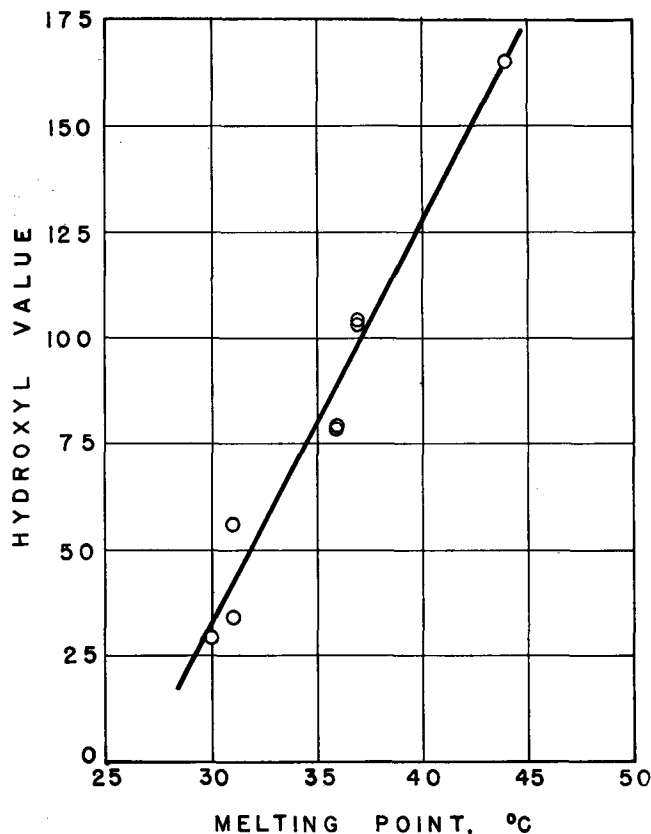


FIG. 3. Relationship between melting point and hydroxyl value of acetostearin made by acetylating monostearin B.

is a relationship between the melting point and hydroxyl value.

A number of acetostearins other than those given in Table III and Figure 3 were found to have melting points higher and lower than those shown. Some products were liquid at room temperature and others

melted as high as 60°C. It is evident that, within limits, acetostearins can be prepared with any desired melting range by the proper choice of monostearin and proportion of acetic anhydride.

### Summary

1. Acetostearins were prepared by reacting various proportions of acetic anhydride with a monostearin of 99.2% purity, a commercially available monostearin containing 91.5% monoglycerides, and a technical grade monostearin containing 61% monoglycerides. The last mentioned product was prepared from a completely hydrogenated cottonseed oil. After the removal of unreacted acetic anhydride and acetic acid from the reaction products, the flexibility and melting characteristics were determined.

2. All of the acetostearins tested were non-greasy solids at room temperature yet were highly flexible. At a temperature of 22°C. most of them could be stretched more than 800% under the test conditions. Bending tests revealed that some of the products possessed good flexibility even at 4°C.

3. The melting characteristics of the products were dependent on the purity of the monostearin used and the degree of acetylation. Some products melted completely below body temperature (37°C.), and others melted at temperatures up to 60°C. The temperature interval over which melting occurred was usually very short (1-3°); however products made from technical grade monostearin melted over a temperature range of 10-20°C.

### Acknowledgment

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## Effect of Winterization on the Composition and Stability of Cottonseed Oil

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DESPITE the fact that winterization of cottonseed oil has been practiced on an industrial scale for nearly half a century, no information could be found in the literature with respect to the effect of this process on the composition and autoxidative stability of the products. The two most important factors affecting the autoxidative stability of cottonseed oil are its content of unsaturation and tocopherols. It is known that the saturated components of the glycerides are decreased when cottonseed oil is winterized (1), but no data are available regarding the effect of this practice on the tocopherols. Consequently no correlation of tocopherol content and composition of the

glycerides with autoxidative stability has been made.

In order to investigate the relationship of the three factors mentioned above, a series of oils consisting of refined and bleached cottonseed oil, the same oil after winterization, and the stearine press cake remaining after winterization was analyzed with respect to the compositions of the glycerides, total tocopherol contents, autoxidative stability, and color. The samples were obtained from three refineries located in different cotton-producing states, namely, Tennessee, Louisiana, and South Texas. Before being analyzed, the samples were freed of soaps, when necessary, and deodorized in a laboratory deodorizer (2).

### Methods of Analysis and Calculations

Iodine values were determined by the American Oil Chemists' Society modification of the Wijs method

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TABLE 1  
 Characteristics and Composition of Original and Winterized Cottonseed Oils and Stearine Press Cake

Characteristic or constituent	Processor A Louisiana			Processor B Texas			Processor C Tennessee		
	Original	Winter- ized	Press cake	Original	Winter- ized	Press cake	Original	Winter- ized	Press cake
Peroxide value <sup>a</sup> .....	0.0	0.0	1.0	0.0	1.0	0.0	1.0	1.0	0.0
Iodine value.....	105.9	109.7	83.8	104.2	108.4	87.2	114.6	116.8	99.4
Thiocyanogen value.....	64.4	67.4	50.6	66.1	68.0	54.9	69.6	71.0	59.9
Color (yellow/red).....	35/3.92	35/3.86	20/2.27	70/6.05	70/4.05	70/3.96	35/3.22	35/3.22	35/2.27
Unsaturated acids expressed as									
Linolein, %.....	51.4	52.4	41.2	47.0	49.8	39.7	55.6	56.6	48.8
Olein, %.....	19.6	22.0	14.6	26.3	25.5	21.0	21.2	21.9	17.2
Saturated acids expressed as glycerides									
Determined, % <sup>b</sup> .....	27.4	25.0	42.3	27.2	23.4	38.0	23.1	21.6	34.0
Tocopherols, %.....	0.079	0.098	0.049	0.079	0.084	0.059	0.087	0.097	0.068
Stability, AOM hrs. <sup>c</sup> .....	8.8	9.3	9.8	9.9	8.8	8.6	7.0	9.2	9.5

<sup>a</sup> Milliequivalents peroxide per kilogram of oil.

<sup>b</sup> Determined by the modified Bertram oxidation method.

<sup>c</sup> Time required by substrate to attain a peroxide value of 100 milliequivalents during aeration at 97.7°C. with an air flow of 2.33 ml./sec.

(11), using a 100% excess of reagent and a 30-minute reaction time. Thiocyanogen values were determined with a 0.2 N solution of thiocyanogen, prepared by bromination of dry lead thiocyanate (9) suspended in a mixture of purified and dried glacial acetic acid and carbon tetrachloride. A 200% excess of reagent was used with a reaction time of 24 hours at 19°C. (8). Total tocopherols were determined by the Parker and McFarlane modification (12) of the Emmerie and Engel method (4). Autoxidative stability was determined by the active oxygen method (3, 6, 7, 10). Color was determined and expressed according to the official method of the American Oil Chemists' Society (11).

The percentages of saturated constituents, expressed as glycerides, were determined by the Pellikan and von Mikusch (13) modification of the Bertram oxidation method, using sintered glass filter sticks for the filtrations (5). The percentages of olein and linolein were calculated as prescribed in the Official Methods of the American Oil Chemists' Society (Cd 2-38) by substituting the iodine and thiocyanogen values in the following equations:

$$\% \text{ Olein} = 2.525 T - 1.348 I$$

$$\% \text{ Linolein} = 1.246 I - 1.253 T$$

where T and I represent thiocyanogen and iodine values respectively (11).

The peroxide values were determined by the method described by Moore and Bickford (10) and are reported as milliequivalents of peroxide oxygen per kilogram of oil.

### Results and Discussion

Data for the characteristics, glyceride composition, tocopherol content, and autoxidative stability, determined by the methods described above are given in Table 1. The total unsaturation, expressed as iodine values, of the winterized oil increased approximately 3% and that of the stearine press cake decreased approximately 20% compared to the original oil. A slight increase in the content of oleoyl and linoleoyl portions of the glycerides occurred in the winterized oil, and a marked decrease occurred in the stearine press cake compared to the original oil whereas the reverse was true in the case of saturated constituents.

The tocopherol content increased in the winterized oil and decreased in the stearine press cake compared to the original oil. At the temperature used for winterization the tocopherols are apparently more soluble in the unsaturated than in the saturated glycerides.

These results might have been expected on the basis of the work reported by Singleton and Bailey (14), who found it impossible to prepare high concentrations of tocopherols by low temperature crystallizations of unhydrogenated cottonseed oil owing to the fact that the tocopherols remained in solution with the more highly unsaturated portion of the glycerides.

The stabilities of the original cottonseed oil, winterized oil, and stearine press cake are essentially the same. In two cases reported the stability was slightly increased in both the winterized oil and the stearine press cake, and in the other case there was a slight decrease. It is apparent therefore that the two factors affecting the autoxidative stability of the oils tend to counterbalance one another. When the unsaturation increases, there is a corresponding increase in the tocopherol content and vice versa. Moore and Bickford (10) observed that the stability of cottonseed oil is decreased when alpha and gamma tocopherols are added to cottonseed oil. However the increase in the concentration of total tocopherols in the winterized oil was accompanied by a change in fatty acid composition.

The color of the original and winterized oils and stearine press cake remained unchanged, indicating that the pigment bodies were not disproportionately distributed between the winterized oil and press cake by this process.

### Summary

The relationship between tocopherol content, fatty acid composition, and autoxidative stability has been investigated for a series of three cottonseed oils representing a commercially refined and bleached oil, the same oil after winterization, and the corresponding stearine press cake. The results indicate that an increase occurs in unsaturation of the glycerides, which is accompanied by an increase in the tocopherol content of the winterized, compared to the unwinterized oil. The reverse is true of the stearine press cake fraction. The changes in fatty acid composition and tocopherol content are such that they tend to counterbalance one another and lead to the same final autoxidative stability in each product. The red and yellow color components of the products are unaffected by the winterization process.

