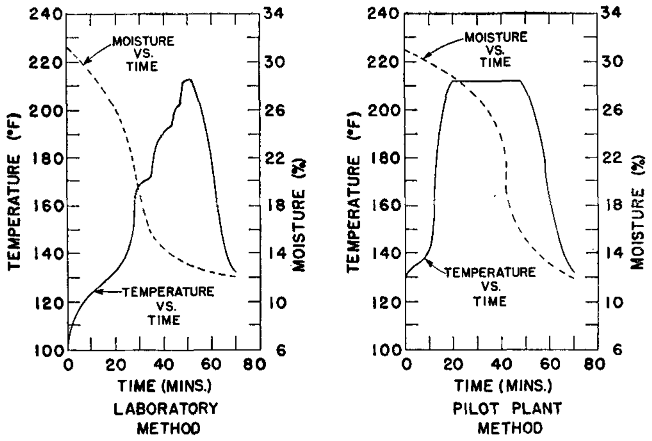

FIG. 4. Comparison of moisture-temperature relationship in laboratory and pilot plant cooking operations.

that the conditions of processing must be carefully selected and carefully controlled if cottonseed meals of the highest nutritive value are to be produced.

None of the variables studied had any significant effect on the neutral oil content of the extracted crude oils. Only three of the 27 oils produced had neutral oil content below 97%. Lower refined and bleached colors were obtained with the oils from the alkali cooks than with the hydraulic type of cooking. Raising the moisture content in the alkali cooks resulted in improved refined and bleached color as well as a lower refining loss by the DeLaval centrifuge refining method.

Summary and Conclusions

Results obtained from alkaline cooking experiments show that all of the four variables studied—cooking moisture content, temperature, time and flake thickness—influenced the properties of the resultant meals in varying degrees. Under the experimental conditions used a high initial moisture content, above 18%, is necessary to lower the free gossypol content in the finished meal to less than 0.04%. When this amount of moisture is used, a plastic mass results at the beginning of the process which requires special equipment to supply the mechanical action necessary to break the pigment glands at a low temperature. In the presence of high moisture content and alkali the gossypol, which is released when the glands are ruptured, is bound to the meal. When sufficient initial moisture is present (24–31%), only traces of gossypol (0.010% or less) are found in the extracted crude oil.

TABLE IV

Chemical Properties of Typical Meals

Run no.	Moisture content %	Residual oil %	Nitrogen solubility %	Free gossypol %	Total gossypol[b] %
33	9.0	2.86	74.8	0.127	1.18
40	8.7	2.66	63.7	0.024	1.20
44	8.8	2.51	61.7	0.068	1.23
Hydraulic[a]	9.1	6.43	76.3	0.103	1.28

[a] Pilot-plant processing.
[b] 46% protein basis.

High temperatures in the presence of high moisture content reduce the solubility of the meal protein (in 0.02 N NaOH). Under the conditions of moisture, temperature, and time of cooking used in the experiments the maximum nitrogen solubility obtained under conditions necessary to produce low free gossypol content was 64%. This differs from results obtained in previous work performed under different conditions. A probable reason for the difference is given based on the interrelationship of the three variables.

The results demonstrated further that finer comminution of the raw meats by rolling to 0.005-in. thick flakes results in lower free gossypol content in the finished meal and lower gossypol content of the oils as well as more complete removal of the oil by the filtration-extraction procedure used.

Acknowledgment

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Dilatometric Errors and an Application to Volume Changes For the Solid State of Methyl Stearate[1, 2]

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A PREVIOUS PUBLICATION from this laboratory dealt with the volume changes associated with the heating and cooling cycles for the solid state of methyl esters of fatty acids (1). These data showed a difference in the shape of curves representing the heating and cooling cycles although the same volume change occurred on both cycles between —38°C. and a temperature a few degrees below the melting point of the particular ester.

The present work involves the establishing of standard errors in dilatometric measurements and the use of these error figures to test the validity of differences found in specific volumes for the solid state of methyl stearate. The effect of past history on

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[1] Presented at the fall meeting, American Oil Chemists' Society, Philadelphia, Pa., Oct. 10–12, 1955.
[2] Issued as N.R.C. No. 4178.

specific volume is studied by measuring on the heating and cooling cycles between different temperature intervals in the solid state.

Experimental

The methyl stearate was from the same sample as used in the previous study.

