glycerides and completely saturated triglycerides is roughly comparable to that existing between the branched-chain and straight-chain hydrocarbons.

Summary

1. The heat contents of cottonseed oil, a hydrogenated cottonseed oil, and a mixture of cottonseed oil and petroleum naphtha have been measured over ranges of temperature within which there is transformation of the glycerides of the oils from a completely solid to a completely liquid form.

2. From the heat content data determinations have been made of the heats of fusion of the oils and of the specific heats of the oils in both solid and liquid states.

3. Equations have been derived for expressing the heat capacities of the oils and the oil-solvent mixture, with the oil in either the liquid or solid form.

4. Values found for the specific heat of the liquid oils are in general agreement with values found by previous investigators. The values calculated for the heat of fusion of the oils are much lower than values reported by other workers for highly saturated glycerides. However, a low value for mixed glycerides of saturated and unsaturated fatty acids is to be expected, from considerations of molecular structure.

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Thermal Properties of Fats and Oils

III. Calorimetric Estimation of Solid and Liquid Glycerides in Cottonseed Oil and Hydrogenated Cottonseed Oil[1]

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IT has previously been pointed out (1) that plastic fats, such as lard, shortenings, butter, and margarine are at ordinary temperatures multi-phase, liquid-solid systems, and that the consistency of such fats depends upon the relative proportions of solid crystals and liquid oil, as determined by the temperature of the material.

From the calorimetric data reported in a previous communication (4), it has been possible to estimate the proportions of solids and liquid over the entire melting range of both cottonseed oil (iodine value, 108.3) and a hydrogenated cottonseed oil (iodine value, 59.5). In addition, from micropenetration measurements made upon the hydrogenated oil and similar measurements made previously on other fats (1), estimates have been made of the probable proportions of solids and liquid in typical commercial products, and some information has been obtained relative to the effect of hydrogenation on the proportions of the two at different temperatures.

It should be pointed out that the amounts of solids and liquids can be accurately estimated only if the calorimetric examination is extended to a sufficiently low temperature to insure that the specific heat and heat of fusion data are based upon the initial existence of the fat in a completely solid state. In general, plastic fats require rather low temperatures for complete solidification; the hydrogenated cottonseed oil chosen for the present investigation was not wholly solidified except at temperatures below —38° C.

Straub and Malotaux (5) have published "consistency curves" for a number of plastic fats, in which melting (in terms of heat content) is represented as a function of temperature, and recently Jack and Brunner (3) have reported similar data on butterfat. It is apparent, however, that in neither case did these workers achieve complete solidification of their materials, hence ther data cannot be considered adequate for a quantitative analysis of the fats in terms of solids and liquids.

Method of Making the Calculations

CALCULATIONS of the amount of solid glycerides melting in the oil in a specific temperature interval were made by distributing the increment in heat content during the interval to heat of fusion and sensible or specific heat, and then translating the heat of fusion to percent glycerides melting, upon the basis of the previously determined average heat of fusion of all the glycerides in the sample. The individually calculated percentages were accumulated at successive temperatures through the melting range, and the accumulated percentages were uniformly adjusted to make the final accumulated value equal to exactly 100 percent.

In estimating the sensible heat, it was necessary to make an arbitrary assumption regarding the changing proportions of solids and liquids over the interval. If it is assumed that all melting occurs at the temperature corresponding to the end of the interval, a maximum value will be obtained for the amount of solids melting, since the heat capacity of the liquid was found to be greater than that of the solid. If all melting is assumed to occur at the beginning of the interval, a minimum value will be obtained. Actually, there was in any case but a slight difference between the maximum and minimum values, and for

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purposes of calculation it was considered satisfactory to take the arithmetical average of the two.

