

Phase Relations in the Solvent Winterization of Cottonseed Oil in 85-15 Acetone-Hexane Mixture at Reduced Holding-Times

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PREVIOUSLY published phase relation data on the solvent winterization of cottonseed oil in an 85-15 acetone-hexane mixture showed that this mixed solvent has definite advantages over either acetone or hexane alone (1). A 3-hour holding-time was used in obtaining the data because, although the separation of solid was not complete in that time, three hours was considered to be the longest holding-time practicable for a continuous process. It is apparent that the shorter the holding-time which can be tolerated, the greater will be the capacity of the chilling units, generally votators,² in a commercial solvent winterization process. Shorter holding-times would afford the additional advantage of reducing the refrigeration costs since the miscella would be under refrigeration for a shorter period. It was the purpose of this investigation therefore to determine whether and under what conditions it would be possible to use holding-times shorter than three hours in the solvent winterization of cottonseed oil in 85-15 acetone-hexane mixture.

Materials. The cottonseed oil used was a commercial refined oil having the following analysis: iodine value (Wijs), 110.0; free fatty acids as oleic, 0.44%; peroxide value, 16.9 millimoles per kg.; and moisture and volatiles, 0.12%. The commercial hexane was Skellysolve B² and the acetone a commercial C.P. grade containing 0.4% of moisture as determined by a special Karl Fischer reagent for ketones (2).

Winterization Procedure. Laboratory bench-scale experiments were performed by the same procedure as previously described (1). 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. They were then centrifuged at the same temperature for 10 minutes. The clear supernatant liquid was then quickly decanted into a tared flask and the residual solid fraction weighed. From the weights and oil contents of the supernatant and solid fractions the total amount of solid which had separated during the chilling could be calculated. The "percentage of solid removed" is reported as the percentage of the total oil present in the original solution.

Effect of Holding-Time on Percent Solid Removed. Winterization experiments were performed with holding-times ranging from 0.5 to 3.0 hours on oil concentrations of 30% and 40% by weight, using chilling temperatures of -12° , -13° , and -14° C. From the graphical representation of these data, Figure 1, it is apparent that for each concentration and temperature the amount of solid separating in the first 30 minutes was comparatively small, that it increased rapidly up to the first hour, and then increased relatively slowly in the next two hours. The curve is still rising at the end of three hours, showing that still more solid will

separate for longer holding-times. This confirms the fact previously reported (1) that the percentage of solid separating after 24 hours of chilling is slightly greater than that after three hours. For the family of curves for the 30% oil concentration, the percentage of solid separating in one hour was less than in three hours by about 0.8%, 0.9%, and 1.7% at -14° , -13° , and -12° C., respectively. It would thus be impossible to remove the same amount of solid with a shorter holding-time at a given chilling temperature.

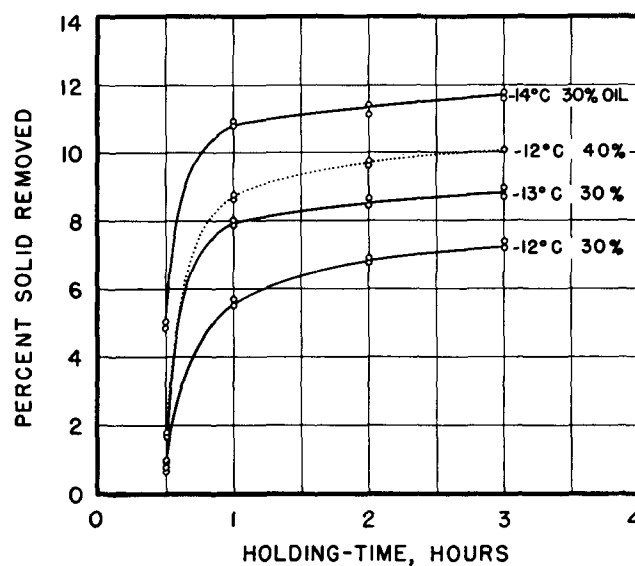


FIG. 1. Relation between holding-time and percentage of solid removed at various chilling temperatures and oil-solvent ratios.

