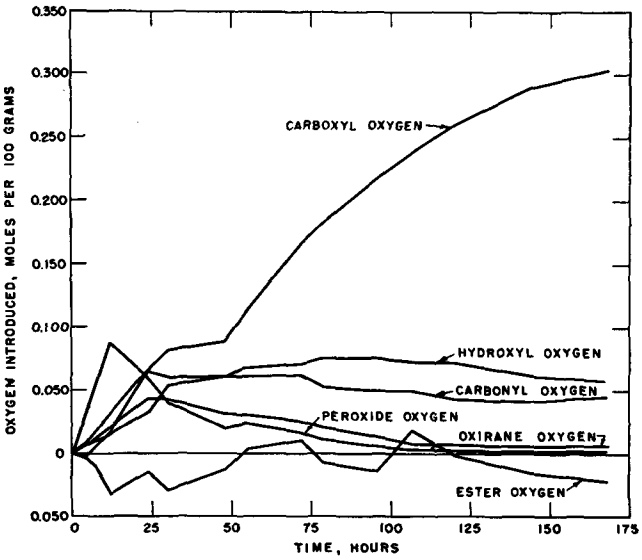


FIG. 3.

The iodine number (Wijs method) of the methyl oleate decreased smoothly with autoxidation time, more rapidly, of course, at the higher temperatures. When the oxidations were concluded, the iodine numbers of the methyl oleate autoxidized at 35°, 70°, and 100° were 22, 6, and 6, respectively. Attempts to correlate oxygen introduced with double bond disappearance gave no simple or understandable relationship.

The data presented and discussed indicate that the course of the autoxidation is exceedingly complex and that investigation of unfractionated oxidation mixtures is less likely to be productive of useful information for mechanism elucidation or the preparation of useful chemicals than fractionation followed by investigation of the behavior of pure intermediates. Fractionation work is now in progress and will be the subject of future reports. Furthermore, to direct the oxidation reactions along preferred paths, highly selective oxidation conditions must be found.

### Acknowledgment

The authors thank Ronald E. Koos for some of the chemical analyses and Jane Dixon for carbon and hydrogen analyses.

### Summary

Methyl oleate, irradiated with ultraviolet, has been autoxidized at 35°, 70°, and 100°C. for 2,000, 264, and 168 hours, respectively. Samples were withdrawn at intervals and total oxygen introduced was determined by chemical analysis for peroxide, carbonyl, hydroxyl, oxirane, ester, and carboxyl oxygen.

Total oxygen introduced was also determined by difference from carbon and hydrogen analyses. In the autoxidation at 35° good agreement was obtained between the two methods for determining total oxygen introduced, over the entire time period studied. At 70° and 100° however good agreement was noted only during the early stages, after which the combustion values were higher and the spread between them became progressively larger. This difference is accounted for by formation of ethers, which could not be determined chemically. At all three temperatures about 2.5 to 3.0 atoms of oxygen were introduced per molecule of methyl oleate.

Even with such a comparatively simple substrate as methyl oleate the autoxidation reaction is exceedingly complex.

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# Phase Relations Pertaining to the Solvent Winterization of Peanut Oil in Acetone-Hexane Mixtures[1]

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COMPLETE phase relation data on the solvent winterization of peanut oil in acetone (3) showed that commercial C.P. acetone did not show promise as a winterization solvent for peanut oil because of the formation of two liquid layers in the concentration and temperature ranges necessary for adequate winterization. It was found in the case of cottonseed oil (2) that separation into two liquid phases can be counteracted by the presence of a small proportion of a hydrocarbon, such as hexane, in the acetone.

The present report gives the phase relation data pertinent to the solvent winterization of a refined peanut oil in a solvent mixture consisting of 85 parts by weight of acetone and 15 parts of hexane. The results show that with this solvent mixture a well-winterized peanut oil can be obtained without encountering two-liquid-layer formation.

