holes and holds an overflow tube V (Figure 4). In operation the lower end of this tube is sealed by the oil accumulated on the plate X with the result that the water vapor must pass upward through the perforations and through the oil layer. The column is so modified that oil from the lowest plate drains into the oil receiver C (Figure 3). Each plate is 26 mm. in diameter, and the distance between plates is 30 mm.

The column is electrically heated by means of a heating element Y (Figure 4), composed of 30 feet of No. 26 resistance wire wrapped in a spiral on a close fitting glass tube enclosing the column. An outer jacket Z (Figure 4) of glass encloses the entire column and heating element.

The flow of water vapor is controlled by a small ring heater J (Figure 3), which is kept just below the water level in the water reservoir D. It is composed of a strip of sheet metal insulated with asbestos and wrapped with No. 26 resistance wire. The water reservoir consists of a 250-cc. graduate equipped with a baffle as shown. The trap K is necessary to catch the small amount of oil which drains from the column upon completion of deodorization. The vapor from the column passes through the spray trap E, into dry ice traps F and I. A vacuum pump is attached at I through a pressure regulator. Pressures are determined by means of the manometers G and L.

Temperatures are measured at the top of the column by means of the thermometer H and at any point on the column by means of a movable iron-constantan thermocouple inserted between the wall of the column and the heating jacket.

In operation the column is heated to the desired deodorization temperature, which is measured by means of the thermocouple. Then oil is allowed to flow through the preheater into the column, and the temperature of the preheater is varied until the thermometer and the thermocouple indicate the same temperature, showing that the oil is entering the column at the desired temperature.

A sample of the same reverted soybean oil used in testing the bubble-cap deodorizer was deodorized at 200°C. in the modified Oldershaw column deodorizer. The data are shown in Table III. A bland oil was produced at an oil flow rate as high as 17.5 g./min.

TABLE III

Oil Quality—Modified Oldershaw Column Deodorizer

Pressure (mm. Hg.)	Oil Flow (g./min.)	Steam (% of oil)	Score and Standard Deviation	
			Oil	Control
0.5	10.0	6.0	8.0±0.90	8.2±0.45
1.0	14.0	2.5	7.7±0.84	8.2±0.45
0.5	17.5	2.5	7.3±0.90	7.9±0.71

TABLE IV

F.F.A. Removal—Modified Oldershaw Column Deodorizer

Pressure (mm. Hg.)	Oil Flow (g./min.	Steam (% of oil)	% F.F.A.		% Removal
			Before	After	
0.7	23.0	2.0	0.52	0.08	85.0
4.5	7.2	8.7	1.51	0.32	79.0
9.0	5.5	10.0	0.45	0.13	71.0
7.0	7.5	6.6	1.51	0.54	63.5
3.3	24.0	2.0	0.45	0.26	42.0
3.5	21.0	2.0	0.45	0.32	29.0

Table IV shows the percentage of free stearic acid removed in the modified Oldershaw column deodorizer at 200°C. It is obvious that the best results were obtained at low oil flow rates or at low pressures. The rate at which free acid is removed is indicated by the data recorded for the second sample. Seventy-nine per cent of the free fatty acid was removed in one pass through the column even though there was an extraordinary high percentage (1.51) present in the original oil.

Summary

Two semi-continuous all-glass vacuum deodorizers have been constructed and tested. One operates on a bubble-cap principle. The other is constructed from a modified 15-plate Oldershaw distillation column. Both columns effectively deodorize oils and remove fatty acids, but the latter has the higher capacity.

Acknowledgment

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Phase Relations in the Solvent Winterization of Molecularly Rearranged Peanut Oil and Cottonseed Oil

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ONE of the major problems in the solvent winterization of cottonseed and peanut oils has been the production of more easily filterable crystals. The filtration behavior when hexane is the solvent is very unsatisfactory, especially for peanut oil. It has recently been shown that improved crystals can be obtained from acetone and from a solvent mixture consisting of 85 parts by weight of acetone and 15 parts of hexane and that these solvents have other advantages over hexane (2, 3, 7). Preliminary short-run pilot plant experiments by Holzenthal *et al.* (5) in this laboratory indicated that the crystals formed in the solvent winterization of cottonseed oil in this acetone-hexane mixture had excellent filtration characteristics.