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## Cottonseed and Peanut Meal Glues. Resistance of Plywood Bonds to Chemical Reagents<sup>1</sup>

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THE preparation and strength properties (4, 6), viscosity (1, 2, 5, 8), and resistance to accelerated service tests (7) of cottonseed and peanut meal glues have been described in previous reports from this laboratory. It was indicated that cottonseed and peanut meal glues prepared from solvent-extracted meals compare favorably with commercial casein glues in static strength properties and that cottonseed meal glue is superior to peanut meal glue and compares favorably with commercial casein glue on an interior test basis for 5 cycles, the strength of the casein bond changing from 384 to 283 pounds per square inch and of the cottonseed meal bond changing from 375 to 264 pounds per square inch.

The purpose of this report is to present data on the resistance of cottonseed and peanut meal plywood bonds to chemical reagents and to suggest fundamental interpretations of these data relative to the chemical factors affecting adhesion of cottonseed and peanut protein to wood.

### Experimental

**Glue formulation.** Cottonseed meal glue, consisting of 100 parts of hexane-extracted meal, 4 parts of sodium hydroxide, 15 parts of sodium silicate, 15 parts of calcium hydroxide, and 3 parts of carbon disulfide-carbon tetrachloride, was prepared as previously described (6). Peanut meal glue was prepared from solvent-extracted peanut meal in a similar manner (4). The casein glue was a commercially available glue mix which required only the addition of water.

**Plywood preparation.** The method used was similar to that described in other reports (4, 6). Each glue mix was prepared and applied to birch veneer to form 3-ply panels as recommended to give maximum shear strengths. These recommended conditions were selected in order that each glue could be compared under its optimum utilization. The cottonseed meal glue was applied at a rate of 21 pounds of glue (dry basis) per 1,000 square feet of glue line, cold pressed at 80°F. and 200 p.s.i. for 1,440 minutes, and followed by hot pressing at 237°F. and 200 p.s.i. for 10 minutes. The peanut meal glue was applied at a rate of 28 pounds of glue (dry basis) per 1,000 square feet of glue line and cold pressed at 80°F. and 200

p.s.i. for 1,440 minutes. The commercial casein glue was applied at a rate of 26 pounds of glue (dry basis) per 1,000 square feet of glue line, cold pressed at 80°F. and 200 p.s.i. for 10 minutes. The press opening during these operations was five 3/16-inch panels. Test pieces, 3/16 inch, 3 1/4 inches by 1 inch, cross-slotted to give a center section of 1 square inch, were cut from the plywood panels; then they were conditioned at 77°F. and 32% relative humidity for 6 days (3).

**Method of testing.** The method of testing the chemical resistance of cottonseed and peanut meal glue

TABLE I  
Effects of Organic Reagents on Tensile Shear Strengths of Birch Veneer Bonded with Cottonseed Meal, Peanut Meal, and Casein Glues

Reagent	Number of Days Immersed	Tensile Shear Strengths - Wood Failure (lbs./in. <sup>2</sup> - %)		
		Cottonseed Meal Glue	Peanut Meal Glue	Casein Glue
Carbon Tetrachloride	0	343 - 55	321 - 65	368 - 90
	1	152 - 30	175 - 60	182 - 30
	2	180 - 25	.....	188 - 25
	4	168 - 30	202 - 40	195 - 35
	8	176 - 35	.....	206 - 40
	10	.....	206 - 35	.....
Benzene	12	178 - 25	.....	210 - 40
	14	183 - 30	225 - 40	231 - 40
	1	184 - 35	165 - 50	224 - 45
	2	189 - 25	171 - 55	214 - 40
	4	201 - 20	180 - 35	.....
	8	194 - 35	.....	217 - 30
Acetone	10	.....	205 - 25	.....
	12	185 - 40	.....	215 - 30
	14	195 - 30	183 - 45	221 - 35
	1	141 - 30	126 - 40	194 - 30
	2	153 - 25	131 - 40	197 - 40
	4	160 - 20	141 - 35	206 - 45
Ethanol 95%	8	169 - 20	148 - 30	212 - 25
	10	.....	157 - 35	.....
	12	175 - 30	.....	224 - 40
	14	174 - 25	166 - 30	241 - 35
	1	159 - 25	146 - 40	205 - 30
	2	172 - 30	157 - 45	203 - 30
Ethanol 50%	4	171 - 25	154 - 35	201 - 35
	8	163 - 35	160 - 30	204 - 30
	10	.....	173 - 15	.....
	12	174 - 30	.....	197 - 25
	14	155 - 20	159 - 50	209 - 30
	1	143 - 25	114 - 15	192 - 40
(Water)	2	139 - 5	113 - 10	174 - 20
	4	114 - 0	101 - 0	155 - 15
	8	81 - 0	68 - 0	101 - 0
	1	144 - 25	129 - 10	181 - 30
Methanol	2	131 - 20	105 - 0	153 - 30
	4	75 - 0	50 - 0	124 - 20
	1	126 - 30	117 - 25	137 - 40
	4	134 - 35	126 - 30	145 - 35
10	142 - 30	136 - 30	140 - 30	
14	135 - 25	142 - 25	151 - 30	

<sup>1</sup>Presented at the 42nd Annual Meeting of the American Oil Chemists' Society, New Orleans, La., May 1-3, 1951.

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TABLE II

Effects of Inorganic Reagents on Tensile Shear Strengths of Birch Veneer Bonded with Cottonseed Meal, Peanut Meal, and Casein Glues

Reagent	Number of Days Immersed	Tensile Shear Strengths - Wood Failure (lbs./in. <sup>2</sup> - %)		
		Cottonseed Meal Glue	Peanut Meal Glue	Casein Glue
Sulfuric Acid 3%	0	343 - 55	321 - 65	368 - 90
	1	109 - 10	101 - 0	137 - 20
	2	69 - 0	63 - 0	87 - 10
	3	38 - 0	36 - 0	51 - 0
Sulfuric Acid 30%	1	91 - 15	83 - 0	111 - 15
	2	44 - 0	41 - 0	57 - 0
	3	23 - 0	20 - 0	31 - 0
	4	22 - 0	20 - 0	24 - 0
Sodium Hydroxide 1%	1	68 - 5	61 - 10	80 - 20
	2	53 - 0	47 - 0	58 - 10
	3	37 - 0	31 - 0	41 - 0
	4	27 - 0	.....	27 - 0
Sodium Hydroxide 10%	1	30 - 0	25 - 0	59 - 0
	2	.....	.....	23 - 0
Nitric Acid 10%	1	63 - 0	58 - 0	81 - 25
	2	40 - 0	35 - 0	52 - 5
	3	29 - 0	23 - 0	37 - 0
Hydrochloric Acid 10%	1	70 - 0	57 - 0	84 - 0
	2	52 - 0	40 - 0	59 - 0
	3	27 - 0	22 - 0	36 - 0
Sodium Chloride 10%	1	56 - 0	51 - 0	91 - 15
	2	47 - 0	42 - 0	61 - 0
	3	28 - 0	23 - 0	37 - 0
Sodium Sulfate 10%	1	65 - 0	65 - 0	115 - 10
	2	51 - 0	52 - 0	78 - 0
	3	34 - 0	37 - 0	53 - 0

bonds consisted of totally immersing the conditioned test pieces in a reagent for a specified period of time and, on removing 20 of the pieces from the reagent, immediately determining their tensile shear strengths. Then the remaining unbroken pieces, which were still immersed in the reagent, were removed at a specified time, and their strengths were determined in a similar manner. The tests were similar to A.S.T.M. Designation D896-46T and D906-49 methods for testing adhesives (3).

Shear strengths reported are averages of at least 20 values. The coefficients of variation of these averages were 10-20%. Wood failure, which was evaluated by visual observation, was reported, and the percentage of the total number of pieces tested showing wood failure was calculated.

### Results

The effects of organic reagents (carbon tetrachloride, benzene, acetone, ethanol 95 and 50%, methanol, and water) and inorganic reagents (sulfuric acid 3 and 30%, sodium hydroxide 1 and 10%, nitric acid 10%, hydrochloric acid 10%, sodium chloride 10%, and sodium sulfate 10%) on the strength properties of plywood glue joints are shown in Tables I and II. These reagents were selected from the lists of standard and supplementary reagents of A.S.T.M. Designation D896-46T (3).

From these data it is observed that on immersion of the test pieces in carbon tetrachloride and acetone solvents there was an initial decrease in the tensile strengths of the bonds followed by an increase in their strengths. On immersion of the test pieces in aqueous ethanol, methanol, and water, the tensile strengths of the bonds decreased with increasing time in contact with the solvents until a minimum value was reached. On immersion of the test pieces in benzene, an initial decrease in tensile strength of the bonds was noted; then there was no significant change

in the strengths of the bonds for periods of immersion ranging from 1 to 14 days.

It is also observed that the resistance of the bonds to inorganic reagents was low. The effects of salts, acids, or bases on the tensile strengths of the bonds were about equal.

### Discussion

There are probably four classes of forces involved in the adhesive bond, a) ionic or valence resulting from the polar groups, b) hydrogen bonding, c) van der Waal attractions, and d) dipolar interactions depending on the orientation of the protein molecules in the bond.

The strength of the bond corresponds to the weakest attractive force. For the moment neglecting the chemical nature of the adhesive forces, there are probably three bonds involved: a) the cohesion of the glue bond, b) the cohesion of the wood veneer, and c) the adhesion between the glue bond and the veneer. When the forces of adhesion and of cohesion of the glue bond are greater than the forces of cohesion of the wood, wood failure results during testing.

The data presented in Table III indicate that the tensile strengths of the bonds, determined after they have reached a reasonably constant value during immersion in the reagents, vary inversely as the dielectric constant of the reagents in which the test pieces were immersed.

