Phase Relations Pertaining to the Solvent Winterization of Cottonseed and Peanut Oils in Acetone

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KNOWLEDGE of the phase relations at reduced temperatures between solvents and cottonseed and peanut oils is of fundamental importance in establishing the conditions required for their solvent winterization. Only a few scattered pertinent data are found in the literature. Adams, Parkhurst, and Voorhees (1) reported that stearines could be removed and a winterized cottonseed oil obtained from self-refrigerating liquefied hydrocarbon gas solution. Bailey, Feuge, Kraemer, and Bauer (2) showed that cottonseed and peanut oils could be solvent winterized from commercial hexane but that with peanut oil filtration difficulties were encountered unless the oil was first subjected to a molecular rearrangement treatment. Preliminary tests by these authors indicated improved crystallization behavior in acetone. This solvent was chosen also by Hilditch and Maddison (3) and by Riemenschneider, Swift, and Sando (6) for systematic fractional solvent crystallization of cottonseed oil. The present report deals with the pertinent phase behavior in the solvent winterization of cottonseed and peanut oils in acetone.

Oils and Solvents

Cottonseed oil No. 1 was a continuous solvent-extracted oil of high iodine value obtained from a single variety of cottonseed. Cottonseed oils Nos. 2 and 3 were commercial oils. The peanut oils were solvent-extracted oils. These oils had been refined and bleached. As is apparent from the pertinent characteristics given in Table I, the cottonseed oils were chosen to cover the upper range of iodine values, which oils are most suitable for use in producing winterized oils in high yields. While cottonseed oils having an iodine value of 116.4 are not now generally available commercially, such oils are actually obtainable from selected lots of seed and may conceivably be available in the future. The peanut oils were of average iodine value.

TABLE I

Analysis of Oils

Oil	Iodine value (Wijs)	Free fatty acids (as oleic)	Perox-ide value	Unsa-ponifi-able	Moisture and vol-atiles
		%	*milli-mols./kg.*	%	%
Cottonseed No. 1	116.4	0.26	38.8	0.55	0.23
Cottonseed No. 2	108.2	0.27	39.6	0.50	0.002
Cottonseed No. 3	106.1	0.23	0.3	0.52	0.04
Peanut No. 1	91.3	0.47	68.0	0.27	0.07
Peanut No. 2	92.5	0.25	9.7	0.26	0.12

A commercial C. P. acetone was used except for some of the cloud point determinations which were made with a purified anhydrous acetone prepared by treating exhaustively with potassium permanganate, drying over potassium carbonate, and finally rectifying through an efficient column. The commercial hexane was Skellysolve B.[5]

Cloud Points

The initial phase of the investigation involved a study of the cloud point as a function of the oil-solvent ratio for cottonseed oil No. 1 and peanut oil No. 1 in purified anhydrous acetone and for cottonseed oil No. 1 in C. P. acetone.

The cloud point was determined as follows: A 25-ml. portion of the solution to be tested was placed in a double-walled test tube (2.5 cm. inside diameter and 20 cm. length). The thermometer and a reciprocating stirrer operating at one cycle per second were fitted to the tube by means of a stopper, which also served to retard loss of solvent and absorption of moisture. The tube was immersed in a cooling bath, the temperature of which was controlled to ±0.1°C., and regulated not to exceed 2.0°C. below the cloud point temperature of the solution under test. A beam of light was focused on the tube through the bath from behind. At concentrations of 60% of oil and less the cloud point temperature was indicated by a sharp, distinct appearance of another phase and was reproducible to within a few tenths of a degree centigrade. At higher concentrations the cloud point tended to become less distinct. The 100% peanut oil showed a very gradual increase in cloudiness on cooling, the first appearance of which was difficult to determine even by frequent comparison with a clear standard. The temperature of appearance of the first detectable trace of cloudiness or, in the case of cottonseed oil, the appearance of minute solid particles, was taken as the cloud point.

For each system cloud point determinations were made for a number of concentrations between 10 and 100% oil. The temperatures observed are plotted as a function of concentration in Figure 1.

For concentrations between 10 and 70% of cottonseed oil the cloud point varies by only 4°C., and for the peanut oil system between 10 and 90% the change is less than 1°C. Thus the cloud point, as determined, is little affected by concentration over a wide range in either case.

Though the cloud point for the 100% peanut oil is some 10°C. above that for the 100% cottonseed oil, the two curves cross at about 80% so that below 70% the cloud points of cottonseed oil mixtures are from 10° to 14°C. higher than for peanut oil mixtures. When the cottonseed oil No. 1 system was rerun, using C. P. acetone, the individual cloud points agreed within a few tenths of a degree in all cases.

When commercial hexane was used as the solvent, the cloud points for each oil were far less distinct than with acetone. The points were indicated by the development of a slight turbidity which did not change perceptibly over a range of several degrees. Though reproducible data could not be obtained, it

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[5] The mention of trade products does not imply that they are endorsed or recommended by the Department of Agriculture over similar products not mentioned.

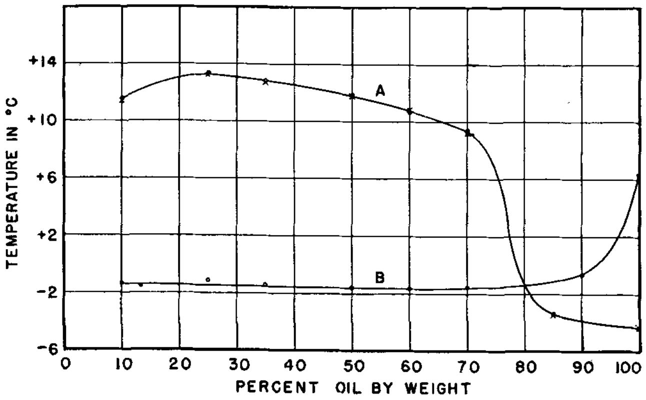

FIG. 1. Cloud point curves: Curve A, cottonseed oil No. 1 in anhydrous acetone (o) and in C. P. acetone (x); Curve B, peanut oil No. 1 in anhydrous acetone.

was apparent that the cloud-point curves lie somewhat lower than those with acetone. Since the cloud points indicate only the temperatures at which the initial separation of solid occurs, they offer no criterion for selecting operating conditions for winterization.

Liquid-Liquid Equilibria

Within certain ranges of concentration at low temperatures, cottonseed oil-acetone and peanut oil-acetone mixtures separate into two liquid phases in addition to the solid phase. Since this phenomenon occurs near or within the temperature range required for winterization and since the presence of a second liquid phase would be expected to cause difficulties in the filtration process, the approximate boundaries of the region of immiscibility were determined in each case.