Dilatometers. Gravimetric dilatometers of approximately 14.0-ml. volume were constructed from Vycor glass and are illustrated in Figure 1A. The capillary tubing of 1.0-mm. bore was sealed to 6-mm. tubing which was sealed to 16-mm. diameter tubing; the latter section formed the bulb of the dilatometer. Two-mm. capillary tubing was sealed to the top of the bulb. The top of the capillary was ground flat and fitted with a sealing arrangement (Figure 1D) patterned after that used by Hofgaard (2). The gasket was made from silicon rubber and was held in place by a machined metal retainer. A Pyrex glass dilatometer with a flattened cylindrical bulb was also constructed (Figure 1B) to study the effects of the shape of the bulb and amount of mercury on the results. A third style of dilatometer bulb was made with an expanded section as illustrated in Figure 1C. With the latter type the fat was solidified in the lower section and then allowed to float freely in the upper part of the dilatometer bulb. The fat sample touched the glass only at the top of the bulb whereas in other dilatometers the fat sample was in close contact with the glass and tended to adhere to it.

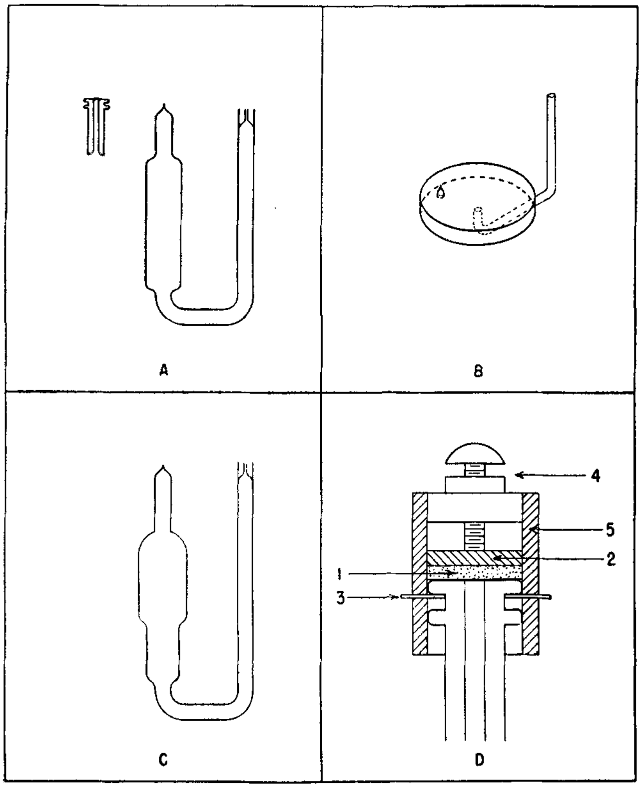

FIG. 1. Styles of dilatometer bulbs and sealing arrangement.
D—1. Silicone rubber gasket
2. Threaded brass plate
3. Spring retainer
4. Screw and lock nut
5. Threaded brass holder

Preparation of Sample. A quantity of liquid methyl stearate (10–20 g.) was placed in a round bottom flask, and the air was removed by repeated solidification and melting under vacuum with violent agitation. A portion of the liquid sample was transferred under atmospheric pressure to the dilatometer bulb where the evacuation of air was repeated. Preliminary removal of air from the sample prevented excessive splashing in the dilatometer bulb. The liquid sample was then slowly solidified from the mercury surface upwards to eliminate as much as possible any crevices or vacuoles in the solid plug of sample. The dilatometers were equilibrated at 37.5°C. until successive 12-hr. measurements indicated negligible volume changes.

Heating and Cooling Cycles. The dilatometers used in the study and the amounts of mercury and sample are listed in Table I. Six successive measurements of heating and cooling cycles without melting the fat sample were made on dilatometers 2 and 4, two on dilatometer 10 (large sample of methyl stearate), and four on dilatometers 5 and 6. Dilatometers 7, 8, and 11 were filled with mercury and used as checks to measure reproducibility. The variation in the controlled temperature baths was from ±0.004 to ±0.008°C. as measured with a platinum resistance thermometer and Mueller bridge circuit.