TABLE III

Effects of the Dielectric Constants of the Reagents on Tensile Shear Strengths of Glue Bonded Birch Veneer

Reagent	Dielectric Constant <sup>1</sup> (20°C.)	Tensile Shear Strengths <sup>2</sup> (lbs./in. <sup>2</sup> )		
		Cottonseed Meal Glue	Peanut Meal Glue	Casein Glue
Carbon Tetrachloride.....	2.24	183	225	231
Benzene.....	2.28	195	183	221
Acetone.....	21.4	174	166	241
Ethanol, 95%.....	25.79	155	159	209
Methanol.....	33.7	135	142	151
Ethanol, 50%.....	.....	114	101	155
Water.....	80.0	75	50	124
Inorganic, aqueous.....	.....	20-30	20-40	20-60

<sup>1</sup>From "International Critical Tables of Numerical Data, Physics, Chemistry, and Technology," Natl. Res. Council of the U.S.A., McGraw-Hill Book Co. Inc., New York, 1933

<sup>2</sup>Pieces immersed for 14 days except for 50% ethanol and water which were immersed for 4 days before testing.

<sup>3</sup>Value for absolute alcohol.

This may be interpreted to indicate that ionic or valence forces are the primary attractive forces involved in the bond.

The chemical nature of the dielectric medium as well as its dielectric constant must also be considered in evaluating the effect of reagents on the bonds. The effect of benzene is to decrease the strengths of the bonds to a constant value in about 24 hours. On the other hand, immersion in carbon tetrachloride and acetone results in a decrease in strength in 24 hours below that caused by immersion in benzene. On continued immersion there is an increase in the strengths until the values obtained after 14 days of immersion are about equal to those obtained after immersion in benzene. One possible explanation is that new attractive forces are introduced by the reaction of carbon tetrachloride and acetone with the protein. To support further the concept of reaction when test pieces, which are removed from these reagents after 14 days, are reconditioned and tested, the

wet strengths of the bonds are significantly increased. This possibility of modifying the glue bonds to increase their wet strengths, i.e., to increase the forces of adhesion by substituting other attractive forces for ionic forces, is the subject of another investigation.

### Summary

The resistance of cottonseed and peanut meal and casein birch plywood glue bonds to organic and inorganic reagents for periods ranging from 1 to 14 days was determined. It was suggested that the principal attractive forces involved in the protein bonds were ionic or valence forces and that differences observed in the resistance of the glues to chemical reagents

were probably due to variations in the amino acid constitution of the proteins.

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## Fatty Acid Amides. IV.<sup>1</sup> Reaction of Fats With Ammonia and Amines<sup>2</sup>

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FATTY acid amides have a well-established industrial position, and their use is widespread and increasing (7, 11). In the commercial preparation of fatty acid amides, fatty acids, rather than fats, are treated with ammonia or amines. The main reason for this is probably the availability of inexpensive, purified fatty acids, notably from vegetable oil foots and inedible animal fats. A large increase in the demand for amides, coupled with the need for utilizing fatty acids in other applications, would probably require that fats themselves be employed as starting materials. The direct conversion of fats to amides and glycerol by reaction with ammonia or amines appears to be an attractive reaction because of its apparent simplicity and the ready availability and low cost of the starting materials. Numerous studies of this reaction have been published in the patent literature, but only a few reports have appeared in technical journals describing systematic investigations (1, 7, 8, 11).

Study of the published reports reveals considerable difference of opinion regarding the best techniques for quantitative conversions of fats to amides and glycerol. The points in question are the time and temperature of reaction, the desirability of operating under anhydrous or aqueous conditions, the need for catalysts, such as ammonium chloride and other salts, and the quantity of ammonia or amines required. Furthermore the basis for assuming that high yields have been obtained is not clear from much of the published work and, in some cases, is open to serious question. In most patents the assertion that quantitative yields are obtained is usually unsubstantiated by actual experimental data.

As part of a systematic investigation of the preparation and characteristics of nitrogen-containing fatty materials in progress in our laboratory (12, 13, 14, 15, 17), it was considered desirable to study the direct conversion of some selected fats to amides and glycerol to define conditions for obtaining quantitative yields

of products. A major portion of the present investigation was devoted to a study of the direct conversion of beef fat (in this study, oleo oil) to amides and glycerol since the most plentiful inexpensive domestic industrial fats are of animal origin. To demonstrate the generality of this work and to extend its utility, olive, castor, and tobacco seed oils were included. The direct preparation of N-(*n*-dodecyl)- and N-(2-hydroxyethyl)- as well as unsubstituted amides was also studied.

An additional line of work investigated, after conditions had been developed for quantitative conversion of fats to amides and glycerol, was the fractionation of amides by crystallization techniques in an attempt to prepare purified fatty acid amides. These could presumably then be readily converted to fatty acids by hydrolysis or employed in applications where their specialized properties made them valuable. The reasons for employing amides for the preparation of purified fatty acids, particularly the unsaturated ones, were that they are among the highest melting fatty acid derivatives, and their solubility in organic solvents is usually so low that they can be conveniently crystallized at or above 0°C. In general, crystallization for purification of unsaturated acids requires temperatures in the range of -40° to -80°C. (7, 11), and it would be a considerable advantage to be able to conduct the purifications at higher temperatures. With the exception of ricinoleamide from castor oil, oleamide from olive oil, and perhaps N-(2-hydroxyethyl) oleamide from oleo oil, amides of high purity (above 90%) were not obtained, presumably because the solubility of all the components of the mixtures were considerably reduced and, more important, the differences in solubility of the various amide types (based on degree of unsaturation) were probably too small for efficient fractionation. Some degree of fractionation was achieved however in all cases.

### Experimental

All reactions with amines were conducted in an atmosphere of nitrogen; those with ammonia in an ammonia atmosphere.

<sup>1</sup> The previous paper in this series is reference 14.

<sup>2</sup> Presented at the Fall Meeting of the American Oil Chemists' Society, Chicago, Ill., Oct. 8-10, 1951.

<sup>3</sup> One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE I  
 Reaction of Methyl Oleate With Ammonia

28% Aqueous Ammonia					
Expt. No.	Temp., °C.	Time, Hours	Quantity of NH <sub>3</sub>	Yield of Oleamide Isolated %	Special Conditions and Remarks
1.....	25	25	..... <sup>a</sup>	0	Oleic acid added in an amount equal to 2% by weight of methyl oleate.
2.....	25	25	..... <sup>a</sup>	0	Methanol present in an amount equal to that of methyl oleate.
3.....	100	6	..... <sup>a</sup>	0.7-2.5	Conducted both in absence and presence of 2% of oleic acid.
4.....	150	1	..... <sup>a</sup>	1	
5.....	150	3	..... <sup>a</sup>	25	
6.....	150	6	..... <sup>a</sup>	45	
7.....	150	6	..... <sup>a</sup>	50	2% of oleic acid present.
8.....	150	6	..... <sup>a</sup>	32	135 g. of ammonium chloride present per 100 g. of methyl oleate. Reaction product darkly colored.
9.....	175	6	..... <sup>a</sup>	50	Conducted both in absence and presence of 2% of oleic acid.
Anhydrous Liquid Ammonia					
10.....	25	6	..... <sup>b</sup>	Trace	
11.....	100	7	..... <sup>c</sup>	7.8-9.2	
12.....	135	6	..... <sup>c</sup>	40	
13.....	135	12	..... <sup>c</sup>	62	
14.....	165	6-12	..... <sup>c</sup>	86-90	The shorter time gave the slightly lower yield.
15.....	175	3	..... <sup>c</sup>	78	
16.....	175	6-12	..... <sup>c</sup>	85-89	
17.....	175	6	..... <sup>d</sup>	86	
18.....	200	6-12	..... <sup>c</sup>	79-83	Reaction product darkly colored.
19.....	200	12	..... <sup>d</sup>	75	Reaction product darkly colored.

<sup>a</sup> 900% excess.  
<sup>b</sup> 3 ml. NH<sub>3</sub>; 2 ml. methyl oleate (approx. 22 moles NH<sub>3</sub> per mole methyl oleate)  
<sup>c</sup> 1 ml. NH<sub>3</sub>; 1 ml. methyl oleate (approx. 15 moles NH<sub>3</sub> per mole methyl oleate)  
<sup>d</sup> 1 ml. NH<sub>3</sub>; 2 ml. methyl oleate (approx. 7.5 moles NH<sub>3</sub> per mole methyl oleate)

**Starting Materials.** Beef fat (edible "oleo oil"): acid number, 0.8; saponification number, 195; iodine number, 43.7-39.7 (changed during storage and handling; polyunsaturated acids, 3.3% (2).

Olive oil (edible grade): acid number, 1.5; saponification number, 193; iodine number, 80.9.

Castor oil (U.S.P. grade): acid number, 2.1; saponification number, 183; iodine number, 86.1; hydroxyl, 4.79%.

Tobacco seed oil was prepared by extracting the ground tobacco seed with petroleum naphtha (hexane fraction) in a Soxhlet extractor. The solvent-free oil had the following characteristics: saponification number, 195; iodine number, 132.0.

Methyl oleate, iodine number, 83.5, methyl oleate content, 97.5%, was prepared by the esterification of purified oleic acid obtained from olive oil by multiple low-temperature fractional crystallization and distillation (3, 16).

*n*-Dodecylamine and monoethanolamine were obtained by fractional distillation of the purest commercial grades through efficient columns. They had the correct physical and chemical characteristics. Anhydrous liquid ammonia was the purest commercial grade. It was purchased in cylinders and was used without further purification. The 28% aqueous ammonia was the A.C.S. grade.

**Preparation of Amides.** Before investigating the reaction of fats with ammonia, a systematic study was conducted on the ammonolysis of methyl oleate. This compound was selected because the determination of yield is simpler when a single amide is produced and

the reaction conditions can be translated directly to the ammonolysis of triglycerides.