According to Bailey and coworkers (1), much better crystals are obtained in the solvent winterization

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of peanut oil from hexane if the oil is first molecularly rearranged or randomized. The purpose of the present investigation was to make a more thorough study of the advantages and disadvantages of introducing this preliminary rearrangement step. Systematic phase-relation data pertaining to the solvent winterization of rearranged peanut oil in 85-15 acetone-hexane mixture and of rearranged cottonseed oil in acetone have been obtained and compared with the corresponding data for the original oils.

Oils and Experimental Procedures

The peanut and cottonseed oils used were commercial refined and bleached oils for which complete solvent-winterization data have already been published; the former in 85-15 acetone-hexane mixture (3) and the latter (previously designated as Cottonseed Oil No. 3) in acetone (2, 7). Their iodine values by the Wijs method were 94.1 and 106.1, respectively. The commercial hexane used was Skellysolve B[2] and the acetone a commercial C.P. grade containing 0.4% of moisture as determined by a special Karl Fischer reagent for ketones (6).

Molecular Rearrangement. The procedure used was essentially that of Eckey (4). The catalyst was prepared by dissolving 2.5 grams of sodium in absolute methanol and adding 350 ml. of dried cyclohexane. Two liquid layers were formed. The excess methanol was distilled from the mixture in a stream of nitrogen leaving about 200 ml. of cyclohexane in which solid sodium methylate was suspended. A portion of this suspension corresponding to 0.2% by weight of sodium methylate was added to the deodorized (peroxide value = 0) and dried oil which had previously been heated to 96°C. After two hours of vigorous stirring at this temperature in a nitrogen atmosphere the oil was cooled and treated with an excess of hydrochloric acid to destroy the catalyst. It was then thoroughly washed with water and, using bubbling nitrogen for agitation, the cyclohexane and moisture were removed in a 20-mm. vacuum at 100°C. The cloud points of the resulting molecularly rearranged oils by the A.O.C.S. Method Cc 6-25 were 14.5° and 14.0°C. for the peanut and the cottonseed oils, respectively, as compared to 2.0 and 0.0°C. for the original oils. An increase in color was noted in both cases.

Winterization Procedure. Laboratory bench-scale winterization experiments were performed by the same procedure as previously described (2, 3, 7). In brief, duplicate weighed samples of the oil in definite oil-solvent ratios were chilled without agitation in a bath at the desired temperature for a definite holding-time. A 3-hour holding time was used unless otherwise mentioned. They were then centrifuged at the same temperature for 10 minutes in the case of the cottonseed oils and for 30 minutes in the case of the peanut oils. From the weights and oil contents of the clear supernatant layer and the residual layer the total amount of solid which had separated during chilling was calculated. The "percentage of solid removed" was based upon the amount of oil present in the given oil-solvent mixture. Cold tests were obtained by a modification (7) of the A.O.C.S. Official Method Cc 11-42 Cold Test.

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

Winterization of Molecularly Rearranged Peanut Oil in 85-15 Acetone-Hexane Mixture

The resulting data from the winterization experiments on the molecularly rearranged peanut oil at —12°C. are plotted in Figure 1, with the corresponding curve previously obtained for the original oil (3) shown as a dotted line. Comparison shows that molecular rearrangement caused an increase in the percentage of solid removed at any given oil-solvent ratio and that the increase is greater at the higher oil concentrations.

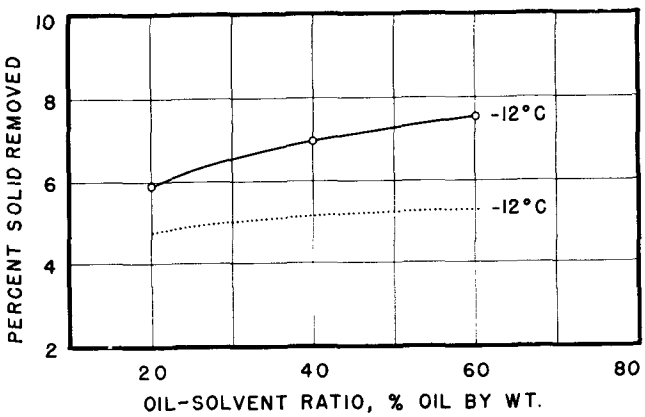

FIG. 1. Solvent-winterization data for peanut oil in 85-15 acetone-hexane mixture (3-hour holding-time): ....., original oil; ————, after molecular rearrangement (cloud point, 14.5°C.).