In order to make the desired calculations it was necessary to assume that there were no substantial differences in the heats of fusion of glycerides melting in the oils at different temperatures. It is recognized that this assumption may not be strictly valid, for there are considerable variations in the latent heats of different individual glycerides. Completely saturated glycerides are known to have much higher heats of fusion than mixed glycerides containing unsaturated acids (4), and in the case of the present samples the average heat of fusion of the glycerides comprising the unhydrogenated oil was 25 percent lower than that of the glycerides of the hydrogenated oil (20.6 and 27.4 cals. per g., respectively). However, it may be assumed from the data of Hilditch and Jones (2), and from the selectivity with which the hydrogenation was conducted, that the hydrogenated oil contained a negligible amount of fully saturated glycerides. Furthermore, the tendency of glyceride mixtures to deposit mixed crystals would certainly operate against any marked segregation of individual glycerides in the crystals. It is believed, therefore, that this method gives a reasonably reliable estimate of the actual composition of the samples, in terms of solids and liquid. If there is any considerable difference in the heats of fusion of the low- and high-melting glycerides, the latter probably have the higher value; hence, the calculated values for percentage of solids are probably maximum values.

Liquid-Solid Composition of the Oils and Relationship Between Percent Solids and Micropenetrations

THE calculated compositions of the two oils at different temperatures, in terms of solids and liquid, are shown in Tables 1 and 2 and Figure 1. In this figure there is also shown for comparison, the consistency of the hydrogenated oil at different temperatures, as measured by micropenetrations.

TABLE 1

Calculation of Proportions of Solid and Liquid Glycerides in Cottonseed Oil at Different Temperatures.

Temp., °K.	Heat content, accumulated, cal./g.	Distribution of heat content in the interval		Liquid phase, accumulated and adjusted to 100 percent total
		To sensible heat, cal./g.	To latent heat, cal./g.	
173.10	0	.....	.....	0
198.30	7.33	7.33	0	0
210.00	11.11	3.77	0.014	0.07
217.70	13.83	2.69	0.024	0.19
222.47	15.54	1.66	0.051	0.44
228.23	17.67	2.06	0.072	0.79
233.73	19.80	2.02	0.106	1.31
239.10	21.91	2.02	0.086	1.73
244.27	24.01	1.99	0.108	2.26
249.10	26.11	1.90	0.195	3.22
252.89	28.26	1.53	0.621	6.26
254.78	30.54	0.77	1.504	13.63
256.35	32.83	0.65	1.638	21.65
258.05	35.10	0.72	1.557	29.27
259.97	37.34	0.82	1.423	36.24
261.89	39.58	0.83	1.409	43.14
263.66	41.81	0.77	1.465	50.33
265.24	44.05	0.70	1.544	57.89
266.69	46.30	0.65	1.597	65.72
268.61	48.50	0.86	1.336	72.27
271.07	50.64	1.12	1.028	77.30
273.89	52.74	1.29	0.816	81.30
277.09	54.80	1.47	0.586	84.17
280.06	56.85	1.37	0.683	87.52
282.67	58.92	1.21	0.855	91.71
284.99	60.99	1.09	0.982	96.52
288.24	62.97	1.53	0.453	98.74
291.99	64.89	1.77	0.149	99.48
297.36	67.52	2.55	0.077	99.86
306.50	71.93	4.38	0.030	100.00
340.00	88.42	16.49	0	100.00

TABLE 2

Calculation of Proportions of Solid and Liquid Glycerides in a Hydrogenated Cottonseed Oil at Different Temperatures