**Reaction of Methyl Oleate With 28% Aqueous Ammonia.** Fifty-nine grams (0.2 mole) of methyl oleate and 123 g. of 28% aqueous ammonia (2.0 moles of NH<sub>3</sub>) were placed in a specially constructed stainless steel bomb (400 ml. capacity), which was then rotated end over end in a thermostatically controlled oil bath (9). Experiments were conducted from 25° to 175°C. for various reaction times (Table I). After the bomb had cooled, the contents were transferred to a beaker and agitated while being warmed on the steam bath to expel excess ammonia. The mixture was then made slightly acid by the addition of 6N hydrochloric acid, and the melted layer of fatty material was washed with warm water until free of acid. It was then dissolved in petroleum naphtha (hexane fraction) (3 ml./g.), treated with activated carbon, and filtered. The filtrate was adjusted to 5 ml. of solvent per gram of solute and cooled to 0°C. to precipitate oleamide. Table I shows the results of these experiments. The yield of oleamide given is that isolated as precipitate from petroleum naphtha at 0°C. Based upon recrystallization experiments with crude and pure samples of oleamide, it is estimated that approximately 85 to 90% of the oleamide present was isolated.

Evaporation of the filtrate after separation of oleamide yielded a liquid product consisting almost entirely of free acids.

**Reaction of Methyl Oleate With Liquid Ammonia.** Thirty grams of methyl oleate (0.1 mole) were placed in a stainless steel bomb (400-ml. capacity) and cooled



TABLE II  
 Characteristics of Mixed Amides From Fats

Amides	M. P., °C.	Iodine No.		Ester No.	Acid No.
		Calcd.	Found		
Unsubstituted amides (from oleo oil)	78-84	41.8	41.7	2.9	2.6
Unsubstituted amides (from olive oil)	73-74	84.9	83.2	3.0	1.5
Unsubstituted amides <sup>a</sup> (from castor oil)	62-64	90.1	85.6	4.3	1.5
Unsubstituted amides (from tobacco seed oil)	59-65	138.6	136.5	2.7	3.4
N-( <i>n</i> -Dodecyl) amides (from oleo oil)	62-68	28.4	28.1	3.2	4.1
N-(2-Hydroxyethyl) am- ides <sup>b</sup> (from oleo oil)	76-85	39.4	38.4	3.2 <sup>c</sup>	.....

<sup>a</sup> Hydroxyl, 4.69% (calcd. 5.0%).

<sup>b</sup> Hydroxyl, 5.46% (calcd. 5.4%).

<sup>c</sup> Saponification number.

to  $-45^{\circ}\text{C}$ . Thirty ml. of liquid ammonia were drawn off into a graduated cylinder (4, 6), packed in solid carbon dioxide, and added to the cold methyl oleate. The lid (also cooled to  $-45^{\circ}\text{C}$ .) was then quickly put in place and screwed down. Experiments were conducted from  $25^{\circ}$  to  $200^{\circ}\text{C}$ . for various reaction times (Table I), as described in the previous paragraph. After cooling, the excess ammonia was vented through a needle valve before the bomb was opened. The granular solid was dissolved in petroleum naphtha and then decolorized and crystallized at  $0^{\circ}\text{C}$ . using 7 ml. of solvent per gram of solute. Substantially quantitative conversion of methyl oleate to oleamide was accomplished by heating it for 6 hours at  $170^{\circ} \pm 5^{\circ}\text{C}$ . with one-half its volume of liquid ammonia (experiment nos. 14, 16, and 17; Table I).

**Reaction of Fats With Liquid Ammonia.** In the initial experiments the volume of liquid ammonia was one-half that of the fat since it had been shown with methyl oleate that quantitative conversion to amides was obtained in this way (Table I). Similar results were obtained however even when the volume of liquid ammonia was one-fourth that of the fat, and all subsequent work was conducted with this ratio.

The preparation of unsubstituted amides from oleo oil is typical of the reaction of all the triglycerides with liquid ammonia.

Three hundred and fifty ml. (314 g., 0.364 mole) of oleo oil (iodine number 39.7) were placed in a stainless steel bomb (700-ml. capacity), and the lid,

which was provided with a needle valve, was put in place and securely tightened. The bomb was cooled to  $-50^{\circ}\text{C}$ . and evacuated by means of a mechanical pump. Ninety ml. of liquid ammonia were drawn off into a graduated separatory funnel packed in solid carbon dioxide, and the ammonia was then introduced into the bomb through the needle valve. The bomb was then heated to  $170^{\circ} \pm 5^{\circ}\text{C}$ . for six hours with rocking (calculated pressure, approximately 2,500 lb./sq. in.), after which it was cooled to room temperature. The excess ammonia was allowed to escape through the needle valve, and the yellow solid remaining in the bomb was transferred to a beaker and washed free of glycerol with several hot water washes. On cooling, the oily layer formed a hard cake which was broken up and dried, yielding 294 g. (98%) of mixed amides, characteristics of which are given in Table II.

By the same procedure unsubstituted amides of olive oil, tobacco seed oil, and castor oil were also prepared in substantially quantitative yield (Table II).

Glycerol was readily recovered in high yield from the aqueous washes by evaporation of the water and vacuum distillation of the crude glycerol concentrates.

**N-(*n*-Dodecyl) Amides of Oleo Oil.** A mixture of 43 g. (0.05 mole) of oleo oil (iodine number 43.7) and 30 g. (0.156 mole) of *n*-dodecylamine was heated for three hours at  $230^{\circ}\text{C}$ . When the mixture had cooled below  $100^{\circ}\text{C}$ ., 1N hydrochloric acid was added with stirring. The layers were allowed to separate, and the aqueous layer was removed after the amides had solidified. The amide cake was remelted and washed several times with hot water until free of acid, yielding 65.6 g. (98%) of mixed dodecyl amides; m.p.  $62^{\circ}$  to  $68^{\circ}\text{C}$ . (Table II). Glycerol was readily isolated by distillation of the combined aqueous layers.

In a larger run consisting of 500 g. of oleo oil and 325 g. of *n*-dodecylamine, an approximately 90% conversion to amides, m.p.  $62^{\circ}$  to  $68^{\circ}\text{C}$ ., was obtained. This material was employed in the fractionation reported in Table III.

**N-(2-Hydroxyethyl) Amides of Oleo Oil.** A mixture of 500 g. (0.58 mole) of oleo oil (iodine number 43.7) and 159 g. (2.1 moles) of monoethanolamine was refluxed for 15 minutes. The cooled reaction mixture was dissolved in warm petroleum naphtha (10 ml./g.) and washed several times with warm 10% sodium sulfate solution to remove the excess monoethanolamine and

 TABLE III  
 Fractional Crystallization of Mixed Amides From Fats

	Mixed Amides		Crystallized Amides															
			Solvent <sup>a</sup>	Fraction I				Fraction II				Fraction III				Filtrate		
				Crystn. Temp. °C.	Yield %	M.p. °C.	Iodine no.	Crystn. Temp. °C.	Yield %	M.p. °C.	Iodine no.	Crystn. Temp. °C.	Yield %	M.p. °C.	Iodine no.	Yield %	M.p. °C.	Iodine no.
Unsubstituted amides	M.p.	Iodine no.																
Oleo oil.....	78-84	41.7	A, 5/1	25	46.8	95-97	13.4	-20	37.0	67-72	69.6	.....	.....	.....	.....	11.2	39-40	67.1
Olive oil <sup>b</sup> .....	73-74	83.2	A, 8/1	24	8.8	87-88	34.2	0	74.9	74-75	82.9	-30	8.0	69-73	98.6	4.7	39-53	157.9
Castor oil <sup>c</sup> .....	62-64	85.6	A, 5/1	0	69.0	65-66	86.3	-20	13.3	62-63	91.2	-40	4.4	59-60	99.5	5.7	39-43	107.5
Tobacco seed oil.....	59-65	136.5	A, 5/1	15	8.0	85-90	43.3	5	11.0	67-71	116.2	-40	70.0	52-63	150.7	11.0	semi-solid	119.2
N-( <i>n</i> -dodecyl) amides																		
Oleo oil <sup>d</sup> .....	62-68	28.4	E, 25/1	24	45.2	78-79	6.1	-20	37.7	45-55	46.6	.....	.....	.....	.....	16.3	semi-solid	39.2
N-(2-hydroxyethyl) amides																		
Oleo oil <sup>e</sup> .....	76-85	38.4	A, 15/1	0	54.8	86-92	9.2	-20	27.2	57-59	71.0	.....	.....	.....	.....	15.5	32-36	73.0

<sup>a</sup>A = acetone, E = 95% ethanol. The numbers indicate solvent ratio in ml./g.

<sup>b</sup>Calcd. for oleamide: iodine number 90.2.

<sup>c</sup>Calcd. for ricinoleamide: iodine no. 85.3; % OH 5.72. The % OH of the mixed amides was 4.69; Fraction I, 5.39; Fraction II, 4.82; Fraction III, 4.39; and Filtrate, 4.32.

<sup>d</sup>The acid number of the mixed amides was 6.0; Fraction I, 1.0; Fraction II, 1.7; Filtrate, 30.0.

<sup>e</sup>Calcd. for N-(2-hydroxyethyl) oleamide: iodine number 78.0.

the glycerol formed. The solvent was evaporated, yielding 525 g. (95%) of N-(2-hydroxyethyl) amides, m.p. 76.3° to 85.1°C. (Table II).

**Fractional Crystallization of Amides.** Table III summarizes the results obtained in the crystallization of the amides prepared from the various fats. Crystallization temperatures above 0°C. were maintained for two hours; 0°C. or below, overnight.