*Materials.* A commercial refined and bleached peanut oil was used in the investigations. Its characteristics were: iodine value (Wijs), 94.1; free fatty acids as oleic, 0.34%; peroxide value, 4.2 millimoles per kg.; unsaponifiable matter, 0.35%; and moisture and volatiles, 0.04%.

Several hydrocarbon solvents were used with the commercial C.P. acetone in preparing the solvent mixtures. The commercial hexane and pentane used were Skellysolve B and F, respectively.[3] The isooctane was "99 mole % pure," and the cyclohexane was an Eastman Kodak Company product.[3]

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[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

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

*Winterization Procedure.* Winterization procedure was essentially the same as that previously described (3) with the following modifications: Duration of centrifugation was increased from 10 to 30 minutes to get a more effective separation of the solid from the supernatant liquid. The centrifuge was modified so that the brushes could be pulled away from the armature of the motor at the end of the centrifugation period. This resulted in smooth deceleration and eliminated a slight swirl of solid up into the clear supernatant liquid previously noted in the case of peanut oil solutions. Both of these latter modifications prevented the remixing of some of the solid with the decanted liquid, a source of error which had previously caused considerable error in the cold test for the winterized product, so that the calculated percentage of solid which had to be removed to attain a given cold test was slightly high. The rubber stoppers for the centrifuge bottles were wrapped in tin foil to avoid sorption of hexane. The "percentage of solid removed" is based on the amount of oil present in a given oil-solvent mixture.

*Effect of Oil-Solvent Ratio and Temperature (3-Hour Holding-Time).* Bench-scale winterizations in a mixed solvent consisting of 85% of acetone and 15% of hexane by weight were carried out at concentrations of 20 to 60% oil by weight at temperatures of −6.5°, −8°, −10°, and −12°C. The resulting data, plotted in Figure 1, show that the percentage of solid removed at a given chilling temperature is affected only slightly by the oil-solvent ratio. This is in direct contrast to the behavior of cottonseed oil in the same solvent as can be seen by comparison with the corresponding −8°C. curve for that oil (2), shown in Figure 1 as a broken line. Thus, for a 50% concentration,

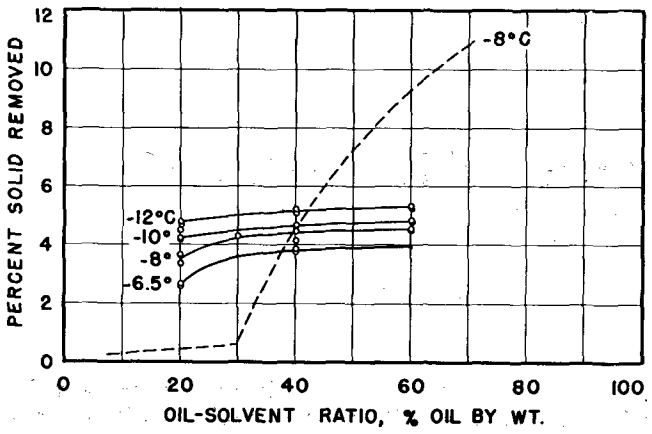


FIG. 1. Solvent-winterization data for oil in 85-15 acetone-hexane mixture: ————, peanut oil; — — — —, cottonseed oil (3-hour holding-time).

a variation of 10% in the concentration would result in only a 0.1% variation in the percentage of solid removed in the case of peanut oil but would cause a variation of over 2% in the case of the cottonseed oil.