TABLE I

Description of Dilatometers

Dilatometer	Glass	Style	Weight of methyl stearate, g.	Initial weight of mercury, g. at 25°C.
2	Pyrex	B	2.0002	497.945
4	Pyrex	A	1.1163	174.634
10	Pyrex	C	6.9362	160.035
10	Pyrex	C	1.4270	234.238
11	Pyrex	A	....	136.408
5	Vycor	A	1.3357	190.376
6	Vycor	A	1.1508	173.745
7	Vycor	A	....	187.208
8	Vycor	A	....	208.742

The effect of the previous history of the sample on the specific volume of the solid state was studied by measuring heating and cooling cycles between the following temperatures: −38°C. and 7°C.; −38°C. and −14°C.; 35°C. and −10°C.; 35°C. and 10°C. in the following sequence:

a) Cooling cycle from +35°C. to −38°C.
b) Heating cycle from −38°C. to +7°C.
c) Cooling cycle from +7°C. to −38°C.
d) Heating cycle from −38°C. to −14°C.
e) Cooling cycle from −14°C. to −38°C.
f) Heating cycle from −38°C. to +35°C.
g) Cooling cycle from +35°C. to −11°C.
h) Heating cycle from −11°C. to +35°C.
i) Cooling cycle from +35°C. to +10°C.
j) Heating cycle from +10°C. to +35°C.
k) Heating cycle from +35°C. to +58°C. for determination of melting dilation and coefficient of expansion of the liquid state.

During the first complete heating and cooling cycle the temperatures of the baths were measured with a platinum resistance thermometer and a Mueller Bridge in addition to the mercury thermometer. Volume change with temperature or slope of lines in the solid and liquid states and standard errors were calculated by the method of least squares.

Determination of Standard Errors. The dilatometers were filled with mercury, and the specific volumes were measured at 5° intervals between −35°C. and 55°C. The regression coefficient, standard error, and standard error of the regression coefficient (Table II) for each dilatometer were then calculated.

TABLE II

Coefficients of Expansion, Melting Dilations, and Standard Error for Dilatometers

Dilatometer	Coefficient of expansion, ml. per gram per degree x 10^6		Melting dilation, ml. per gram	Standard error, ml. per gram x 10^5		
	Solid	Liquid		Mercury	Solid	Liquid
2[a]	232	1,003	.1736	42.0	13.5	5.5
4[a]	180	1,003	.1752	7.8	5.3	4.5
4[b]	181				7.3	
10[a]	176	1,010	.1726	15.0	3.5	4.4
10[c]	196	....	....		13.0	....
5[a]	186	1,010	.1740	4.7	5.4	4.1
5[b]	184				9.4	
6[a]	188	....	....	3.6	11.4	3.5
	183				6.1	

[a] Temperatures measured with mercury thermometers.
[b] Temperatures measured with platinum-resistant thermometer.
[c] With 1-g. sample.

The standard errors of the dilatometers filled with mercury range from 3.6 x 10^{-5} ml. for the Vycor dilatometer to 42 x 10^{-5} ml. for the flat cylindrical dilatometer. Some of this difference in standard error results from the difference in the weights of mercury. However the standard error for measurements of the methyl stearate either in the solid or liquid state should be related to the standard error for the dilatometer in which the measurements were made. Since the results are expressed as expansion per gram, the standard error should be reduced by increasing the size of the sample. This is shown in Table II by the results on dilatometer 10. The standard error with a 1-g. sample is the same as the standard error for the dilatometer alone, whereas the standard error with a 7-g. sample is 3.5 x 10^{-5} ml./g. It is seen from the data in Table II that the standard error for the solid state is appreciably greater than the standard error for the liquid state. The standard errors for Vycor glass dilatometers were lower than for those of Pyrex glass although the variations in specific volumes at —38°C., as seen in Table III, are not much different. The specific volumes at —38°C. of dilatometers 7, 8, and 11 for four consecutive cycles between —38°C. and 35°C. are given in Table III. The maximum variation in volume for the Pyrex dilatometer was 0.0009 ml. whereas the Vycor dilatometers showed variations of 0.0008 and 0.0004 ml., respectively. There was no regular increase or decrease in the volumes with consecutive measurements.