**Hydrolysis of Amides to Free Acids.** One mole of amide fraction, obtained by crystallization as just described, was refluxed with 1 l. of constant boiling (approximately 20%) aqueous hydrochloric acid. Analytical samples were removed at intervals, dissolved in petroleum naphtha, and washed with warm water until free of hydrochloric acid. Iodine and acid numbers were then determined on the dried samples.

An oleamide-rich fraction (iodine number 85.5; acid number, 1.4) required only two hours refluxing to yield free acids with an iodine number of 78.4 (calcd. 85.2) and an acid number of 192. Longer hydrolysis, up to 24 hours, did not increase the acid number.

An N-(2-hydroxyethyl) oleamide-rich fraction (iodine number, 62.0; acid number, 0.8) was also completely hydrolyzed in two hours, yielding free acids with an iodine number of 70.3 (calcd. 71.5) and an acid number of 191.

On the other hand, an N-(*n*-dodecyl) oleamide-rich fraction (iodine number, 44.9; acid number, 1.4) required 24 hours to obtain an acid number as high as 183.2. The iodine number of the free acids was 28.5 (calcd. 56.4). Their chlorine content was 6.35%, indicating substantial addition of hydrochloric acid to the double bond.

Hydrolysis of the amides with aqueous sulfuric acid or alcoholic potassium hydroxide proceeded too slowly for practical use. With the former considerable increase in color was noted.

### Discussion

Table I shows that the maximum yield of oleamide isolated from the reaction of methyl oleate with excess 28% aqueous ammonia was about 50% (6 hours reaction at 150° to 175°C., experiment nos. 6, 7, and 9). This yield appeared to be a limiting value probably because of the competition between the hydrolytic and ammonolytic reactions. Evidence for this conclusion is the fact that evaporation of solvent from the acidified filtrate after separation of oleamide yielded a liquid product consisting almost entirely of free acids.

Emulsions were frequently encountered in working up the products from experiments in which water was present apparently because of the formation of ammonium soaps. In the early experiments (nos. 1, 3, 7, and 9, Table I) a small amount of oleic acid was added to the methyl oleate to obtain ammonium oleate immediately, which would presumably favor contact between the ester and the aqueous system, thus speeding up the reaction. This was soon abandoned because it had no beneficial effect and soaps were being formed anyway. Addition of ammonium chloride did not favor amide formation (experiment no. 8) and resulted in a dark reaction product. Oleamide was not formed or was obtained only in traces at or below 100°C. (experiment nos. 1, 2, and 3).

With anhydrous ammonia, quantitative conversion of methyl oleate to oleamide was obtained (6 to 12 hours at 165° to 175°C., experiment nos. 14, 16, and 17, Table I). Above 175°C. (experiment nos. 18 and

19), the yield was lower and the reaction product was darkly colored. Oleo oil, olive oil, castor oil and tobacco seed oil were also converted to amides and glycerol in substantially quantitative yields in the same way (Table II). The ester numbers of the crude mixed amides from the fats were about 3 to 4. These values are not significant because even with rigorously purified amides, such as oleamide, ester numbers in this range are usually obtained when the compounds are refluxed with 0.2N alcoholic potassium hydroxide for 30 minutes.

It can be concluded from these studies that anhydrous liquid ammonia is preferable to 28% aqueous ammonia for the conversion of fatty esters to amides, a reaction temperature of 170° ± 5°C. for 6 hours is sufficient, ammonium chloride is not required and is actually deleterious and, in the case of glycerides, glycerol is readily recovered in high yield.

A disadvantage to the use of anhydrous liquid ammonia was the relatively high pressures involved. It may be possible however to conduct the reaction at moderate pressures by simultaneously introducing and venting ammonia. In the conversion of fats to N-(*n*-dodecyl)- and N-(2-hydroxyethyl) amides however atmospheric pressure reaction conditions were employed (Table II). Particularly significant was the quantitative conversion of oleo oil to N-(2-hydroxyethyl) amides in only 15 minutes by refluxing with ethanalamine. The conversion to N-(*n*-dodecyl) amides however required 3 hours heating at 230°C. with *n*-dodecylamine, and conversion to unsubstituted amides required 6 hours heating at 170°C. under pressure with liquid ammonia.

Crystallization of the amides from the various fats gave some interesting results although fractionation was not as clear-cut in all cases as had been hoped when this work was initiated.

In Table III are shown results of the fractional crystallization from acetone of the unsubstituted amides of oleo oil. Two main precipitate fractions were obtained at room temperature and -20°C., respectively. These can be described as predominantly saturated (iodine number 13.4) and predominantly monounsaturated (iodine number 69.6), but no separation into pure amides could be achieved under a variety of conditions, including recombination of selected fractions and recrystallization. Petroleum naphtha and 95% ethanol were also employed as solvents. Petroleum naphtha gave results similar to those with acetone with respect to crystallization temperatures and yields, but the precipitates were difficult to filter and dry. Ethanol also gave results similar to those with acetone, but lower crystallization temperatures were required. Acetone was the best all-round solvent.

Both acetone and 95% ethanol were employed with the unsubstituted amides of olive oil. Acetone was superior. As shown in Table III, after removal at room temperature of a small amount (8.8%) of amide fraction, which was predominantly saturated (iodine number 34.2), a substantial precipitate amounting to about 75% of the starting material and consisting mainly of oleamide (estimated purity 92%) was then obtained at 0°C. Thus a high recovery (93% yield based on the assumption that olive oil contains 80% oleic acid) of oleamide was readily obtained from olive oil amides by precipitation at 0°C. whereas precipitation of oleic acid from olive oil acids requires temper-

atures of about  $-60^{\circ}\text{C}$ . The filtrate amides (iodine number, 157.9) were predominantly linoleamide.

In Table III are shown the results obtained in the crystallization from acetone of the unsubstituted amides of castor oil. An 86% yield (based on the assumption that castor oil contains 80% ricinoleic acid) of ricinoleamide (estimated purity,  $>95\%$ ) (5) was obtained by a single crystallization of the amides at  $0^{\circ}\text{C}$ . Ethanol was not as satisfactory for this fractionation as was acetone.

The results obtained in the crystallization from acetone of unsubstituted amides of tobacco seed oil were not as good as had been anticipated, considering the predominance of linoleic acid (as glycerides) in this oil (Table III). It is estimated that the precipitate obtained at  $-40^{\circ}\text{C}$ . (iodine number, 150.7) contained only about 70% of linoleamide. Petroleum naphtha as solvent gave even less satisfactory results.

The N-(*n*-dodecyl) amides of oleo oil were fractionated (Table III) only from 95% ethanol because of their extremely low solubility in acetone and petroleum naphtha. An approximately equal division into two fractions was obtained: one consisting predominantly of saturated dodecyl amides (iodine number 6.1) and the other (iodine number 46.6) predominantly of dodecyloleamide.

In Table III are shown the results obtained in the fractional crystallization from acetone of the N-(2-hydroxyethyl) amides of oleo oil. Acetone was superior for one reason or another to 95% ethanol, petroleum naphtha, isopropyl alcohol, and mixtures of acetone and petroleum naphtha. In crystallizing N-(2-hydroxyethyl) amides from acetone, care should be exercised to remove free monoethanolamine completely from the amides because of its reaction with acetone. We avoided the use of hydrochloric acid to neutralize excess monoethanolamine because of the possibility of an acid-induced rearrangement of N-(2-hydroxyethyl) amides to amino esters (10).

The N-(2-hydroxyethyl) amides yielded a fraction predominantly saturated (iodine number 9.2) and a fraction (iodine number 71.0) consisting of about 90% N-(2-hydroxyethyl) oleamide.

Attempts were made to isolate fractions even richer in oleamide or substituted oleamides by recrystallization of fractions rich in these substances. These experiments were unsuccessful.

The hydrolysis of unsubstituted amides and N-(2-hydroxyethyl) amides with constant boiling aqueous hydrochloric acid was rapid and complete within two hours, and the parent fatty acids could be readily isolated. N-(*n*-Dodecyl) amides however hydrolyzed slowly (24 hours), and chlorine-containing products were obtained when the hydrolysis was carried to completion.

### Summary

Conditions have been worked out for the quantitative conversion of oleo oil, olive oil, castor oil, and tobacco seed oil to amides and glycerol by reaction with liquid ammonia under pressure. Similarly methyl ole-

ate has been converted to oleamide in excellent yield. The reaction of aqueous ammonia with methyl oleate, however, gives a maximum yield of isolated oleamide of only 50%, apparently because of competition between hydrolytic and ammonolytic reactions.

N-(2-hydroxyethyl)- and N-(*n*-dodecyl) amides have also been prepared by the reaction of oleo oil with monoethanolamine and *n*-dodecylamine, respectively, at atmospheric pressure. Particularly significant is the quantitative conversion of oleo oil to N-(2-hydroxyethyl) amides by refluxing with monoethanolamine for only 15 minutes. The conversion to N-(*n*-dodecyl) amides however required three hours heating at  $230^{\circ}\text{C}$ . with *n*-dodecylamine, and conversion to unsubstituted amides required six hours heating at  $170^{\circ}\text{C}$ . under pressure with liquid ammonia.

Crystallization of the amides obtained from the various fats yielded oleamide (purity, 92%) from olive oil, ricinoleamide (purity,  $>95\%$ ) from castor oil, and N-(2-hydroxyethyl) oleamide (purity, 90%) from oleo oil. Little fractionation was accomplished with the amides of tobacco seed oil however. In the fractionation of the unsubstituted and N-(*n*-dodecyl) amides from oleo oil, fractions which were predominantly saturated and monounsaturated were obtained readily, but no greater purification could be effected by recrystallization.

Unsubstituted and N-(2-hydroxyethyl) amides were readily converted to the corresponding free acids by refluxing for two hours with constant boiling (approximately 20%) aqueous hydrochloric acid.