The dependency of the percentage of solid removed upon the temperature is shown in Figure 2, which indicates that over the temperature range considered the effect of lowering the chilling temperature is only slight. For a 40% oil solution, for example, the variation in the percentage of solid separating is only about 0.2% per degree change in temperature. Again the corresponding curve for the 40% cottonseed oil

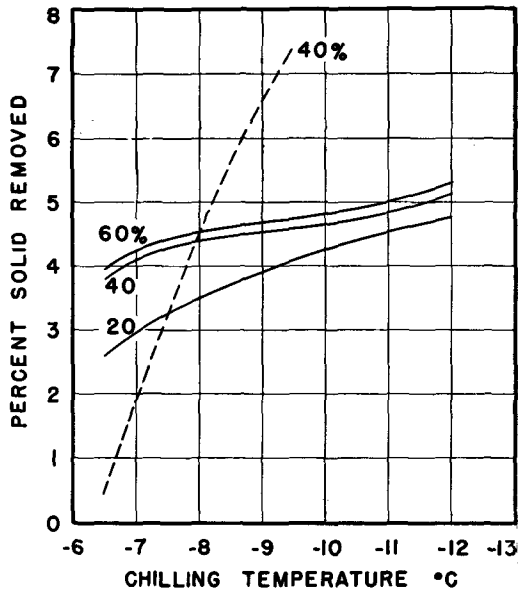


FIG. 2. Percentage of solid removed at various chilling temperatures at constant oil-solvent ratios: ————, peanut oil; — — — —, cottonseed oil (3-hour holding time).

in the same solvent (2) is included as a broken line to show the marked difference in behavior.

*Effect of Holding-Time and Agitation.* Determinations were made using concentrations of 40% oil by weight in the 85-15 acetone-hexane mixture, a chilling temperature of −10°C., and holding-times ranging from 0.5 hour to 24 hours. Duplicate tests were made for each holding-time, one with and the other without agitation. The agitation was accomplished by gently swirling the sample every 10 minutes during the chilling period. As can be seen from the data in Table I, a holding-time longer than 30 minutes is unnecessary. Nor does agitation have any effect at any of the holding-times. This is again in direct contrast to the behavior observed for cottonseed oil (2), which shows a definite increase in the percentage of solid removed with agitation and with increased holding-time up to 24 hours or more in this solvent.

TABLE I

Effect of Holding-Time and Agitation Upon Amount of Solid Removed 40% Peanut Oil in 85-15 Acetone-Hexane Mixture

| Holding-time | Solid removed | |
|---|---|---|
| | Unagitated | Agitated |
| *Hrs.* | % | % |
| 0.5 | 4.7 | 4.8 |
| 1.0 | 4.9 | 4.8 |
| 1.5 | 4.4 | 4.6 |
| 2.0 | 4.9 | 5.2 |
| 3.0 | 5.1 | 5.0 |
| 24.0 | 4.8 | .... |

*Degree of Winterization.* Figure 3 shows the degree of winterization attained as the amount of solid removed is increased. It is apparent that approximately 3.5% of solid must be removed from this peanut oil to produce a winterized oil having a cold test of 15 hours. Removal of another 0.6% of solid extends the cold test to 72 hours.

*Effect of Oil-Solvent Ratio and Temperature on Settling.* Using the experimental procedure previously described (3), the relative settling capacities of the solid separating were determined for the same chilling-temperature and oil-solvent ranges as were used for the winterization experiments. Figure 4

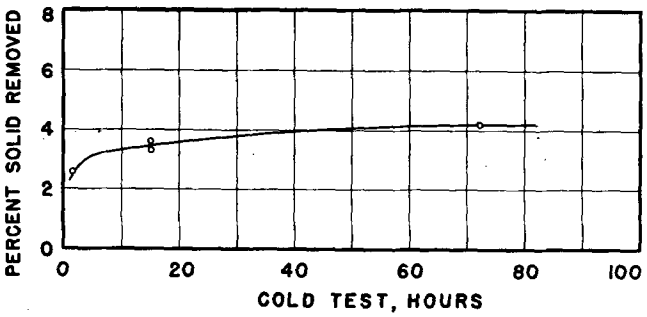


FIG. 3. Cold test after removal of various percentages of solid from peanut oil.