TABLE III

Volumes of Pyrex and Vycor Dilatometers at —38°C. for Successive Cycles

	Pyrex No. 11	Vycor No. 7	No. 8
April	10.0726	13.8292	15.4213
May	10.0730	13.8288	15.4209
June	10.0735	13.8290	15.4209
July	10.0731	13.8296	15.4209

The coefficients of expansion for the solid and liquid states for methyl stearate in the various dilatometers are given in Table II. There is good agreement between the coefficients for expansion in the solid state except for dilatometer 2 and dilatometer 10 with a 1-g. sample. The calculated standard error of the regression coefficient was 6 x 10^{-7} ml./g./°C. for dilatometer 4 and 5 x 10^{-7} ml./g./°C. for dilatometer 5. The differences in the coefficients for the solid state as measured by mercury and platinum resistance thermometers for dilatometers 4, 5, and 6 are barely significant as measured by the standard errors of the regression coefficients, indicating that no appreciable error was introduced by the use of the mercury in glass thermometers. The coefficients of expansion of the solid state for the consecutive runs which are not shown in Table II were as follows (ml./g./°C. x 10^6): dilatometer 4—187, 169, 183, 178, 183, and 184; dilatometer 5—184, 186, 187, and 171; dilatometer 6—188, 171, 184, and 161; dilatometer 10—180 and 176. The agreement for coefficients is as good between dilatometers as between different runs on the same dilatometer. The coefficients of expansion of the liquid state and the melting dilations (Table II) show good agreement between dilatometers. No values are reported for dilatometer 6 because of a leak in the system at 38.5°C.

Effect of Previous History on Specific Volume. The curves for the heating and cooling cycles are illustrated in Figure 2, and specific volumes at approximately 10° intervals are given in Table IV. These data are taken from the measurements made with Vycor dilatometer 5. The complete heating and cooling cycles from —38°C. to 35°C. corroborate the data previously reported (1). The partial cooling cyles which were started from +35°C. agreed with the complete cooling curve from +35°C. to —38°C., whereas the cooling curves from +7°C. and —14°C. did not coincide with the complete cooling curve. These latter curves approached the complete cooling curve as the temperature approached —38°C. and reached the same value at —38°C. A number of the experimental points on the cooling curve from —14° C. to —38°C. are significantly different from the points on the heating curve.

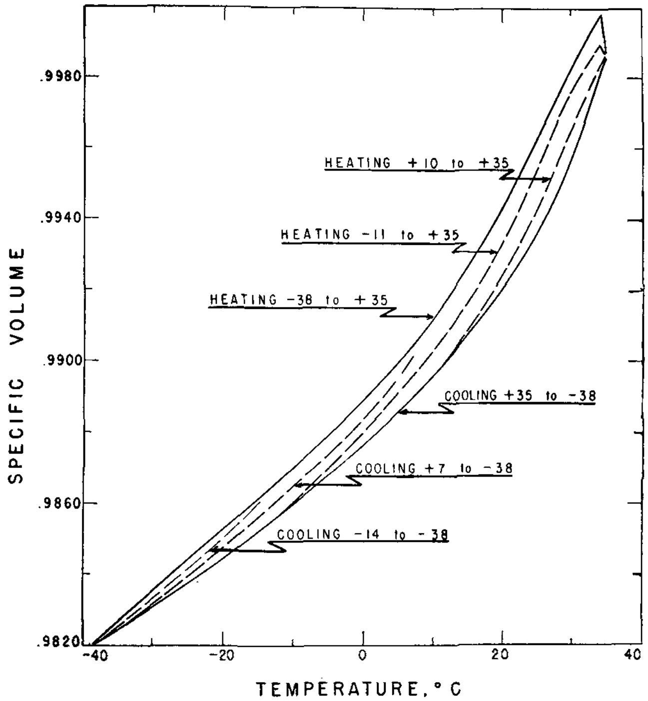

FIG. 2. Dilatometric curves for heating and cooling cycles of methyl stearate.