The experimental procedure was as follows: oil-acetone solutions of concentrations between 10 and 60% of oil were prepared at 5% concentration intervals. Ten ml. of each were placed in a 15-ml. graduated centrifuge tube. The tubes were stoppered and placed in a cooling bath at the desired temperature for 3 hours. They were then quickly transferred to a refrigerated centrifuge at the same temperature and centrifuged for 10 minutes at about 500 times gravity. It was usually apparent on inspection which concentrations separated into two liquid phases in addition to the solid phase. In the case of mixtures of low oil concentrations however the heavy liquid phase, if present, was of course small, and the line of demarcation between the two liquid layers was obscured by the solid phase. Whenever possible, each clear liquid phase was sampled and the concentration of oil in each determined by stripping *in vacuo.* The concentration of the oil in each of the two liquid phases was thus determined at each selected temperature for a number of oil-solvent ratios and averaged.

The resulting phase diagrams for cottonseed oil No. 1 and peanut oil No. 1 are shown in Figure 2 with the temperature plotted against the oil-solvent ratio. It was found that at any one temperature the concentrations within the two liquid phases were approximately constant so long as two layers were present though the relative amounts of the two liquid phases varied with the overall concentrations. In this respect the multicomponent oil-acetone system exhibited a behavior similar to that of a binary system.

The boundaries of the region of immiscibility are however quite sensitive to impurities and may vary slightly with the oil sample. For example, about 0.4% of water was added to the acetone used in making up a 40-60 peanut oil-acetone mixture. On chilling to —3°C. and centrifuging at the same temperature, this mixture gave two distinct liquid phases in addition to a solid phase though the diagram (Figure 2) indicates no liquid-liquid separation until the temperature is lowered to about —4.5°C. Peanut oil No. 2, which had approximately the same analysis but which was slightly turbid, also gave two liquid layers in a 40% oil mixture with the ordinary acetone at —3°C. Crude peanut oil showed the opposite effect; a lower temperature was required for liquid-liquid separation. From other tests it was found that 35 and 45% solutions of cottonseed oil No. 3 in acetone tended to form two liquid layers at —10°C., which is 1.5°C. higher than expected from the curve in Figure 2. It is thus apparent that the regions delineated by the curves in Figure 2 can be considered only an approximation of the areas in which separation into two liquid phases occurs.

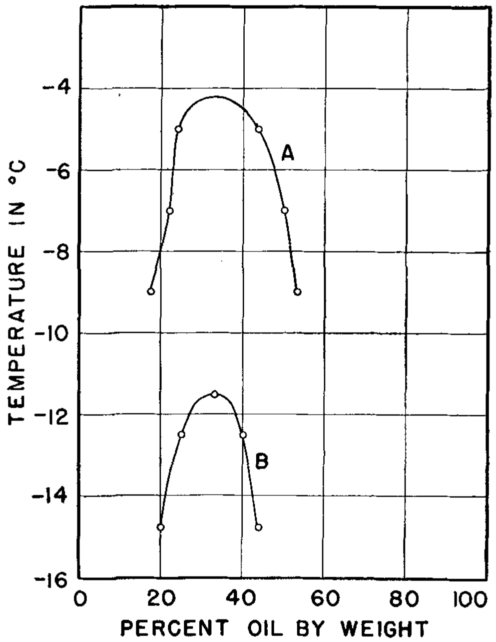

FIG. 2. Liquid-liquid phase diagrams: Curve A, peanut oil No. 1-acetone system; Curve B, cottonseed oil No. 1-acetone system.

Solvent Winterization in Acetone

Laboratory bench-scale winterization tests were carried out between —3.0° and —11.0°C. for oil concentrations varying from 15 to 75% by weight on three cottonseed and two peanut oils to survey the yields obtainable, degree of winterization, and other properties of the fractionated oils as functions of temperature, concentration, holding-time, agitation, and iodine value.

Winterization Procedure. Duplicate samples of approximately 200 ml. of the desired concentrations of oil in acetone were weighed into tared 250-ml. stoppered centrifuge bottles. The samples were chilled at the desired temperature for a definite time (holding-time) by immersion in a constant temperature bath regulated to within ±0.1°C. They were then quickly transferred to a refrigerated centrifuge and centrifuged at the same temperature for 10 minutes at a speed corresponding to about 350 and 700 times gravity at the top and bottom of the solutions, respectively. The temperature of the centrifuge was so regulated that the liquid in the spinning bottles was within 0.3°C. of the desired temperature. This required that the experiments be performed in a constant temperature room.

The clear supernatant liquid was quickly and carefully decanted into a tared flask. The centrifuge bottle with the residual solid fraction was weighed, and the weights of supernatant and solid fractions were obtained by difference. It was sometimes necessary to leave a considerable amount of the supernatant liquid with the solid fraction to prevent suspended particles of the solid from being decanted.

The amount and concentration of the oil in both the supernatant and the residual solid fractions were determined quantitatively by removing the acetone and heating to constant weight at 100°C. and 10 mm. pressure under a stream of nitrogen. The weight of oil in the solid fraction was corrected by subtracting the weight of the oil in the supernatant entrained by the solid fraction, which can be calculated from the weight of acetone in the solid fraction and the concentration of the supernatant. The corrected value so obtained is the "per cent solid removed," and is reported as the percentage of the total oil present in the original solution.

The duplicate results for the percentage of solid removed usually checked within 0.3 unit for cottonseed oil mixtures. For peanut oil mixtures the agreement was not quite so good, probably because the magnitude of the correction was in general greater as the centrifuge separation and the decantation were much less efficient and a greater amount of supernatant was entrained in the solid fraction.

Modified Cold Test. As a criterion of the degree of winterization, a modification of the A.O.C.S. Official Method Cc 11-42 Cold Test was used which was suitable for testing the small samples encountered. After removing the last traces of acetone and moisture by heating at 120°C. and 10 mm. pressure in a stream of nitrogen, 8 ml. of the oil was placed in a 10-ml. specimen vial with a plastic screw cap and a cap liner. The cap was tightly affixed and given a paraffin coating. The vial was then immersed upright in a water-ice mixture (at 0°C.). At definite periods it was removed for a moment and compared with a clear standard against a fluorescent light as a background.

Comparative tests proved this modified A.O.C.S. method to be as satisfactory as the Official Method. Cottonseed and peanut oils differed markedly in the manner in which they showed failure by either of these two methods. Small discrete solid particles formed in cottonseed oil which were readily detectable. In peanut oil a slight haze formed which was not readily discernible and was best detected by the loss of brilliance as compared to the control.