Considerably more solid had to be removed from the molecularly rearranged oil to attain a given degree of winterization. It was necessary to remove only 3.2% of solid from the original oil to produce an oil having a 6-hour cold test (3). The molecularly rearranged oil, on the other hand, failed a 2-hour cold test after removing 7.5% of solid, and a 0.5-hour cold test when 7.0% was removed.

A considerably lower chilling temperature was required to produce a winterized oil from the rearranged oil. With a chilling temperature of —6.5°C. and an oil-solvent ratio of 30 to 70, about 3.5% of solid was removed from the original oil, producing an oil having a cold test of 8 hours (3). Using the same oil-solvent ratio and a chilling temperature of —12°C. for the rearranged oil, about 6.5% of solid was removed, but the resulting oil had a cold test of less than 0.5 hour. Thus the chilling temperature necessary to obtain an adequately winterized oil from the rearranged oil would have to be considerably more than 6 Centigrade degrees below that for the original oil. This is disadvantageous not only because of the additional refrigeration required but also because at these lower chilling temperatures there is an increased tendency for two liquid layers to form, which can be expected to cause filtration difficulties.

Using the experimental procedure previously described (3, 7) the relative settling capacities of the solid separating in a 3-hour holding-time were determined for the various oil-solvent ratios at —12°C. These data are plotted in Figure 2, which shows the percentage by volume of clear supernatant liquid after

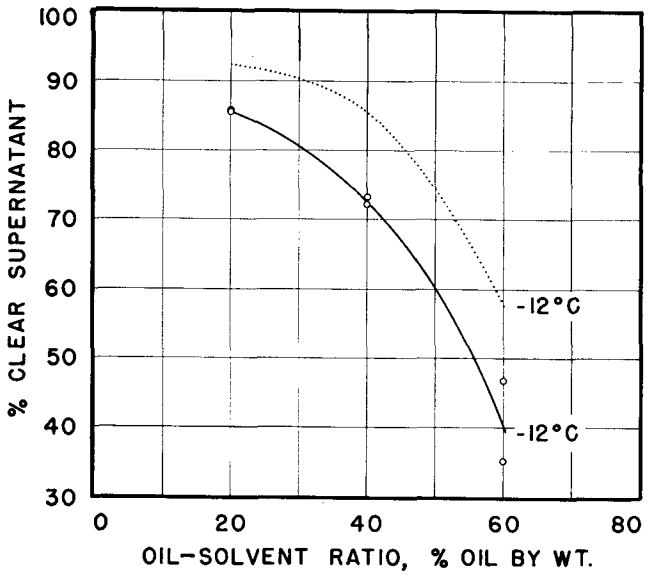

FIG. 2. Percentage by volume of clear supernatant layer after centrifuging chilled mixtures of peanut oil in 85-15 acetone-hexane at 2,100 × gravity (3-hour holding-time): ....., original oil; ————, after molecular rearrangement (cloud point, 14.5°C.).

centrifuging the chilled sample at a speed equivalent to 2,100 times gravity. The corresponding curve for the original oil (3) is shown as a dotted line. It is apparent that the settleability for the rearranged oil was not as good as for the original oil. This is more conclusively illustrated by Figure 3 which can be derived (2) from Figures 1 and 2. Figure 3 shows the "degree of packing" as influenced by the oil-solvent ratio and the chilling temperature; the degree of packing is defined as the ratio between the weight in grams of solid separating and the volume in cc. it occupies after centrifuging. The dotted curve is for the original oil under the same conditions (3).

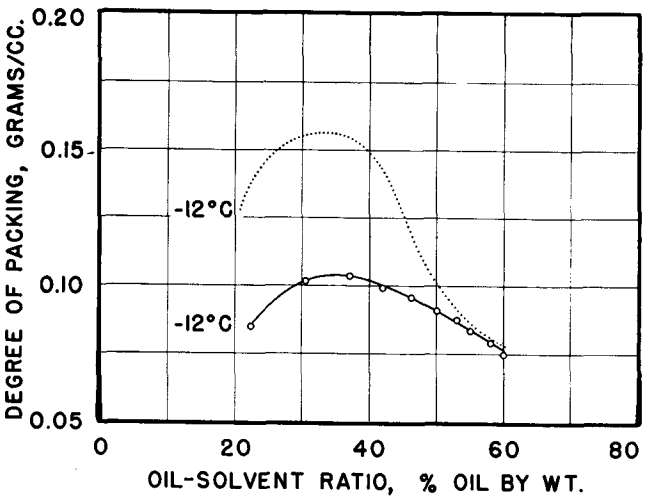

FIG. 3. Degree of packing of the solid as influenced by the oil-solvent ratio for mixtures of peanut oil in 85-15 acetone-hexane (3-hour holding-time): ....., original oil; ————, after molecular rearrangement (cloud point, 14.5°C.).