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# Spaced Spiral Weave Metallic Cloth as a Column Packing Material for Stripping Soybean Oil

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PACKED columns, using such packings as Raschig rings and Berl saddles, are in common use in the steam stripping of solvent-extracted oils, such as soybean oil, for the removal of the last traces of the solvent. Efficient operation of the columns is desirable to obtain low steam consumption, together with effective removal of the solvent without heat damage to the oil. Investigations within the past 50 years have resulted in an increasing appreciation of the very pronounced effect of liquid distribution on the efficient performance of a packed column. Tour and Lerman (4, 5), in a study of liquid flow through a dumped packing, found that liquid introduced at the top of a column by a center-point feed source flowed down through a dumped packing in a manner conforming to the normal law of probability, or frequency distribution, providing the flow of liquid was independent of both redistribution equipment and the tower wall. The normal law may be expressed mathematically as:

$$Q_x = k e^{-h^2x^2}$$

where  $Q_x$  is the fraction of the total liquid starting down the center line of the packing that would fall into a trough of unit width located at a given distance down the packing and displaced horizontally a distance  $x$  from the center line. The factors  $h$  and  $k$  are constants which depend only on the packing height and on the type and size of the packing units;  $e$  is the base of the natural logarithmic scale.

In applying the normal law equation to experimental data, natural logarithms of the terms on each side of the equation may be taken to give:

$$\ln Q_x = \ln k - h^2x^2$$

When the normal law applies, a plot of  $\ln Q_x$  against  $x^2$  will give a straight line having the intercept  $\ln k$  and slope of  $-h^2$ .

## Development of a Distributor Head

To determine the liquid distribution down through Raschig ring packing, an experimental tower, or column, 12 inches in diameter and 9 feet high was constructed from galvanized sheet iron. The lower end was flanged and bolted to a collecting grid which consisted of 4 concentric sheet metal rings 2 inches high, having diameters of 4, 6, 8, and 10 inches respectively, soldered to a  $\frac{3}{8}$ -inch steel base plate 14 x 14 inches square in such a manner that their centers coincided with the center line of the tower. The tower wall served as a fifth ring, thus providing a total of five compartments. A  $\frac{1}{4}$ -inch iron pipe nipple with 2 feet of attached rubber tubing was connected to each compartment as a drain. A 12-inch diameter piece of 4-mesh galvanized screen was placed on top of the partitioning rings to support the packing.

A constant-head tank was centered at the top of the tower to supply water at a constant feed rate.

Flow rates from each compartment were measured with 250 or 500 cc. graduates and a stop watch. Data for tests employing center-point feeding and packed heights of 2, 4, 6, and 8 feet respectively are shown in Table I.

TABLE I  
Distribution in Columns Packed With  $\frac{3}{4}$ -Inch Raschig Rings

Packing depth, feet	Type of feed <sup>c</sup>	Flow rate, gal. per min.	Actual distribution as percent normal distribution <sup>a</sup>				
			Compartment no. <sup>b</sup>				
			1	2	3	4	5
2	C	0.765	458	193	85	16	4
	D	0.209	262	208	127	39	21
4	C	0.204	413	170	108	62	31
	D	0.201	202	174	148	63	30
6	C	0.197	207	168	120	73	38
	D	.....	.....	.....	.....	.....	.....
8	C	0.346	195	156	121	82	49
	D	0.223	128	137	122	95	64

<sup>a</sup>Average or normal distribution of total liquid over column area.  
<sup>b</sup>Compartments numbered from the center outward.  
<sup>c</sup>C—center feed. D—distributor feed.

Efficient operation of a packed column depends on a uniform distribution of the descending liquid over the surface of the packing. The data in Table I show

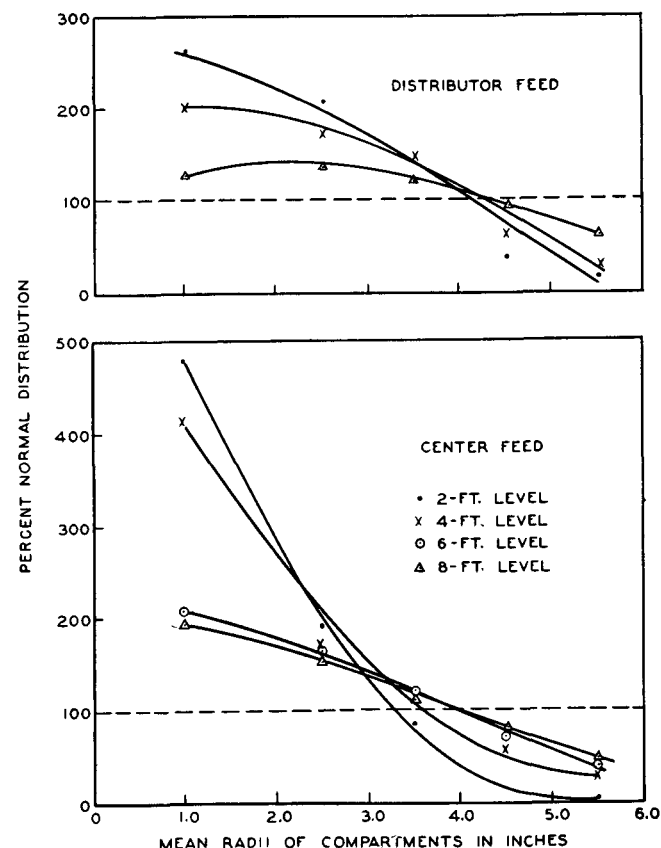


Fig. 1. Distribution as percent of normal in right half of a 12-inch column packed with  $\frac{3}{4}$ -inch Raschig rings.

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that at a depth of two feet the concentration of liquid at the center (compartment No. 1) was 100 times that near the wall (compartment No. 5). The volume of packing covered in the top two feet of height was approximately that of a cone 12 inches in diameter by 24 inches high, or one-third that which would be covered in ideal distribution. Even at the eight-foot level the concentration at the center was four times that near the wall.

The variation from uniform distribution over one-half the column cross-section, that is from the center to the outside wall, is shown graphically in Figure 1, where uniform distribution is shown by the broken line. The average flow per unit area in each compartment has been recalculated as the percentage of the uniformly distributed flow, thus eliminating the variable of flow and allowing a direct comparison of the data for different packing depths. To determine whether or not the data conformed to the normal law of distribution as found by Tour and Lerman (4), logarithms of the percentages of total flows,  $Q_x$ , were plotted against the squares of the horizontal displacements,  $x$ , in Figure 2. The series of approximately straight lines obtained indicates reasonable adherence to the theory, as would be expected since this is a case of center feeding. These results indicated that it should be possible to increase the efficiency of a packed column beyond that secured by center feeding by the use of a suitable distributor.

The application of distributors used in various industrial processes to the feeding of a miscella (sol-

vent-oil mixture) to the column was therefore studied. Circular spray heads and spray nozzles commonly employed in gas absorption equipment were found to plug if solids were present in the miscella. This plugging occurred also, but to a lesser extent, with a hollow cone spray nozzle. A splash plate was found to give very poor distribution over the column area.

Experiments with a slotted cone as a distributor showed that the slots were not receiving uniform quantities of liquid. Flat strips of metal were then attached to the surface of the cone forming radial partitions terminating at individual slots. The strips distributed the liquid uniformly to the slots, but no liquid flowed on the surface of the cone proper. These experiments led to the development of a distributor having no cone but consisting of 20  $\frac{1}{8}$ -inch rods attached to a bullet-shaped brass center and bent to form an umbrella shape. Partitioning rings of sheet metal were soldered to the upper edges of the rods to reduce any tendency of the liquid to fan across from one rod to another. This distributor head is shown in Figures 3 and 4.

The new distributor not only distributed a liquid with good uniformity over a column cross-section but also, because of the open type of construction, was not readily clogged by a liquid containing solids. When used with  $\frac{3}{4}$ -inch Raschig rings, results (Table I, Figure 1) superior to those with center feeding were obtained.

#### Evaluation of Stripping Column Performance

To evaluate the stripping performance of a packed column using the distributor head, test runs were made with a column used in the solvent recovery stage of a pilot plant designed for continuous solvent extraction of soybean oil. Since previous stripping studies (3) using this column had indicated somewhat better results with Berl saddles as packing than Raschig rings, the former were used. The arrangement of the equipment used is shown in the flow diagram, Figure 5.

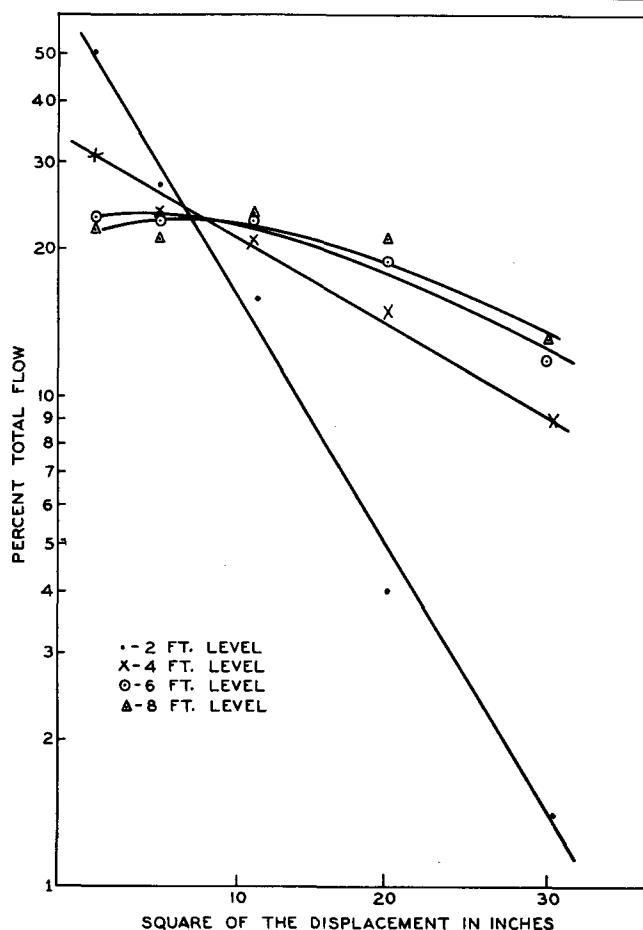


Fig. 2. Distribution in the right half of a 12-inch column packed with  $\frac{3}{4}$ -inch Raschig rings and with center feed. Relation of percent of total to square of displacement.