Effect of Holding-Time and Temperature. The effect of holding-time on the degree of winterization was determined by chilling samples of 35% cottonseed oil No. 1 in acetone for 3, 8, 16, and 24 hours at —5.0°, —6.5°, —8.0°, and —11.0°C. As shown in Figure 3 the amount of solid removed increased with an increase in holding-time. The total overall gain as well as the percentage gain in solid yield caused by increasing the holding-time from 3 to 24 hours diminished as the chilling temperature was lowered. An approximately linear relationship was observed between the chilling temperature and the percentage of solid removed for each holding-time in the temperature range considered. These data show that, under the experimental conditions maintained, the same degree of winterization can be attained at different temperatures by varying the holding-time.

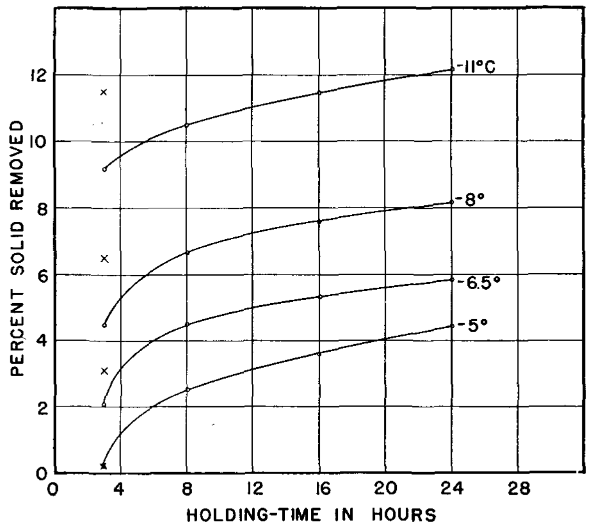

FIG. 3. Relation of percentage of solid removed to holding-time at various temperatures for 35% mixture of cottonseed oil No. 1 in acetone; (o) without agitation; (x) with agitation.

Effect of Agitation and Temperature. In order to determine the effect of agitation on the percentage of solid separating, duplicate samples with agitation were included in each of the above 3-hour runs. The agitation was accomplished by swirling the bottles intermittently (about every 10 minutes) during chilling, causing the solid that separated to be mixed with the supernatant. The agitation effect may be caused partly by a more rapid attainment of the bath temperature by the sample.

The values for the agitated samples are included in Figure 3 as crosses. No effect was perceptible at —5.0°C., but it is apparent that agitation at the lower temperatures caused a marked increase in the amount of solid separating. At —11.0°C. the percentage of solid removed after chilling with agitation was as great as in a similar solution chilled statically for 16 hours at the same temperature.

Effect of Oil-Solvent Ratio and Temperature. Winterizations were run by the standard procedure on cottonseed oil-acetone mixtures between 15 and 75% of oil by weight and at several chilling temperatures with a 3-hour holding-time without agitation. The percentage of solid removed and the corresponding degrees of winterization attained were thus determined for the three cottonseed oils, whose iodine values were 116.4, 108.2, and 106.1, respectively. The resulting data are shown graphically in Figures 4 and 5.

A 3-hour holding-time was chosen for these experiments since longer periods would not be feasible in a continuous winterization process. Agitation during the chilling was not used because of the experimental difficulties involved. It should be noted therefore

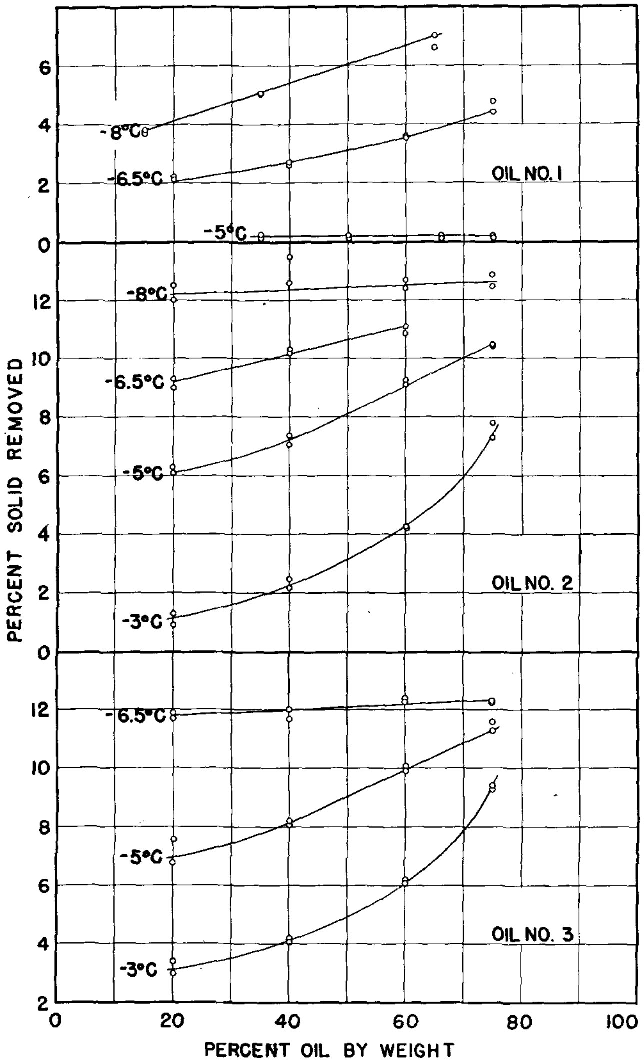

FIG. 4. Solvent-winterization data for cottonseed oils Nos. 1, 2, and 3 in acetone for 3-hour holding-time.

that the values obtained for the percentage of solid removed are in general slightly lower than can be obtained in plant processing equipment, in which the mixtures could be agitated during chilling and be brought to the desired chilling temperature more rapidly.

Five variables are involved in these experiments; namely, a) oil-solvent ratio, b) chilling temperature, c) percentage of solid removed, d) cold test, and e) iodine value of the original cottonseed oil. Their interrelationship can be clarified by interpolating and plotting in various ways to eliminate some of the variables.