Winterization of Molecularly Rearranged Cottonseed Oil in Acetone

Winterization experiments were performed on the molecularly rearranged cottonseed oil at various oil-solvent ratios at —5.0° and —6.5°C. with a 3-hour holding-time. Acetone was used as the solvent since the data for the original oil in that solvent were available (2, 7). The data are plotted in Figure 4 with the corresponding data for the original oil shown as dotted lines. It is apparent that the results obtained differ markedly from those for the original cottonseed oil. Much more solid separated from the molecularly rearranged oil than from the original. Also the shape of the curves was greatly altered, with the rearranged oil showing a minimum in the percentage of solid removed as the concentration of the oil increased. Another apparent inconsistency in the rearranged oil is that between 20 and 40% oil concentrations more solid separated at —5°C. than at —6.5°C. It should be remembered however that these curves do not represent equilibrium conditions between the solid and liquid so that this apparent abnormality may be caused by different rates of crystallization at the various concentrations and temperatures.

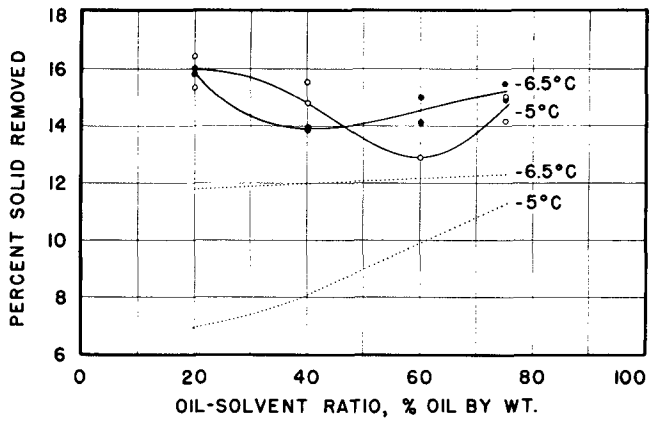

FIG. 4. Solvent-winterization data for cottonseed oil in acetone (3-hour holding-time): ....., original oil; ————, after molecular rearrangement (cloud point, 14.0°C.).

As in the case of the rearranged peanut oil, much more solid had to be removed from the molecularly rearranged oil than from the original oil to attain the same degree of winterization, and a correspondingly lower chilling temperature would be required. Only 7% of solid had to be removed from the original cottonseed oil to produce a winterized oil having a 6-hour cold test, and this could be accomplished with a 3-hour holding-time at a chilling temperature of —5°C. The best cold test attained for the molecularly rearranged cottonseed oil was only 3.5 hours in spite of the fact that as much as 16% of solid had been removed and a chilling temperature of —6.5°C. was used.

The settling data obtained for the same oil concentrations and temperatures are plotted in Figure 5. Comparison with the corresponding curves for the original oil (2, 7), represented by the dotted lines, shows that the molecular rearrangement markedly impaired the settling qualities of the crystals formed. As shown by Figure 6, the degree of packing of the

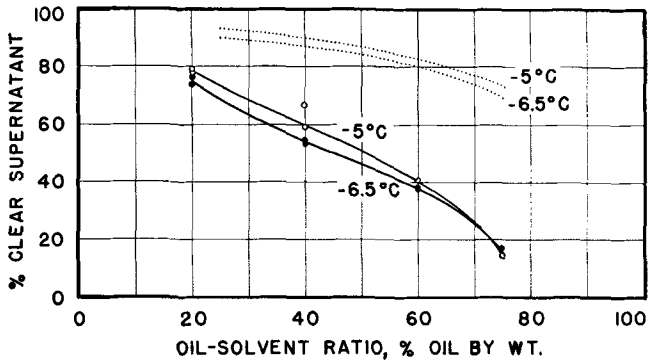

FIG. 5. Percentage by volume of clear supernatant layer after centrifuging chilled cottonseed oil-acetone mixtures at 2,100 × gravity (3-hour holding-time): ....., original oil; ————, after molecular rearrangement (cloud point, 14.0°C.).

original oil was 100 to 300% better than for the molecularly rearranged oil.