TABLE IV

Specific Volumes of Methyl Stearate for Heating and Cooling Cycles

Temperature, °C.	Cooling cycles					Heating cycles				
	+35°C. to −38°C.	+7°C. to −38°C.	−14°C. to −38°C.	+35°C. to −11°C.	+35°C. to +10°C.	+10°C. to +35°C.	−11°C. to +35°C.	−38°C. to −14°C.	−38°C. to +7°C.	−38°C. to +35°C.
−38	.9821	.9819	.9821					.9819	.9821	.9821
−23	.9840	.9842	.9844					.9848	.9848	.9848
−14	.9853	.9859	.9862					.9862	.9862	.9862
−11	.9858	.9862		.9857			.9857		.9869	.9869
− 2	.9873	.9879		.9873			.9877		.9885	.9885
+10	.9898			.9892	.9891	.9891	.9901			.9912
+25	.9938			.9938	.9933	.9943	.9953			.9963
+35	.9988			.9984	.9985	.9985	.9985			.9986

The complete heating cycle and the two partial heating cycles which start at —38°C. are identical. The heating cycles which were started at temperatures above —38°C. are significantly different from the complete heating cycle and from any of the cooling cycles. The volume change per degree in the temperature range 25° to 35°C. also changes as the heating curves are started at temperatures above 0°C. The over-all volume change for any pair of heating and cooling cycles is identical, but the pathway followed on each cycle or individual curve depends on the previous treatment of the sample. It was anticipated that the curves representing the heating and cooling cycles between —38°C. and —14°C. would be identical since previous work and other reports in the literature indicate that methyl stearate is "completely solid" in this temperature region. It would be expected to be in a single crystalline form, whose volume change with temperature on either heating or cooling would be constant. The standard error of measurement of specific volume in this temperature region is ±0.00005 ml. per gram, and a number of the measured points on the cooling cycle differ from the heating cycle by more than three times this figure. This is shown in Table IV, where the points on the cooling cycles at —23°C. are 0.0004 to 0.0008 ml. per gram different from the same points on the heating cycles.

There is a large deviation in the specific volumes given in Table IV at +35°C. than at —38°C. This is explained by the reductions in specific volumes after the completion of successive measurements of a cooling and heating cycle and subsequent equilibration at 35°C. These are given in Table V for dilatometers 5 and 6, where the specific volumes are reduced 0.0029 and 0.0024, respectively, during the four consecutive equilibrations between measurements of complete heating and cooling cycles. A similar trend was found in all other dilatometers. Previous work[3] in this laboratory on other methods of preparing the sample, use of four atmospheres of pressure during measurements, and the use of high pressures after preparation of the samples have not eliminated the reduction in volume found for equilibration or affected the shape of the curves representing heating and cooling cycles. From these data it would be anticipated that the specific volume difference found in Table IV between the first and last cooling cycles (0.0003 ml. per gram) is a real difference. The data for all the four complete heating and cooling cycles for dilatometer 5, plotted on a large graph, showed four almost identical sets of curves which were displaced over the temperature range by the reduction in specific volume which was observed at 35°C. The reduction in specific volume after each equilibration had no apparent effect on the coefficient of expansion in the solid state and on the change in slope of the heating cycle between 25°C. and 35°C. but did result in an increased value for the melting dilation as shown in Table VI, based on the assumption that, since the samples were not melted between consecutive determinations, the specific volume of the liquid state was not affected over the period of time required for the experiment. The melting dilation for dilatometer 5 was calculated as the specific volume difference at 39.1°C. between the liquidus line and the extended line representing expansion of the solid state (—38° C. to —10°C.) calculated by the method of least squares. The melting dilations given in Table VI show progressive increases which are significantly different.

TABLE V

Specific Volumes of Methyl Stearate at —38°C. for Vycor Dilatometers

Run	Dilatometer	
	5	6
April	.9850	.9858
May	.9837	.9853
June	.9829	.9847
July	.9821	.9834

The specific volumes of methyl stearate for the two Vycor dilatometers given in Table V do not show the agreement which would have been expected from the remainder of the data. These differences may have been real and may have been related to the phenomenon of volume reduction found for consecutive equilibrations at 35°C. This would mean that differences in specific volume for the solid state would depend on the extent of equilibration at 35°C.

Discussion

The present work is an attempt to establish the precision and accuracy of dilatometric measurements. This was necessary to assess the validity of differences which were found in this and in previous dilatometric studies. The improvements in the present

TABLE VI

Variation of Melting Dilations with Specific Volumes of Solid State at Different Times

	Specific volume at —38°C.	Coefficient of-expansion of solid ml./gram $\times 10^{-3}$	Melting dilation	Specific volume at 39.1°C.[a]
April	.9850	184	.1740	1.1719
May	.9837	186	.1757	
June	.9829	187	.1761	
July	.9821	171	.1779	

[a] Calculated from liquidus line 42°C. to 58°C.