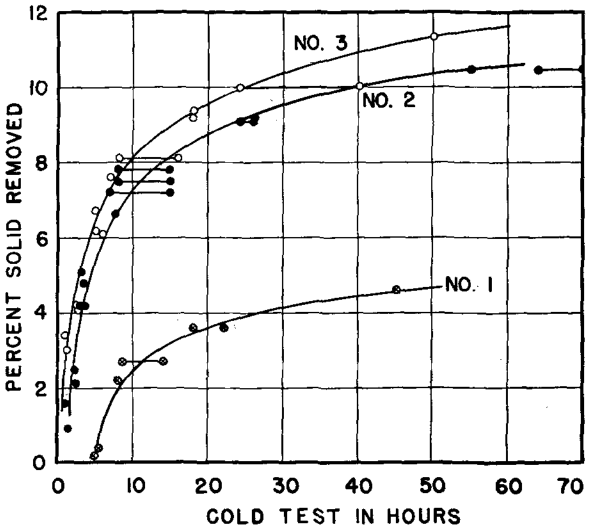

FIG. 5. Cold test after removal of various percentages of solid from cottonseed oils No. 1 (I. V. 116.4), No. 2 (I. V. 108.2), and No. 3 (I. V. 106.1).

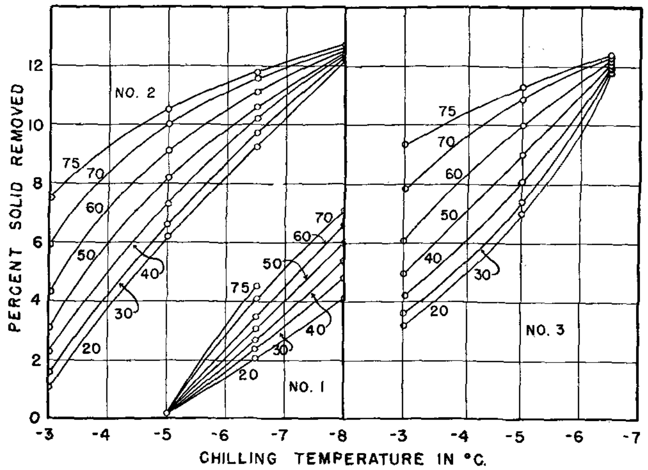

FIG. 6. Percentage of solid removed at various chilling temperatures at constant oil-acetone ratios for cottonseed oils Nos. 1, 2, and 3 (3-hour holding-time).

Figure 6 is a graphical representation of data for each of the three oils obtained by interpolation in Figure 4 and shows the effect of chilling temperature on the percentage of solid removed when the oil-solvent ratio is kept constant. Figure 7 obtained by interpolation in Figure 6 shows for each oil the chilling temperature required to cause the separation of the specified percentages of solid as influenced by the oil-solvent ratio. Table II shows the relation of the iodine value of the original oil to the percentage of

TABLE II

Effect of Iodine Value of Original Cottonseed Oil on the Per Cent Solid Removed at Various Chilling Temperatures and Oil-Acetone Ratios

Oil-solvent ratio by wt.	20% Oil			40% Oil			60% Oil			75% Oil		
Iodine value	106.1	108.2	116.4	106.1	108.2	116.4	106.1	108.2	116.4	106.1	108.2	116.4
Chilling temp. (°C.)	Per cent solid removed											
—3.0	3.2	1.1	....	4.2	2.3	....	6.1	4.3	....	9.3	7.5	....
—4.0	4.9	3.8	....	6.0	5.1	....	8.2	7.2	....	10.4	9.3	....
—5.0	7.0	6.2	0.2	8.1	7.3	0.2	10.0	9.1	0.2	11.3	10.5	0.2
—6.0	9.8	8.2	1.4	10.6	9.3	1.8	11.5	10.5	2.4	12.1	11.4	3.2
—6.5	11.8	9.2	2.1	12.0	10.2	2.7	12.2	11.1	3.5	12.4	11.8	4.5
—7.0	....	10.2	2.8	....	11.0	3.6	....	11.6	4.6	....	12.2	....
—8.0	....	12.2	4.1	....	12.4	5.4	....	12.6	6.6	....	12.9	....

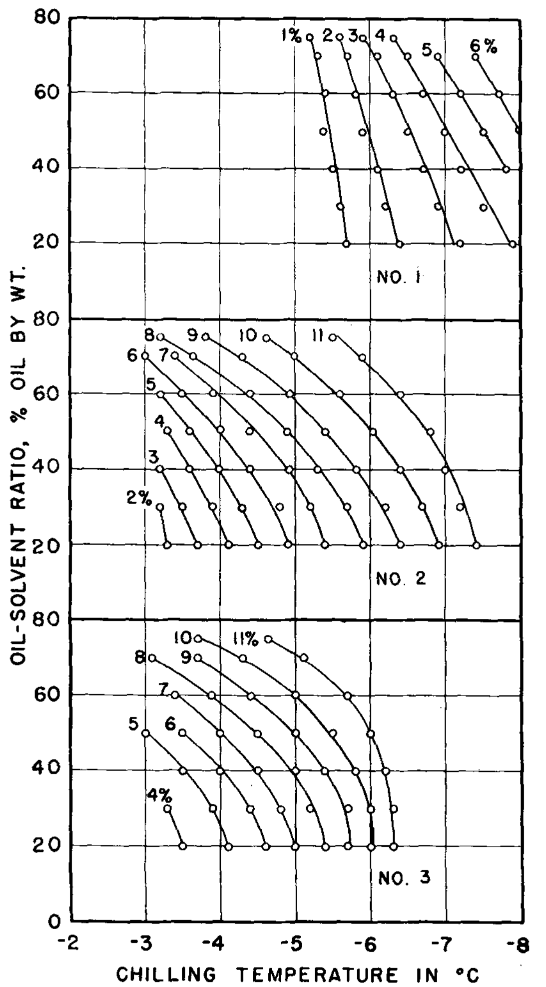

Fig. 7. Relation of chilling temperature to oil-acetone ratio for constant percentage of solid removed from cottonseed oils Nos. 1, 2, and 3 (3-hour holding-time).

solid removed at various constant temperatures or constant oil-solvent ratios.

The following conclusions can be drawn from these data:

For a given oil the percentage of solid removed at a given oil-solvent ratio increases as the chilling temperature is lowered.

For a given oil the percentage of solid removed at a given chilling temperature usually increases as the oil-solvent ratio increases (Figure 4). This increase becomes less marked when the percentage of solid removed becomes very large. The constancy at various oil-solvent ratios in oil No. 1 at —5.0°C. (Figure 4) was perhaps caused by the fact that solid started to separate from these mixtures at the cloud point: that is, the percentage separating per degree lowering was evidently very small until some temperature below —5.0°C. was reached.