Effect of Partial Molecular Rearrangement of Peanut and Cottonseed Oils

The same original peanut and cottonseed oils were subjected to a mild molecular rearrangement using less catalyst, a lower temperature, and a shorter reaction time. The resulting partially rearranged oils had cloud points of 3.0° and 2.5°C. as compared to 2.0° and 0.0°C. for the original peanut and cottonseed oils, respectively. Winterization data, similar to those shown in Figures 1 to 6, were then obtained on these oils, using 85-15 acetone-hexane mixture as solvent and chilling temperatures of —6.5°, —10°, and —13° C. for the peanut oil, and using acetone and a chilling temperature of —5°C. for the cottonseed oil. The results as compared to those for the original oil can be summarized as follows:

Partially Rearranged Peanut Oil. The percentage of solid separating during a 3-hour holding-time was not appreciably affected. However the percentage which had to be removed to attain a given degree of winterization was increased by the partial rearrangement. For example, removal of 6% of solid resulted in a product having a cold test of less than 3 hours while only 3.2% had to be removed from the original oil to attain a 6-hour cold test. It was also found that additional solid separated when the holding-time was increased from 3 to 20 hours. In this respect also the behavior of the partially rearranged oil was less favorable than that of the original oil, for which the percentage of solid separating at a given chilling temperature reached its maximum within a half-hour holding-time (4). These results imply that for a given oil-solvent ratio and chilling temperature the rate of crystallization was lower for the partially rearranged than for the original oil but that the percentage of oil which would crystallize if allowed sufficient time was actually greater.

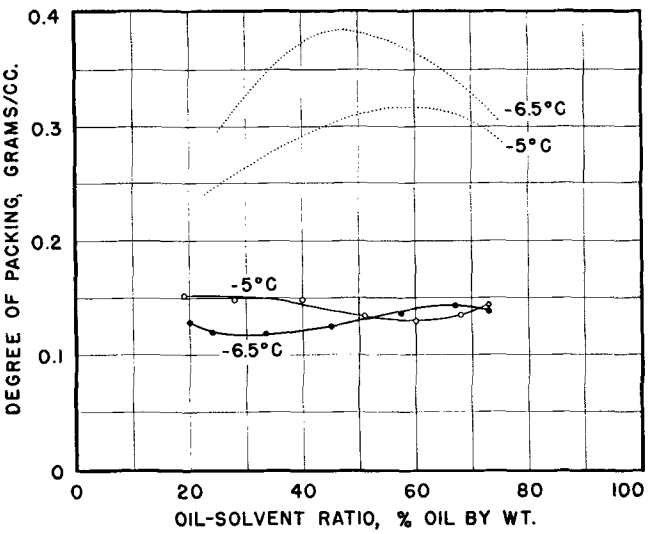

FIG. 6. Degree of packing of the solid as influenced by the cottonseed oil-acetone ratio (3-hour holding-time): ....., original oil; ————, after molecular rearrangement (cloud point, 14.0°C.).

Partially Rearranged Cottonseed Oil. Partial rearrangement caused a slight reduction in the amount of solid separating at a given oil-solvent ratio and chilling temperature in a 3-hour holding-time, probably because, as with peanut oil, the rate of crystallization was decreased. It seems likely that the percentage of the oil which would crystallize if sufficient time were allowed would be greater for the rearranged oil.

The cold test obtained by removal of a given percentage of solid was reduced by the partial rearrangement. For example, to obtain a winterized oil having a 6-hour cold test 9.2% of solid had to be removed from the rearranged oil as compared to 6.8% for the original oil. Thus more solid had to be removed from the rearranged cottonseed oil than from the original oil to attain the same degree of winterization, and this would require a lower chilling temperature if a 3-hour holding-time were used in both cases.

The curves for the settling of the solid separating and its degree of packing showed that the partial rearrangement markedly impaired the settling qualities of the crystals formed. The degree of packing for the original oil was from 66 to 100% better than that for the partially rearranged oil.

Summary

Systematic phase-relation data have been obtained to determine the effect of either mild or extensive molecular rearrangement on the winterization behavior of peanut or cottonseed oils. The results show that the introduction of the molecular rearrangement step before solvent winterization is disadvantageous. A larger percentage of solid must be removed to obtain a winterized oil, especially for cottonseed oil, and lower yields result. Lower chilling temperatures and longer chilling periods are also required, partially because of a lower rate of crystallization. In addition the settling qualities of the solid separating are markedly impaired.

Acknowledgment

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