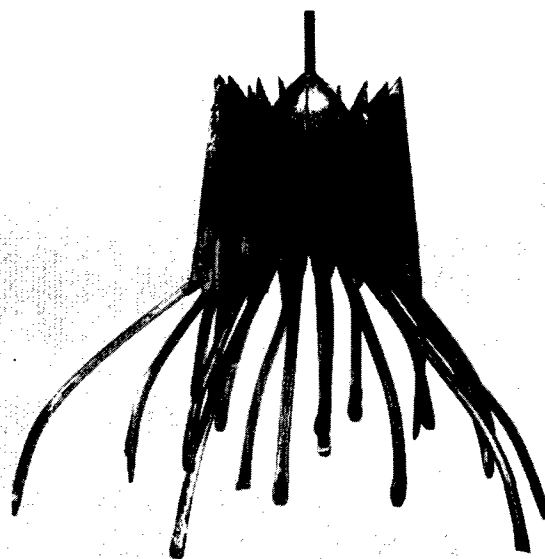


Fig. 3. Distributor head. Side view.

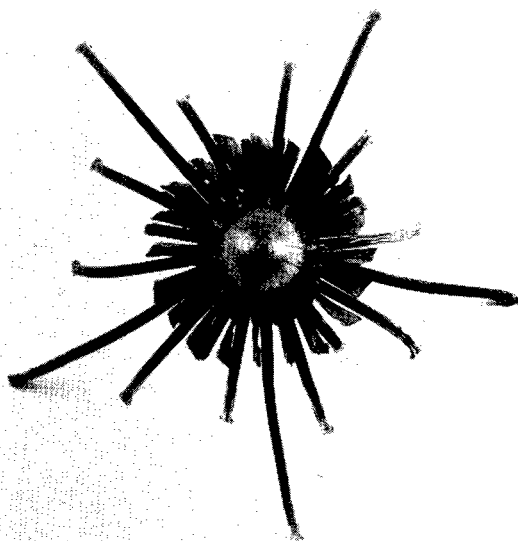


Fig. 4. Distributor head. Top view.

The column consisted of a standard black 8-inch iron pipe 9 feet in length, jacketed by a similar 10-inch pipe, and insulated with 2-inch, 85% magnesia insulation. Connections on the column were provided for the feed inlet, stripped oil outlet, and vapor outlet.

The feed, a miscella consisting of 80% soybean oil and 20% trichloroethylene by weight, was pumped

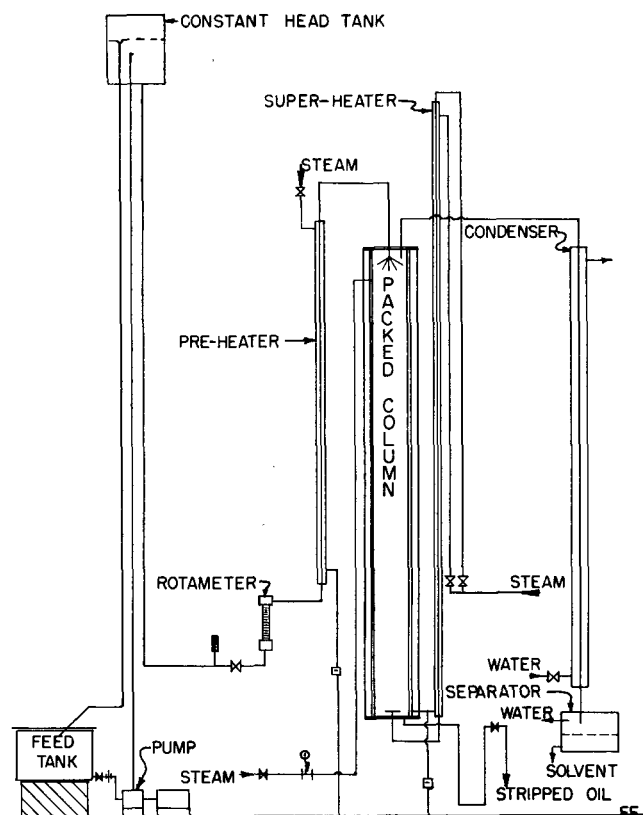


Fig. 5. Flow diagram of stripping equipment.

from the feed reservoir near the base of the column into a constant-head tank. From this tank the liquid fed by gravity through a rotameter to the top of the stripping column; initial distribution of the liquid was made by the distributor head shown in Figure 3. After flowing down the packing, the stripped oil was discharged through a gooseneck at the base of the column. Indirect steam was supplied to the column jacket at 80 lb. per sq. in. gauge. Additional live steam, improved in quality by means of a superheater, was introduced at the column base through a steam distributor having the form of a perforated cross. Vapors leaving the column were condensed and fed to a separator where the solvent was recovered.

Experimental operations were carried out in the following manner. The column was packed to a height of 8 feet with 1-inch Berl saddles by nearly filling it with water and slowly dropping in the packing units so as to obtain uniform packing. After draining the column, assembling the equipment, and allowing sufficient time for the apparatus to warm up, live steam was blown into the column and regulated to give the desired constant flow rate of condensate from the separator. Miscella was then fed to the column at a rate determined by the rotameter. The stripped oil was analyzed colorimetrically for trichloroethylene by a method described by Arnold and Hollowell (1).

Runs were first made with center-point feeding with various amounts of miscella and amounts of stripping steam to produce stripped oils containing the following percentages of solvent: less than 0.02, 0.02, 0.05, and 0.10. Feed temperatures, determined by thermocouples, varied from 100°C. at high feed rates to 120°C. at lower rates. Stripped oil temperatures varied from 140° to 150°C. Similar stripping runs were then made, using the distributor head. The data are presented graphically in Figure 6 showing the relation between the amount of oil stripped and the stripping steam required to reduce the solvent in the oil to a certain level and the limiting capacity of the column when producing stripped oil containing various solvent levels. Curves 1 and 3 show the increase in stripping efficiency and column capacity obtained by substituting distributor feeding for center-point feeding when stripping to a residual solvent content of 0.02%. The increase in stripping efficiency using the distributor head when stripping to 0.02% residual trichloroethylene was approximately 20%; in column capacity approximately 30%.

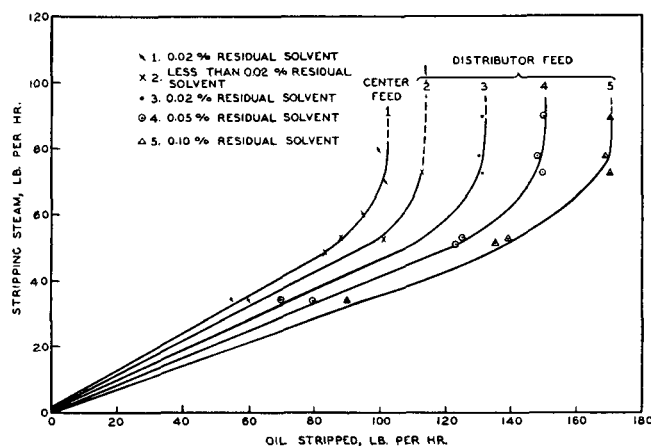


Fig. 6. Steam required for stripping soybean oil in column packed with Berl saddles.

### Liquid Distribution Using Spiral Weave Metallic Cloth

The improvement secured in stripping efficiency by use of a distributor is limited since it merely sets the pattern at the top of the column; the distribution down the column is dependent upon the packing used. Certain types of metallic cloth appeared to possess filming properties which might adapt them for use as a column packing. Vilbrandt (6) reported that a column packed with a hose-knit cloth of flat copper ribbon showed slightly greater efficiency than a bubble cap column for distillation. Spiral weave metallic cloth of the type used for conveyor belts was investigated by Skow (2) as a tower packing for distillation and in this laboratory as a packing for a column used for stripping solvent from soybean oil. Excellent stripping capacities and efficiencies were indicated, but consistent results were not obtained. Distribution studies were therefore undertaken to determine the optimum conditions for the utilization of spiral weave cloth as a stripping column packing.

The material used was 10-mesh stainless steel spiral weave cloth with straight rod reinforcing (Figure 7)

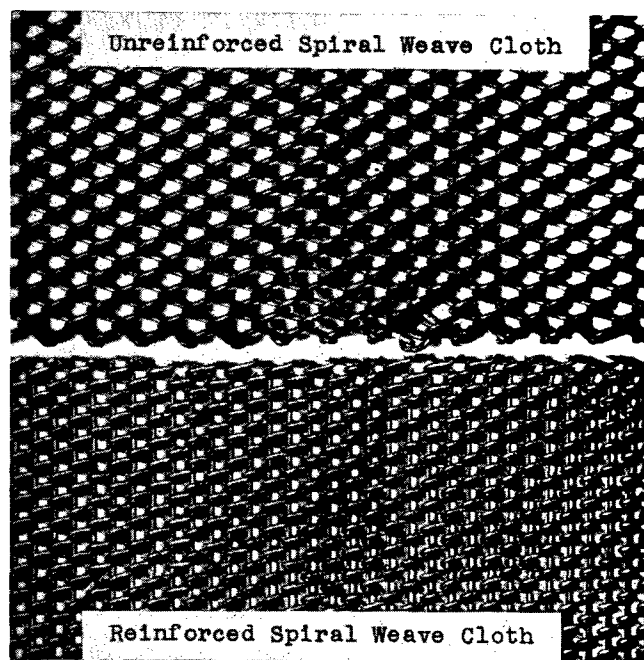


FIG. 7. Wire cloth used in the stripping studies.