The higher the iodine value of a cottonseed oil, the less solid separates from its acetone mixtures at a given chilling temperature. In order to obtain a winterized oil of a given cold test it is necessary to remove a larger percentage of solid from an oil of a low iodine value than from one of a high iodine value (Figure 5). For example, to attain a 6-hour cold test, 1%, 6%, and 7% of solid must be removed from oils Nos. 1, 2, and 3, which have the iodine values 116.4, 108.2, and 106.1, respectively.

The curves for all three oils in Figure 5 show approximately the same curvature so that they can be made practically to coincide by shifting them along the vertical axis. This implies that the same additional percentage of solid must be removed from these to change the final cold test from 6 hours to say 20 hours.

The chilling temperatures necessary to cause the separation of enough solid to give a cold test of 6 hours are shown in Figure 7 by 1%, 6%, and 7% curves for oils Nos. 1, 2, and 3, respectively. The latter two curves, between solvent ratios of 20% to 60% of oil, fall between —5.0° and —3.5°C. and almost coincide. The corresponding curve for oil No. 1 however shows much less variation with oil-solvent ratio, extending only from —5.1° to —5.4°C.

It seems probable that for oil No. 1 the parts of the curves for temperatures between —5.0° and —6.5°C. are slightly in error because they are so drawn in Figure 6 as to converge at —5.0°C. Additional experimentation between these temperatures would probably verify this since, as implied above, the —5.0°C. curve in Figure 4 would practically coincide with a —4.0°C. curve, and also, at least for the lower oil concentrations, with a curve for —5.5°C. Should this be true the 20% line for oil No. 1 in Figure 6 would curve down to reach the 0.2% solid-removed at a lower temperature than the 75% line. This would in turn result in the 1% curve in Figure 7 extending over a slightly wider temperature range.

It will be noted that the curves for the oils Nos. 2 and 3 in Figure 7 are roughly superimposable, the n% curve for oil No. 2 approximating the $(n+1)$% curve for oil No. 3. Since 6% and 7% of solid must be removed from oils Nos. 2 and 3, respectively, it is therefore implied that for these two commercial oils the same chilling temperature is required to obtain a product of any given cold test.

Effect of Winterization on the Iodine Value. It is known that the solids separating out during winterization consist of the more saturated glycerides. They have a lower iodine value and the winterized oil a higher iodine value than the original oil. The magnitude of this effect was determined for a number of winterization experiments. Figure 8 shows the amount by which the iodine value is increased as a

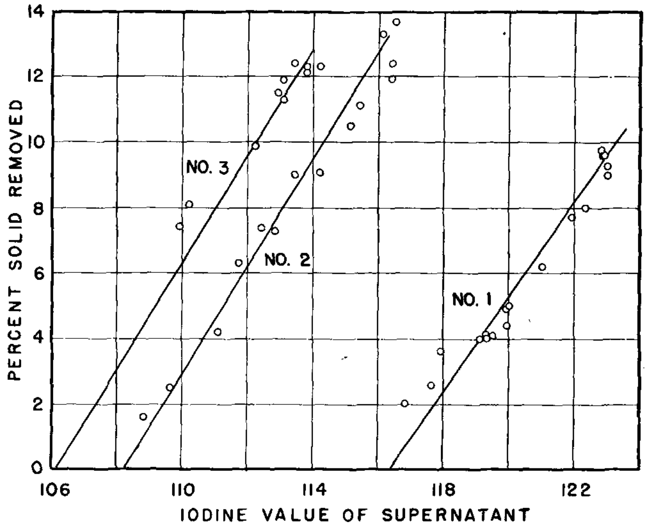

Fig. 8. Change of iodine value with the percentage of solid removed for mixtures of acetone with cottonseed oils Nos. 1, 2, and 3.

greater and greater percentage of solid is removed. The curves for the three oils can be represented roughly by straight lines over the range considered. Their slopes are approximately equal and show a rise of 0.6 to 0.7 points in iodine value for each percentage of solid removed.

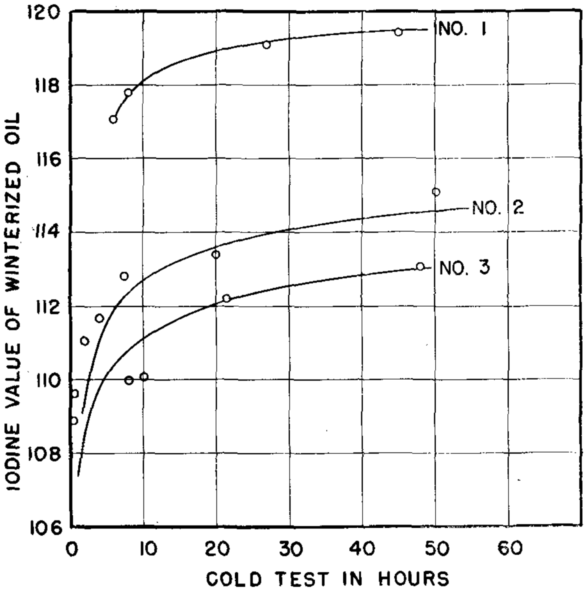

Fig. 9. Relation of cold test to the iodine value of winterized cottonseed oils Nos. 1, 2, and 3.

The change in the iodine value with the cold test or the degree of winterization for each of the three cottonseed oils is shown in Figure 9 which was developed from Figure 5 and the straight lines of Figure 8. The experimental data, shown as circles on the graph, show fair agreement. Figure 9 indicates that in general the higher the iodine value of the original oil the higher the iodine value of the resulting winterized oil having a given cold test value. Thus it is apparent that in producing a winterized oil with a 6-hour cold test the iodine value was changed from 116.4 to about 117 in the case of oil No. 1, from 108.2 to about 112 in the case of oil No. 2, and from 106.1 to about 110.5 in the case of oil No. 3.

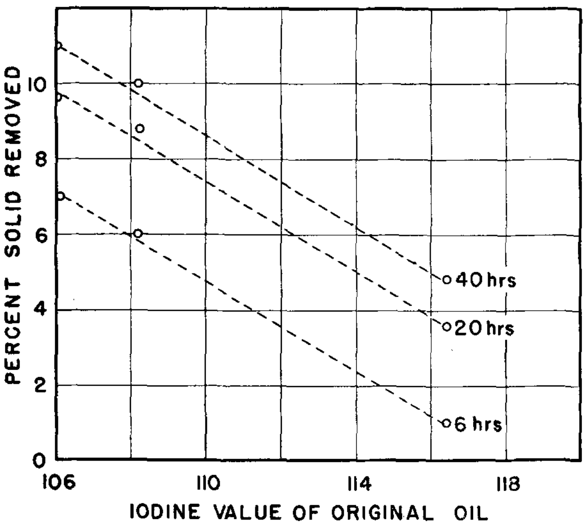

Fig. 10. Relation of iodine value of the original cottonseed oil to the percentage of solid which must be removed to attain cold tests of 6, 20, and 40 hours.