Temp., °K	Heat content, accumulated, cal./g.	Distribution of heat content in the interval		Liquid phase, accumulated and adjusted to 100 percent total
		To sensible heat, cal./g.	To latent heat, cal./g.	
203.1	0	.....	.....	0
220.0	5.25	5.25	0	0
235.0	10.28	5.03	0	0
244.58	13.91	2.48	0.221	.83
250.25	16.14	2.09	0.139	1.34
255.44	18.37	1.96	0.276	2.38
260.08	20.62	1.79	0.459	4.09
264.00	22.89	1.54	0.730	6.82
267.22	25.20	1.30	1.007	10.59
269.78	27.53	1.05	1.291	15.41
271.97	29.88	0.91	1.437	20.78
274.21	32.21	0.95	1.383	25.95
276.69	34.51	1.06	1.235	30.56
279.29	36.78	1.13	1.136	34.81
281.98	39.02	1.19	1.053	38.74
284.58	41.25	1.16	1.070	42.74
286.85	43.48	1.03	1.208	47.26
288.95	45.71	.96	1.271	52.01
291.00	47.93	.94	1.273	56.76
293.08	50.13	.97	1.231	61.36
295.19	52.30	.99	1.192	65.81
297.34	54.46	1.02	1.139	70.07
299.51	56.60	1.04	1.097	74.17
301.74	58.71	1.07	1.042	78.06
304.08	60.79	1.13	0.946	81.60
306.55	62.83	1.20	0.848	84.77
309.11	64.85	1.25	0.765	87.62
311.60	66.85	1.22	0.776	90.52
313.96	68.84	1.17	0.814	93.56
316.26	70.80	1.14	0.825	96.65
318.72	72.73	1.23	0.709	99.30
320.57	73.85	0.93	0.188	100.00
340.00	83.70	9.85	0	100.00

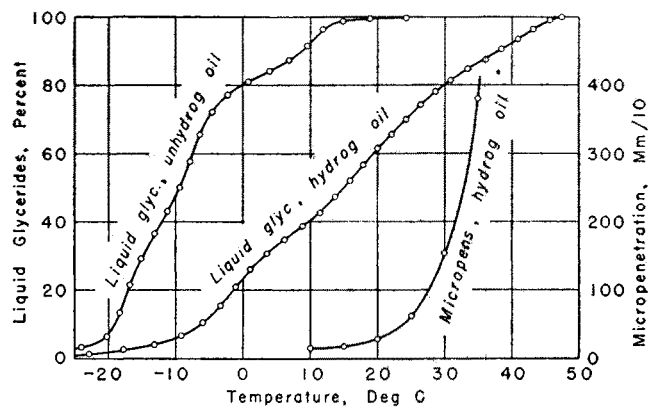

FIG. 1. Liquid glycerides contents of unhydrogenated and hydrogenated cottonseed oil, and micropenetrations of the hydrogenated oil, as functions of the temperature of the oil.

In Table 3 there is presented the correlation between percentage of solids in the fat and micropenetrations, as established from the data of Figure 1.

From the correlation between solids content and micropenetrations, and from the micropenetration measurements recorded in a previous communication (1), estimates have been made of the content of solid glycerides in several commercial hydrogenated vegetable oil products. These are given in Table 4.

It is evident that the range of solids content within which a fat is plastic and readily mixed, spread, or otherwise worked, is comparatively narrow. In the case of hydrogenated vegetable oil products, this range may be said to be roughly about 15 to 35 percent solid glycerides. A difference in the content of solids amounting to as little as 1 percent is sufficient to make a noticeable difference in the consistency of the material. The sensitiveness of hydrogenated products to small differences in content of saturated acids

TABLE 3

Relationship Between Solid Glycerides Content of Hydrogenated Cottonseed Oil and Micropenetrations of the Oil

Solid glycerides, percent	Micropenetration, mm./10
44.0	20
37.5	30
33.0	40
30.5	50
28.5	60
27.0	70
26.0	80
24.0	100
21.5	125
20.0	150
17.5	200
16.0	250
15.0	300
14.0	350

TABLE 4

Estimated Solid Glycerides Content of Commercial Plastic Fat Products at Different Temperatures.

Fat	Percent solid glycerides at indicated temperatures, deg. C.				
	15°	20°	25°	30°	35°
Shortening (Spry)	40.5	32.5	24.5	18.0	14.5
Shortening (Crisco)	41.0	32.0	24.0	17.0	14.5
Shortening (Dexo)	40.5	32.5	24.0	17.5	14.5
Shortening (Scoco)	45.0	39.0	28.0	21.0	16.0
Margarine oil (Parkay)	46.0	35.0	25.5	16.0	.....
Margarine oil (Nucoa)	45.0	33.0	22.5	14.0	.....

or iso-oleic acids is quite understandable, in view of the rapidity with which the consistency changes with variation in the proportion of glycerides in the solid state.