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[3] Unpublished data.

technique resulted from a) the use of Vycor glass which has a lower coefficient of expansion and may have eliminated some of the variations in glass corrections, and b) the use of a solidification procedure which should have eliminated most of the microscopic cracks or vacuoles in the sample. A more rapid equilibration was obtained by the use of a dilatometer bulb with an expanded section which allowed the fat sample to float freely in the mercury and prevented the sample from adhering to the walls of the bulb. Using Vycor dilatometers of 14.0-ml. capacity and a 1.0-g. sample, the error of measurement was ±0.00005 ml. per gram while using Pyrex dilatometers of a similar size and a 1.0-g. sample the error was ±0.00008 ml. The standard error was less for measurements in the liquid state than in the solid state.

The decrease in specific volume after each equilibration at 35°C. was anticipated from previous work, but a numerical value was difficult to obtain since specific volumes were not used. The present work shows that a change in the melting dilation could be expected from the continual decrease in specific volume after each equilibration. The variation in coefficient of expansion for the solid state has a small effect on melting dilation if the decrease in specific volume is neglected. For dilatometer 5, the maximum difference in coefficients of expansion for the solid state (0.000171 and 0.000187) is 0.00016, and if one assumed an equivalent specific volume at —38° C., this would make a difference in melting dilation of 0.0012 ml. per gram.

No explanation is offered for the differences found in the specific volumes of methyl stearate in the solid state. These differences were anticipated from the previous work (1), in which different curves were found for the heating and cooling cycles. The specific volume at a given temperature would depend on the temperature to which the sample was cooled before making the measurement. The present study could be enlarged to include other heating and cooling cycles, but it is expected that a family of curves would be found and the position of each curve would depend on the temperature at which the measurements were started.

The melting dilations and coefficient of expansion in the liquid state are of the same order of magnitude as the previous study (1). The coefficient of expansion for the solid state (0.00018) is lower than previously reported (0.00022 ml.). From the present data it would appear that a dilatometer constructed from Vycor glass containing 100–125 g. of mercury and a 2–3 g. sample should yield data in which the standard error was equal to or less than the standard error found in the present work.

Summary

The dilatometric curves representing heating and cooling cycles for methyl stearate between —38°C. and +35°C. are the same shape as found in the previous study. Cooling cycles which are started from points on the heating curve yield curves which are different from each other and from curves representing the complete heating and cooling cycles. Curves for heating cycles which are started from points on the curve representing the complete cooling cycle will also be different from the curves representing either the heating or cooling cycles in the same temperature region. The specific volumes at any temperature in the solid region depend on the previous history of the sample even though the sample is not melted between determinations. A continual reduction in specific volume was found for successive runs after equilibration at +35°C. This reduction had no apparent effect on the coefficient of expansion of the solid state but did increase the melting dilation. Using the present Vycor dilatometers, the standard error of measurements in the solid state are around ±0.00005 ml. per gram in terms of specific volume. The use of a platinum resistance thermometer and Mueller bridge did not significantly improve the precision of the measurements.

Acknowledgment

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Emulsion Stability[1]

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THE LITERATURE dealing with emulsions is very extensive, and many theories have been expressed concerning their stability (1, 3). It is now generally accepted that a tenuous interfacial film is required for a stable emulsion. This tenuous film has been expressed in terms of surface viscosity (9), condensed films (13), films of considerable thickness (1), and so forth. It is frequently suggested that electric repulsion contributes to the stability of O/W emulsions containing ionic emulsifiers (12, 14), but it is of minor importance with emulsions stabilized with nonionic surfactants (4). The lack of a relationship between electric repulsion and stability has also been noted (2).

It is known that O/W emulsions are best prepared with water-soluble emulsifiers while the oil-soluble emulsifiers are used for stable W/O emulsions. The type of emulsion produced with solids depends upon whether the solid emulsifier is more readily wetted by water or by oil (4). These observations have been extended to relate the degree of stability of emulsions to the non-wetting of the interfacial film by the discontinuous phase (4).

On the basis of insight provided by other investigators, it is possible to present a theory which will account for many observations concerning emulsion stability. That described here concerns emulsion stability only insofar as it relates to coalescence. An emulsion which has creamed or flocculated is considered stable if coalescence does not occur. Minor

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[1] Presented at the 129th Meeting of the American Chemical Society, Dallas, Tex., April 9–13, 1956.