Figure 10 shows the relationship between the iodine value of the original cottonseed oils and the percentage of solid which must be removed to obtain an oil with a cold test of 6, 20, and 40 hours, respectively. For the purpose of comparison the linear relationship is indicated by the dotted lines.

It is possible to calculate roughly the iodine value of the solid removed, $(I.\ V.)_S$, in each case from the iodine value of the desolventized solid fractions with the entrained supernatant liquid, $(I.\ V.)_M$, and that of the oil in the clear supernatant liquid, $(I.\ V.)_L$. The method of calculation is based on the fact that the iodine value is an additive property so that

$$\%S \times (I.\ V.)_S + \%L \times (I.\ V.)_L = 100 \times (I.\ V.)_M$$

where $\%S$ and $\%L$ are the percentages of the solid removed and of the oil from the entrained supernatant liquid, respectively, in the mixture, M. The calculated results showed that the iodine value of the solid removed was in all cases between 48 and 55. This is in good agreement with the iodine value, 52.5, reported by Riemenschneider and coworkers (4) for their most saturated glyceride fraction obtained by systematic fractional solvent recrystallization of cottonseed oil from acetone.

Effect of Oil-Solvent Ratio and Temperature on Settling. The amount of solid separating from a chilled cottonseed oil-acetone mixture at a given temperature increases as the concentration of the oil increases even though, as in the —8.0°C. curve for oil No. 2 (Figure 4), the percentage of solid removed is practically unchanged. Thus in the case mentioned, 2.44 grams of solid would separate from 100 grams of a 20% solution and 9.45 grams from a 75% solution.

Decrease in temperature or increase in oil concentration tend in addition to increase both the viscosity and the density of the solution. Amount, viscosity, and density conspire to decrease the extent to which the solid will settle in solution during the 10-minute centrifugation of the standard procedure. The relative magnitude of this effect with temperature and concentration was determined experimentally for each oil by the following procedure.

Oil-acetone mixtures of various concentrations between 15 and 75% were prepared. Ten ml. of each were placed in a 15-ml. conical graduated centrifuge tube, and the stoppered tubes were immersed in a cooling bath at the desired temperature for 3 hours. They were then centrifuged for 10 minutes in a conical-head refrigerated centrifuge at the same temperature at a speed corresponding to about 1400 and 2800 times gravity at the top and bottom of the liquid, respectively, or 2100 midway. An additional set of samples was run for oils Nos. 2 and 3 at —3.0°C., using a centrifugal speed corresponding to 525 times gravity at the midpoint of the sample.

After centrifuging, the solution had a clear transparent layer on top, referred to as the supernatant layer, and below this a turbid suspension of solid or a solid cake, as the case might be, at the bottom. The amounts of the supernatant layer in percentage by volume are shown in Figure 11 in which the values observed for the lower centrifugal speed at —3.0°C. are shown as broken lines.

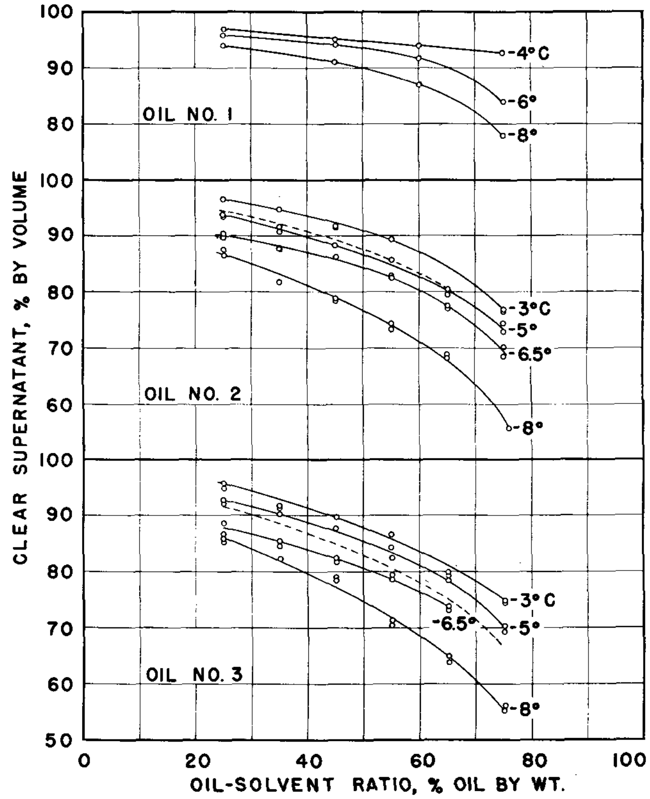

FIG. 11. Percentage by volume of clear supernatant layer after centrifuging cottonseed oil-acetone mixtures at different temperatures (3-hour holding-time). Full lines, 2100 X gravity; broken lines, 525 X gravity at —3.0°C.

The supernatant layers contained all of the winterized oil recoverable by centrifugal separation of this efficiency without washing the crystals. Since the supernatant layers vary in concentration, the values given in percentage by volume cannot be considered as absolute yields.

To estimate the true yields of winterized oil in the clear supernatant it is necessary to consider Figure 11 in conjunction with Figures 5 and 7. For example, Figure 5 shows that 6% of solid must be removed from oil No. 2 to attain a product with a 6-hour cold test. The corresponding chilling temperatures for various oil-solvent ratios can be read from Figure 7. By interpolation between the —3.0° and —5.0°C. curves for oil No. 2 in Figure 11 (shown as broken lines in Figure 12), the full curve A in Figure 12 was obtained. Curve A shows the percentage by volume of clear supernatant liquid at various oil-solvent ratios when 6% of solid separates from oil No. 2. Since the concentration of oil in the supernatant is in all cases 94% of the original oil concentration, the weight per cent of the original oil recovered in each clear supernatant layer can be obtained by applying a factor of 0.94 to the volumes of curve A. For oil No. 2 this gives the values for curve B. Corresponding treatment of the data for oils Nos. 3 and 1 results in curves C and D, respectively.