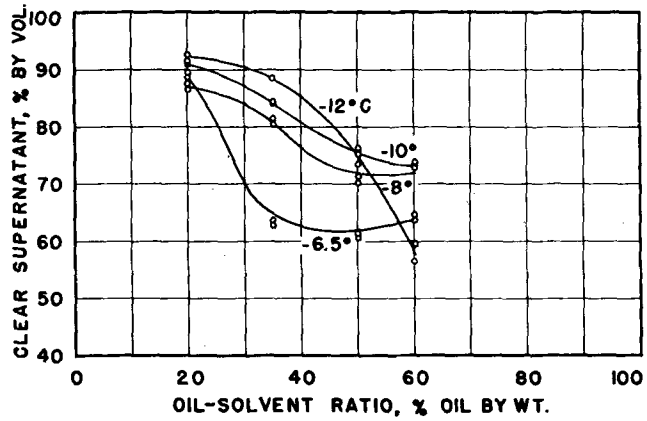


FIG. 4. Percentage by volume of clear supernatant layer after centrifuging peanut oil-solvent mixtures at 2100 × gravity (3-hour holding-time).

summarizes the data obtained for a 3-hour holding-time showing the percentage by volume of clear supernatant liquid after centrifuging at a speed corresponding to 2100 times gravity. For oil concentrations below 50% the percentage of clear supernatant liquid increases as the chilling temperature is lowered. The —6.5°C. curve falls off very rapidly as the oil concentration increases from 20 to 35%. The general shape and relative position of these curves were confirmed by the settling data obtained coincidentally in the various winterization experiments, in which a lower speed and large round-bottom centrifuge bottles were used. At oil concentrations above 50%, the

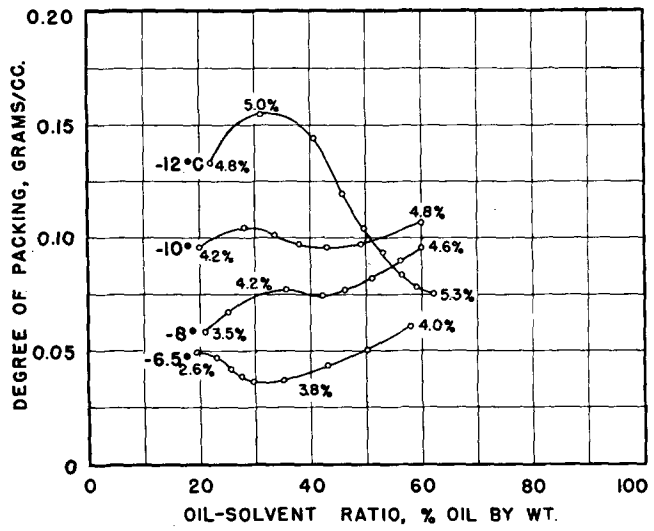


FIG. 5. Degree of packing of the solid for various chilling temperatures as influenced by the peanut oil-solvent ratio and the percentage of solid removed (3-hour holding-time).

—6.5° and —8°C. curves rise slightly and the —12°C. curve continues to fall consistently, crossing all of the other curves. The reason for this behavior becomes clear when consideration is given to the variation in the quantity of solid separating under the different conditions represented by the curves as discussed later.

Analysis of the data represented in Figures 1 and 4 indicates that the first portion of solid which separates does not settle as well as when large proportions are involved. This is demonstrated by Figure 5, which shows the "degree of packing" as influenced by the oil-solvent ratios at various temperatures, the degree of packing being defined as the ratio between the weight in grams of solids removed and the volume in cc. it occupies at the bottom of the chilled solution after centrifuging. The numbers along these curves show the percentage of the original oil separated at the various temperatures and concentrations. For a given percentage of solid removed the degree of packing would be expected to be greater in the 20% oil concentrations than in the 60% mixtures, which have a much higher density and viscosity. Keeping this fact in mind, it is apparent from Figure 5 that the degree of packing increases about threefold to a maximum as the percentage of solid removed (percentage of original oil) increases from 2.6% to 5.0%. The rapid drop in the —12°C. curve as the oil-solvent ratio increases from 30 to 60% of oil may be due to the fact either that at this temperature the effect of increase in viscosity and density with oil concentration is becoming more dominant or that a different type of crystal which settles less readily is making its appearance.