26 inches wide rolled into a loose 8-inch diameter cylinder. The roll was inserted in an 8-inch sheet metal pipe 9 feet high, mounted on a collecting grid similar to that described for use with the 12-inch pipe except that it was equipped with 4 concentric circular compartments 2, 4, 6, and 8 inches respectively in diameter. Water was run onto the top surface of the roll by either center feed or by means of the distributor head.<sup>2</sup>

The results, which are given in Table II, show that, when center feeding was used, most of the liquid remained near the center line of the column as it descended, none of it getting into the third or fourth compartments. Even with the distributor head feed-

ing, the amount of liquid in the fourth compartment was only 55% of the normal amount for uniform distribution. The liquid actually moved toward the center of the column, just the opposite of the movement in the column packed with Raschig rings where the liquid tended to flow toward the column wall.

TABLE II  
Distribution in a Column Packed With Unspaced Rolled Spiral Weave Wire Cloth 26 Inches High

Type of feed	Flow rate, gal. per min.	Actual distribution as percent normal distribution			
		Compartment no.			
		1	2	3	4
C.....	0.504	933	228	0	0
C.....	0.758	902	230	0	0
D.....	0.344	173	173	106	55

It appeared that the increase in liquid concentration at the center of the column was caused chiefly by the transfer of liquid from the outside to the inside of any given turn and thence across between turns to the outside of the adjacent turn on the center side. This transfer of liquid might result if the same amount of liquid were present initially on each of the two sides of the cloth so that the film on the inner or concave side would be slightly thicker than on the convex side, thus producing a tendency to flow towards the center of the column. Movement of liquid around the spirals which make up the cloth would tend to equalize the total amounts on the two sides of the cloth. It seemed probable that this transfer might be avoided by separating the layers from each other so they were not in contact. The use of some spacing device appeared to be the obvious solution.

Preliminary distribution studies using 1/4-inch rubber tubing as spacing material showed that a continuous strip of material was unsatisfactory since the liquid tended to follow the tubing, spiralling towards the center. A spacing material large enough to prevent flooding across layers and of such nature as to prevent as much as possible the channelling of steam between layers was indicated. Three types of spacers were investigated: Raschig rings, Berl saddles, and balls. Rolled packing units composed of the spiral weave metallic cloth and the desired spacers were made by distributing the spacers on the surface of the cloth, laid flat on the floor, in such a manner that they were separated approximately 1/2-inch from one another. A sufficient length of cloth with spacers to form a cylinder which would fit snugly into the column was then rolled into a unit and secured with wire. A sufficient number of these units to give the desired height were placed one on top of the other in the column.

In addition to testing these in a column a simple visual test was devised in which a stream of water was impinged on a layer of the metallic cloth about three inches from the center of a vertically supported packing unit. The layers of cloth yielding streams of water at the base of the roll were checked to determine the horizontal displacement of liquid as it flowed down through the packing unit. This test was used as a check on all liquid distribution runs made in this study.

The results secured in testing the various spacing materials indicated that a spherical shaped particle used as a spacer produced the best liquid distribution

<sup>2</sup>When a change was made in column diameter, the rods in the distributor were readjusted to give proper distribution.

since it made only point contact between layers of metallic cloth. When using any spacer, there was always a better contact surface encountered between the inner surface of the cloth and the spacer than between the outer surface and the spacer. As a result, more liquid was displaced toward the inner layers than toward the outer portion of the rolled packing unit. When the roll diameter approached the diameter of the spacer, as it did near the center of the roll, this effect became more pronounced.

Liquid distribution tests were made with spacing materials ranging in size from  $\frac{1}{4}$  to 1 inch, and it was found that  $\frac{1}{2}$ -inch spacing materials were the most satisfactory in obtaining uniform distribution of liquid in a packing unit. Spacing materials less than  $\frac{1}{2}$  inch in size allowed liquid to flood across from one layer to the next at even moderate feed rates, and rolls spaced with materials larger than  $\frac{1}{2}$  inch gave less uniform distribution over a column cross section. Thus the ideal spacing material, from the standpoint of liquid distribution alone, appeared to be  $\frac{1}{2}$ -inch balls. Representative distribution data on the three types of  $\frac{1}{2}$ -inch spacers given in Table III and Figure 8 show the distribution effectiveness in the following decreasing order: balls, saddles, and rings.

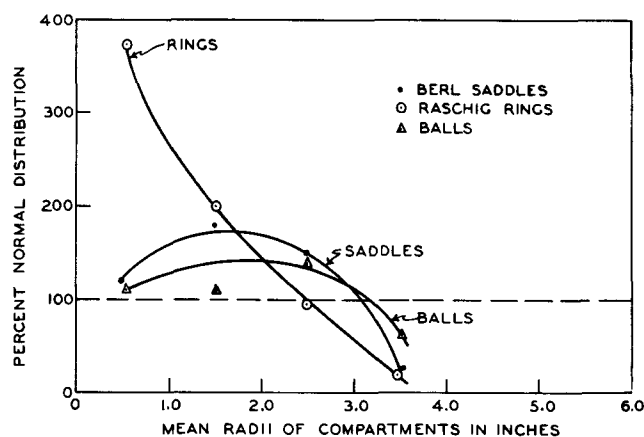


FIG. 8. Percent normal distribution in right half of column packed with spiral-weave metallic cloth spaced by Berl saddles, Raschig rings, and balls.

TABLE III

Distribution in a Column Packed With Spaced Spiral Weave Steel Cloth 52 Inches High With Distributor Feed

Spacing material	Flow rate, gal. per min.	Actual distribution as percent of normal distribution			
		Compartment no.			
$\frac{1}{2}$ " Berl saddles	0.272	104	180	160	18
	0.468	136	181	138	33
$\frac{1}{2}$ " Raschig rings	0.464	372	202	96	20
$\frac{1}{2}$ " Ceramic balls	0.235	112	110	146	63

In addition to the studies using the reinforced spiral weave cloth, distribution was determined on 8-mesh spiral weave cloth without the reinforcing rods (Figure 7) and with  $\frac{1}{2}$ -inch Berl saddles as spacers. A plot of the data showed excellent distribution across the bottom cross section. Some distribution studies were made in which the distributor head was rotated at speeds between 30 and 50 r.p.m. The rotation decreased the tendency of the liquid to be picked up by the Berl saddles and displaced to-

ward the center of the column. The distribution pattern changed less with changes in feed rate when the distributor head was rotated than when it was stationary.

### Stripping Performance with Spaced Spiral Weave Wire Cloth

Stripping performance data (Figure 9) were determined for 10-mesh reinforced spiral weave cloth packing using  $\frac{1}{2}$ -inch Berl saddles,  $\frac{1}{2}$ -inch Raschig rings, and  $\frac{1}{2}$ -inch ceramic balls as spacers. Stripped oil temperatures varied from 128° to 140°C. These data indicated that the Berl saddles rather than ceramic balls gave the best stripping efficiency and capacity. This somewhat better stripping efficiency and capacity of the saddles compared with the balls probably resulted from two factors: greater film surface and film movement on the saddles than on the balls and a better baffling of the steam by the saddles, resulting in a greater turbulence in the steam flow.

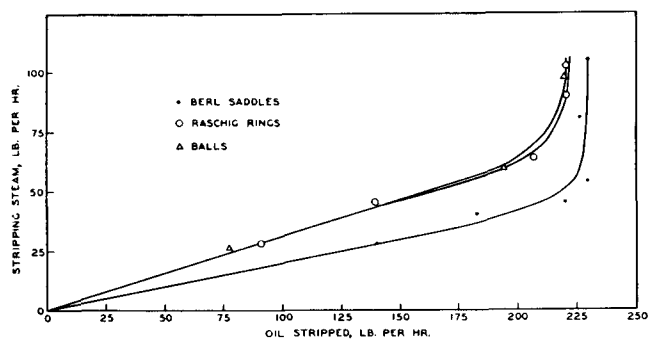


FIG. 9. Steam required for stripping soybean oil in column packed with reinforced spiral weave cloth spaced with Berl saddles, Raschig rings, and balls—residual solvent less than 0.02%.

Stripping data for non-reinforced 8-mesh spiral weave cloth with  $\frac{1}{2}$ -inch Berl saddles as spacers are shown in Figure 10. Comparison of these data with data for the reinforced cloth (lower curve, Figure 10) indicated that the reinforced cloth was definitely superior since it gave greater vaporization efficiencies and an increased capacity. The relative efficiencies of the reinforced and non-reinforced spiral weave wire cloth are evidently not the result of differences in the distribution of the liquid across the column but rather the result of differences in the filming of the liquid down the cloth. Visual observation of the liquid passing down the two types of cloth showed that the liquid was flowing inside the spirals of the non-

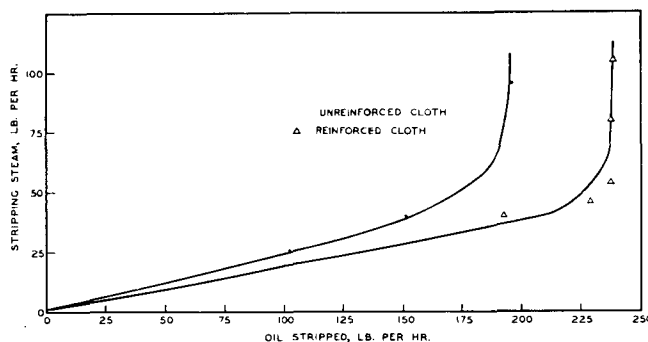


FIG. 10. Steam required for stripping soybean oil in a column packed with unreinforced and reinforced spiral weave cloth spaced with Berl saddles. Residual solvent 0.02%.