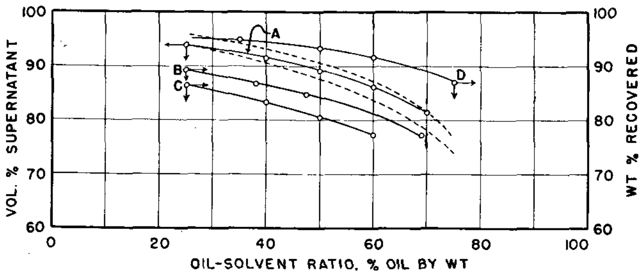

FIG. 12. Settling curves for cottonseed oil-acetone mixtures at 2100 X gravity chilled to give a 6-hour cold test. Curve A, calculated volume percentage of clear supernatant for oil No. 2; Curves B, C, and D, weight percentage of winterized oil recovered from oils Nos. 2, 3, and 1, respectively.

Comparison of curves B, C, and D shows that as the iodine value of the original oil varies from 106.1 to 116.4, the yield of a 6-hour cold test product, as here defined, changes from 86% to 95% for a 25% oil concentration and from 77% to 92% for a 60% oil concentration.

Peanut Oil. The winterization behavior of peanut oil in acetone differs from that of cottonseed oil in two important respects. The crystals which separate on chilling do not settle as well, and the separation into two liquid layers occurs at a higher temperature and within the temperature and concentration ranges necessary for efficient winterization.

These factors made it impossible to obtain complete data over a wide range of temperatures and concentrations by the methods used with cottonseed oil. The presence of the two liquid phases would result in high and erratic calculated values for the percentage of solid removed because at least a part of the liquid entrained by the solid would be more concentrated than the decanted supernatant liquid. If high oil-solvent ratios were used to avoid the region of immiscibility (Figure 2), the amount of clear supernatant after centrifuging would be very small or, in other words, the volume of the supernatant entrained by the solid would be very large. The results obtained would therefore be much less accurate because of the correspondingly large correction factor.

TABLE III

Effect of Oil-Solvent Ratio and Temperature on Per Cent Solid Removed From Peanut Oil-Acetone Mixtures

(Peanut oil No. 1; 3-hour holding-time)

Conc. oil by weight....................	10%	30%	50%
Chilling temp. (°C.)	Per cent solid removed[1]		
—1.0	4.1; 4.1	4.5; 4.4; (4.5)	5.2
—3.0	5.2; 5.2		
—7.0	7.0; 7.3; 7.0; 7.3; (7.6); (7.1)[2]		
—9.0	8.5; 8.4; 8.5; 8.4		

[1] The figures in parentheses are the values for peanut oil No. 2.

[2] The corresponding values for a 16-hour holding-time are 6.7, 6.8, and 7.2; and for a 24-hour holding-time, 6.9 and 7.4.

Table III summarizes the data obtained for peanut oil for the temperatures and concentrations which did not involve separation into two liquid layers. The values for a chilling temperature of —1.0°C. show that, as in the case of cottonseed oil, the percentage of solid separating at a given chilling temperature increased as the oil-solvent ratio increased.

The first two columns in the table are represented by the full line in Figure 13 and show that for mixtures of 10% oil in acetone the percentage of solid removed increases practically linearly as the chilling temperature is decreased over the range considered. The corresponding curves for the three cottonseed

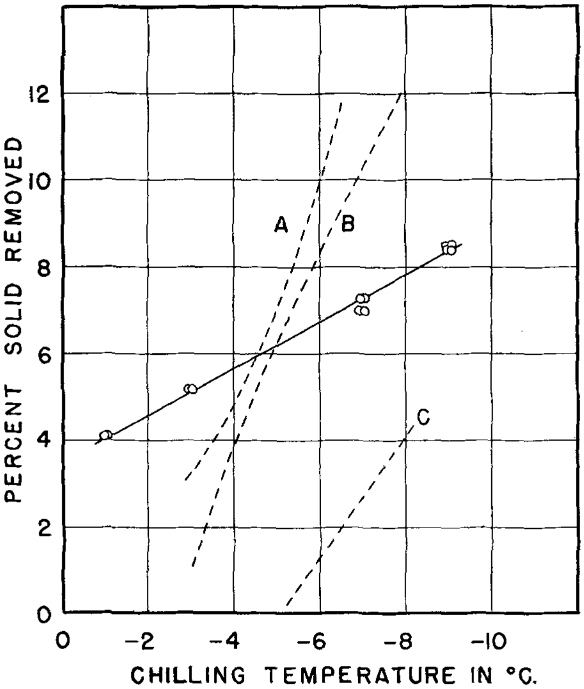

FIG. 13. Relation of chilling temperature to percentage of solid removed from 10% mixture of peanut oil No. 1 in acetone (full line); and corresponding curves for 20% mixtures of cottonseed oils Nos. 1, 2, and 3 in acetone (broken lines C, B, and A, respectively).

oils at a 20% concentration are represented for comparison by the broken lines reproduced from Figure 6. (Figure 6 indicates that for cottonseed oils the slopes at a 10% concentration will not be greatly different.)

The values in Footnote 2 of Table III indicate that an increase in the holding-time beyond 3 hours does not appreciably affect the amount of solid separating. In this respect also peanut oil differs from cottonseed oil. As would be anticipated therefore, agitation was found to have no effect upon the percentage of solid separating in a 3-hour period.

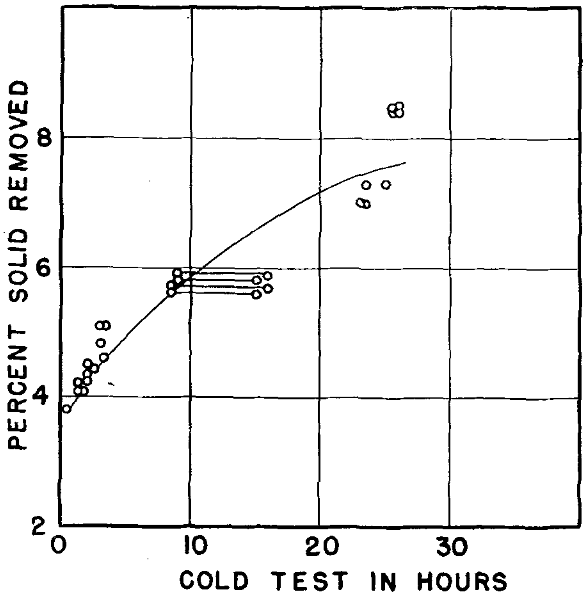

FIG. 14. Cold test after removal of various percentages of solid from peanut oil No. 1.

It will be noted from the figures in parentheses in Table III that at concentrations and temperatures where two liquid layers do not appear, peanut oil No. 2 gave essentially the same results as peanut oil No. 1.

