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 unfractonated 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 Samples were withdrawn at intervals and total oxygen introduced was determined by chemical analysis for peroxide, carbonyl, hydroxyl, oxirane, ester, and carboxyl oxygen.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.

**REFERENCES**


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**Phase Relations Pertaining to the Solvent Winterization of Peanut Oil in Acetone-Hexane Mixtures**

RICHARD E. BOUCHER and EVALD L. SKAU, Southern Regional Research Laboratory,
New Orleans, Louisiana

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. The isooctane was "99 mole % pure," and the cyclohexane was an Eastman Kodak Company product.

1Presented at the 55th Fall Meeting of the American Oil Chemists' Society, Chicago, Ill., Oct. 8-10, 1951.
2One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

2The 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 decaanted 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 $-6.5^\circ$, $-8^\circ$, $-10^\circ$, and $-12^\circ$. 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 $-8^\circ$ curve for that oil (2), shown in Figure 1 as a broken line. Thus, for a 50% concentration, 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 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 $-10^\circ$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 1, 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.

![Figure 1](image1)

![Figure 2](image2)

**TABLE 1**

<table>
<thead>
<tr>
<th>Holding time</th>
<th>Solid removed</th>
<th>Unagitated</th>
<th>Agitated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hrs.</td>
<td>%</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>4.7</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>4.9</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>4.4</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>5.1</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>24.0</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 Settlement. 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