Effect of Hydrogenation on the Solid Glycerides Content of Cottonseed Oil

From the present data and previously recorded micropenetration measurements (1) on samples of a cottonseed oil hydrogenated to different degrees, it is possible to show the typical effect of hydrogenation on the content of solids in hydrogenated oils at ordinary temperatures. The data for hydrogenated cottonseed oil at 25°, 30° and 35° C. are shown in Figure 2. It will be seen that within the range of temperatures and iodine values at which the oil is plastic, reduction of the iodine value by 1 unit causes the content of solids to increase approximately 1 percent.

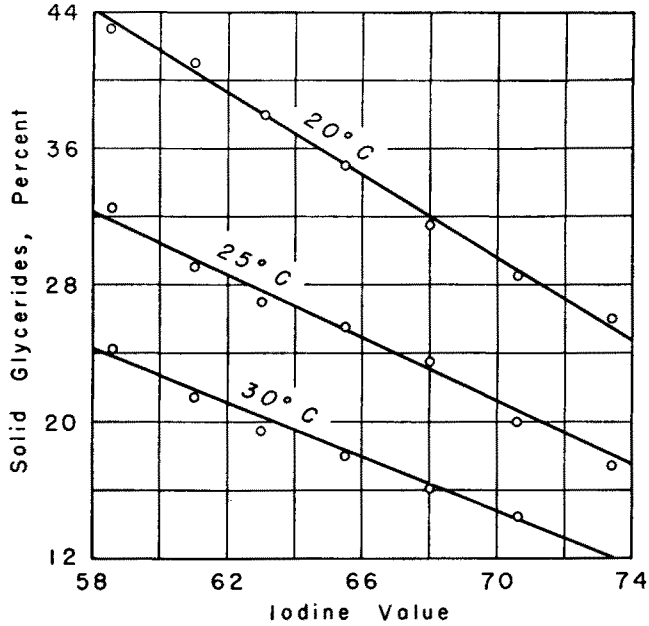

FIG. 2. Effect of hydrogenation on the solid glycerides content of cottonseed oil at different temperatures.

Summary

1. The relative amounts of solid and liquid glycerides in cottonseed oil and a hydrogenated cottonseed oil have been estimated calorimetrically at different temperatures over the melting ranges of the oils.

2. A correlation has been established between the content of solids in hydrogenated cottonseed oil and the consistency of the oil, as measured by micropenetrations.

3. From previous micropenetration data on commercial fat products, it is established that such fats are plastic and easily worked only at solids contents between about 15 and 35 percent. Differences in the content of solids of as little as 1 percent are sufficient to cause noticeable differences in the consistency of plastic fats.

4. Within the ranges of temperature and iodine value at which hydrogenated cottonseed oil is plastic, it is estimated that each decrease in iodine value of 1 unit causes the solid glycerides content of the oil to increase approximately 1 percent.

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Abstract of Color Committee Report, 1943-44

THE work of the Color committee during the year has been confined to that done by a subcommittee consisting of Dr. R. T. Milner, R. C. Stillman, and Procter Thomson, with the exception of some color readings which were made on some special samples of oil sent out by Dr. E. B. Freyer to the whole committee.

The subcommittee has submitted a report, which, in somewhat condensed form, has been turned over to the Uniform Methods and Planning committee. As the work of the committee has not been completed and is therefore a report of progress and contains nothing that needs to be acted upon by the Society at this time, Mr. Stillman, who prepared the report, has suggested the following abstract of the work that has been done:

"The Color Committee, during the past year, has confined itself to (1) a study of the reproducibility of the Lovibond color of a large number of oils and (2) a study of the color characteristics of 19 picked oils as is and made up into shortenings. These studies show that the Lovibond system of reading colors is certainly unreliable for measuring the color of oils widely varying in hue, nor is it improved to any great extent by the use of illuminant C as a light source. Preliminary results indicate that lu-