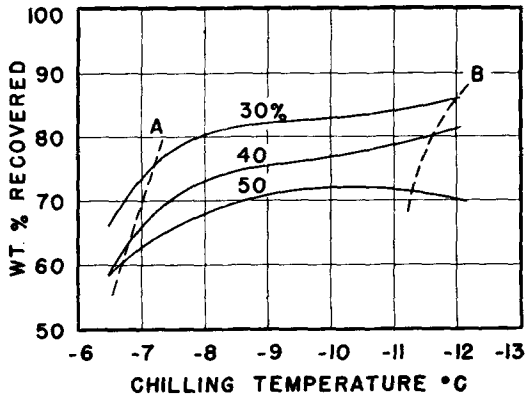


FIG. 6. Weight percentage of winterized oil recoverable from clear supernatant of 30, 40, and 50% peanut oil solutions centrifuged at 2100 × gravity after chilling for 3 hours at various temperatures. Curves A and B show where 4% and 5%, respectively, of solid separates.

Figure 6, obtained by calculation from Figures 1 and 4, shows the weight percentage of the original oil recoverable from the clear supernatant liquid for three of the original oil concentrations at various chilling temperatures. The dotted lines *A* and *B* show where 4% and 5%, respectively, of solid would be separating, 4% being slightly more than the amount necessary to produce a well-winterized oil from this particular peanut oil. These curves show that lower temperatures would give larger yields of winterized oil, assuming that simple centrifugation without washing were used to separate the clear supernatant from the solid layer. For example, using a 40-60 oil-solvent ratio, a yield of only 66% of the original oil could be

realized with a chilling temperature of —7°C., but at —12°C. the yield would be 81%, even though an additional 1% of solid would have been removed from the oil.

*Effect of Other Hydrocarbons in Admixture with Acetone.* In order to determine whether other hydrocarbons would have the same effect as hexane in admixture with acetone, winterization experiments were conducted on approximately 30% oil solutions in a number of such solvent mixtures. The results are given in Table II. From the values of the percentage of solid removed it is apparent that a well winterized oil was obtained in each instance. In all cases, the presence of the hydrocarbon was effective in preventing the formation of the two liquid layers. That cyclohexane is not quite as effective as hexane in lowering the temperature at which two liquid phases appear is shown by the fact that a 30% solution of the oil in an 85-15 acetone-cyclohexane mixture showed a second liquid phase at —12°C. The result for acetone, which had to be obtained at 10% oil concentration to avoid separation into two liquid layers, confirmed previously published data for a peanut oil of slightly lower iodine value (3).

TABLE II

Effect of Various Hydrocarbons in Admixture with Acetone on Amount of Solid Removed from Peanut Oil (3-Hour Holding-Time)

| Solvent mixture | Hydrocarbon | Temperature | Original oil conc. | Solid removed |
|---|---|---|---|---|
| | *Wt.%* | *°C.* | *%* | *%* |
| Acetone | 0 | —6.5 | 10 | 7.0 |
| Acetone-pentane | 13 | —10 | 30 | 5.1 |
| Acetone-isooctane | 20 | —10 | 32 | 4.5 |
| Acetone-hexane | 15 | —10 | 30 | 4.5 |
| Acetone-hexane | 15 | —12 | 30 | 5.0 |
| Acetone-cyclohexane | 20 | —12 | 30 | 5.1 |

Settling experiments were also conducted on various peanut oil-solvent mixtures to which 0.1% of soybean lecithin or various small percentages of cottonseed monoglycerides were added. In no case was an improvement in the settling qualities of the peanut oil solid observed.