Figure 14 shows the cold test in hours obtained by removal of various percentages of solid from peanut oil No. 1. From this curve it is apparent that about 5% of solid must be removed from the oil to attain a cold test of 6 hours. The fact that the curve does not seem to flatten out as rapidly as those for the cottonseed oils (Figure 5) may be caused by the trace of solid which remained in the supernatant layer due to a slight swirl when the centrifuge stopped.

Another difference of practical significance in the winterization behavior of cottonseed and peanut oils is demonstrated by comparing the slope of the peanut oil curve with that of the cottonseed oil curves in Figure 13. It is apparent that 3 to 4 times as much solid separates from the cottonseed oil per degree lowering of chilling temperature as from the peanut oil. It therefore becomes apparent that tolerance to variation in temperature during solvent winterization of peanut oil in acetone, at least for the oil-solvent ratio of 10%, is very much more favorable than with cottonseed oil.

Thus in order to winterize peanut oil No. 1 to pass a cold test of 6 hours, about 5% of solid would have to be removed (Figure 14) and for a 10% oil mixture a chilling temperature of about —3.0°C. would be required (Figure 13). There would be no great disadvantage in this case to set the winterization temperature at —5.0° or —6.0°C. to allow for any fluctuation in temperature (and consequent re-solution of the solid) during the processing between the initial chilling and the completion of the filtration. Winterization at the lower temperature would merely cause an increase in the separated solid from 5% to about 6.2 and 6.8%, an increase of about 25 and 35%, respectively, in the amount of solid to be filtered off. In the case of cottonseed oil No. 2, 6% of solid would have to be removed (Figure 5) and a chilling temperature of about —5.0°C. would be required. In this case if the operating temperature was set 2 or 3 degrees lower, —7.0° or —8.0°C., as a guard against fluctuation, the percentage of solid removed, as shown by Figure 13, would be about 10.4 and 12.2% respectively. The resultant increase in the amount of solid which would have to be filtered off would be over 75 and 100%, respectively. For cottonseed oil No. 1 the corresponding figures would be about 600 and 800%, respectively. This consideration might have to be taken into account in regulating the rate of feed and the speed of the drum filter or centrifuge. Perhaps more important, it might markedly affect the yield and therefore have some economic significance since the solid removed will inevitably entrain some of the supernatant.

Figure 13 also implies that the heat capacity of a peanut oil-acetone mixture for some degrees below and above the temperature required for winterization is considerably less than that of a cottonseed oil-acetone mixture. This follows from the fact that much more solid separates out per degree lowering in the case of cottonseed oil and that the heat of crystallization, 21 cals. per gram (7), is involved.

The validity of this conclusion is corroborated by an examination of the dilatometric data published by Hofgaard (4) and by Kraemer and Bailey (5). It is apparent from their volume-temperature curves for cottonseed and peanut oils that the slope, or the change in volume per degree, is about the same for the two oils in the liquid state but that below the temperature at which solid separates the slope is very much greater for cottonseed than for peanut oil.

Filtration

The use of filtration as a means of separating the solid from the chilled oil-acetone mixtures was examined briefly by means of a small-scale "filter leaf" test, with and without filter aids. These experiments were limited to oil-solvent ratios ranging from 20 to 50% and a chilling temperature of −9.0°C. with a 3-hour holding-time and were only roughly quantitative.

In general there was an extreme contrast between the ease of filtration of the cottonseed oil mixtures and the difficulties encountered with the peanut oil mixtures. The former proved readily filterable over the entire range of concentrations investigated while the latter could be filtered clear at a reasonable rate up to an oil-solvent ratio of only 30%. Successful filtrations of the cottonseed oil-acetone mixtures were made without filter aids while the only satisfactory tests made on peanut oil mixtures involved the use of filter aids either as a precoat or added to the solution.

The most successful filtrations were made by using a No. 8 duck as the filter cloth. The initial rate of filtration (duration one minute) of a 35% solution of cottonseed oil containing about 1% of filter cel kept in suspension by gentle agitation during chilling and using a vacuum of 10 inches of mercury was approximately 530 pounds of oil per square foot per hour. Using the same cloth or a heavy twill with a precoat of the filter aid about one-sixteenth inch thick a 30% solution of peanut oil in acetone filtered at the initial rate of approximately 350 pounds of oil per square foot per hour. A 30% solution of the same oil containing a small amount of filter aid and agitated while cooling filtered at approximately the same rate.

Summary and Conclusions

Systematic physical chemical data on the solvent-winterization behavior of cottonseed and peanut oils with acetone have been obtained which should serve as a basis for selecting the conditions necessary for the effective solvent winterization of these oils in acetone.

Cottonseed and peanut oils are only partially miscible with acetone below certain temperatures which have been determined. In peanut oil this phenomenon may interfere with the winterization process within a certain range of concentrations. For cottonseed oil however the separation into two liquid phases does not occur until some 5°C. below the temperature required for adequate winterization.

Complete data for a 3-hour holding-time have been obtained for three cottonseed oils ranging in iodine value from 106.1 to 116.4. Tables and graphs have been constructed to show the effect of oil-solvent ratio, chilling temperature, holding-time, agitation, and iodine value of the original oil on the percentage of solid removed and on the degree of winterization and iodine value of the winterized oil.

Similar data have been obtained for a refined peanut oil insofar as possible without interference from separation into two liquid phases. It seems probable that if acetone were used as the winterization solvent for peanut oil, the separation into two liquid layers and the sensitivity of this phenomenon to moisture might be a source of processing difficulties especially if filtration instead of centrifugation were used to separate the solid from the supernatant.

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Detergency Evaluation. I. Wash Test Methods[1]

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SURFACE-ACTIVE agents can be evaluated by many different tests, some of which were described in a previous paper (4). Of the many possible, a method for estimation of cleansing ability is necessary since one of the very important uses of these agents is the cleansing of surfaces such as soiled wearing apparel, which alone represents a multi-million pound market in the United States.

Not all surface-active agents possess the same degree of cleansing action, and differentiation between them is a serious problem which becomes more complex when the multitude of mechanical means used to produce washing action are considered. These have varied from hand cleaning to use of mechanical washers and now includes fully automatic washing machines installed both in homes and in power laundries. Duplication of these washing processes in the laboratory on a small scale, under controlled conditions, proves fairly difficult. Mechanical action and its mode of application must be controlled since it directly affects the degree of soil removal, as demonstrated by Bacon and Smith (2) for the Laun-

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[1] Presented at the spring meeting, American Oil Chemists' Society, May 1-3, 1950, Atlanta, Ga.