Figure 1 demonstrates however that the same amount can be removed in a shorter period by either a) lowering the chilling temperature or b) increasing the oil concentration. For example, 7.3% of solid is removed from a 30% solution at -12° C. with a holding-time of three hours. At -13° C. this amount of solid would separate from a solution of the same concentration in about 45 minutes and at -14° C. in about 33 minutes. Similarly, using a 40% oil concentration and a chilling temperature of -12° C., this same percentage of solid separates in slightly less than 45 minutes. It would be predicted on the basis of these curves however that it would not be practicable in a commercial process to use a holding-time of less than about one hour at any of these concentrations and chilling temperatures. This follows from the shape of the curves, which shows that solid is still separating very rapidly at the end of shorter periods; that is, a slight variation in the temperature, concentration, or the time, would cause considerable variation in the percentage of solid removed. To be commercially practical the chilling time used should be such that the curve will already have flattened out so that the rate of additional crystallization is comparatively low.

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

Though these curves indicate a minimum of about one hour for a practical holding-time, it seems quite probable from other available information (1, 3) that still shorter chilling periods can be used when the miscella is agitated during the chilling period. In the present experiments the miscella was chilled from room temperature by setting the centrifuge bottle in a bath at the desired temperature and was not stirred. It has been shown (1, 3) that crystallization proceeds much more rapidly when the solutions are even gently agitated every 10 minutes. It can thus be expected that with the relatively violent agitation in industrial chilling units the curves corresponding to those in Figure 1 would flatten out much sooner and that therefore a chilling period considerably below one hour would be feasible under those conditions.

Cold Tests. Cold tests were obtained by a modification (3) of the A.O.C.S. Official Method Cc 11-42 Cold Test. Winterized oils were obtained in all the above experiments in which a holding-time of one hour or longer was used. There was very good agreement between the cold tests obtained and those predicted for an oil of this particular iodine value (see Ref. 3, Fig. 10). If 5.6% of solid is removed from an oil having an iodine value of 110, like that of the present oil, the winterized oil would be expected to fail the cold test between 6 and 20 hours. The actual failure found when this amount of solid was removed from a 30% oil concentration at -12°C . with a 1-hour holding-time, was between 8 and 15 hours. A 2-hour holding-time at the same concentration and temperature resulted in the removal of 6.8% solid and a cold-test failure somewhere between 24 and 40 hours. The predicted cold test would have been just below 20 hours. All samples that had more than 7.0% solid removed during the winterization experiments passed more than a 40-hour cold test.

Settling Qualities of the Solid Separating. No special settling tests in graduated conical centrifuge tubes

were performed. Measurements of the settling were however made as before (1) on each sample after centrifuging in the 250-ml. centrifuge bottles. The results indicated that the reduction in holding-time did not have an appreciable effect upon the settling characteristics of the solid.

Summary

The purpose of this investigation was to determine whether and under what conditions it would be practicable to use holding-times of less than three hours in the solvent winterization of cottonseed oil in 85-15 acetone-hexane mixture. Since the output of the chilling unit varies inversely as the holding-time required, it is advantageous to use the shortest feasible holding-time. Systematic winterization data were obtained on a laboratory scale for different oil-solvent ratios and temperatures using the technique previously described.

The results indicate that, under the static chilling conditions used in these experiments, the holding-time can be reduced from three hours to 1 hour by using either a higher oil concentration, a lower chilling temperature, or both. However, on the basis of previously reported data it is known that with agitation during chilling, such as would be encountered in commercial continuous chilling units, the rate of crystal formation would be further increased. Under practical conditions therefore the adjustment of temperature and concentrations should make it feasible to use holding-times even shorter than one hour with a corresponding increase in the capacity of the chilling units.

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Influence of Alkali Concentration and Other Factors on the Conjugation of Natural Polyunsaturated Acids as Determined by Ultraviolet Absorption Measurements¹

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ULTRAVIOLET spectrophotometric analysis is the most important method employed today for determination of the polyunsaturated constituents of fats and oils. Since publication in 1943 of a spectrophotometric method for determination of linoleic and linolenic acids in fats and oils (12), the method has been subjected to numerous changes or to suggested changes by various investigators. The method has been extended to include arachidonic acid (2) and modified to increase the transparency of the medium (14, 4). Efforts to improve the sensitivity

and accuracy of the method by including certain correction factors (4, 5, 17) or by variations of the conditions of isomerization (1, 3, 9, 10) have been described. Recently this laboratory has published new and more accurate constants for use in the spectrophotometric analyses of the more common natural fats and oils (6). These new constants were determined on acids isolated by physical means in their natural geometrical configuration whereas the earlier constants were determined on chemically prepared bromination-debromination acids. The latter acids contain substantial proportions of geometrical isomers other than the natural all-cis type (11). Geometrical isomers vary in their rates of conjugation during alkali treatment, resulting in significant dif-

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