TABLE III

Effect of Other Solvents and Various Hydrocarbons in Admixture with Acetone on Settling of Peanut Oil at 2100 × Gravity (3-Hour Holding-Time)

| Solvent wt. ratio | Temperature | Original oil conc. | Vol. clear supernatant |
|---|---|---|---|
| | *°C.* | *%* | *%* |
| Acetone/hexane (85/15) | —10 | 45 | 78 |
| Acetone/hexane (80/20) | —10 | 45 | 75 |
| Acetone/pentane (80/20) | —10 | 45 | 84 |
| Acetone/cyclohexane (80/20) | —10 | 45 | 77 |
| Acetone/benzene (80/20) | —10 | 45 | 57 |
| Acetone/isooctane (80/20) | —10 | 45 | 85 |

Table III shows the comparative effect of hexane and other hydrocarbons in admixture with acetone on the settling in 45% peanut oil solutions at —10°C. with a 3-hour holding-time. The results are not conclusive because of the fact that the percentage of solid removed may not be the same in all cases. However when the data of Table II are considered, there is an indication that acetone-pentane solutions may have advantages over acetone-hexane.

## Discussion

Peanut oil cannot be winterized by the method commonly used for cottonseed oil. The chilled oil has the characteristics of a gel so that the crystals which form do not settle and cannot be removed by filtering or centrifuging (1). Difficulties in filtration are also encountered in the solvent winterization of peanut oil from commercial hexane (1). Much better crystals are formed when acetone is used as the winterization solvent, but at the temperatures and oil-solvent ratios necessary for a practical winterization process two liquid layers are present (3), a fact which interferes with the efficient removal of the solid from the liquid.

Addition of a hydrocarbon, such as hexane, to the acetone used as winterization solvent lowers the chilling temperature required for adequate winterization of peanut oil. This is apparent from the results in Table II. However the presence of the hydrocarbon lowers to a much greater extent the temperature at which two liquid layers form. Thus when a refined peanut oil is winterized in a solvent consisting of 85 parts by weight of acetone and 15 of hexane, good crystals are formed in sufficient quantity without encountering two-liquid-phase formation at the required temperatures.

In many respects peanut oil has a much more favorable behavior than cottonseed oil during solvent winterization in this solvent mixture. The variation in the percentage of solid removed, as either the chilling temperature or the oil-solvent ratio varies, is extremely small. This is very advantageous from a practical point of view. In the first place, a much less rigid regulation of temperature is necessary in the separation and filtration of the crystals. Furthermore the redissolving of the crystals during washing may be less of a problem; even if pure solvent cannot be used for washing, it seems probable that a relatively dilute solution of winterized peanut oil might be used satisfactorily. A winterization temperature 5°C. or more below that required for adequate winterization and the use of a wash liquid still lower in temperature would not be expected to be impractical nor to affect the yield adversely. It has also been shown that when solutions of peanut oil in this acetone-hexane mixture are chilled to a given temperature, the separation of the solid reaches completion in less than 30 minutes as compared to well over 3 hours for cottonseed oil solutions. This would be an important factor in a continuous solvent-winterization process.

## Summary

Systematic phase relation data have been obtained pertaining to the solvent-winterization behavior of a refined peanut oil in a mixed solvent consisting of 85% by weight of acetone and 15% of hexane. Graphs have been constructed to show the effect of oil-solvent ratio, chilling temperature, holding-time, and agitation on the percentage of solid removed, on the degree of winterization, and on the settling qualities of the solid separating.

The results show that it is possible on a laboratory scale to solvent-winterize refined peanut oil in this solvent mixture. The data afford a preliminary basis for pilot plant design, selection of optimum conditions, and recognition of limitations for pilot plant research on the solvent winterization of peanut oil.

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