experience indicates that high-quality soybean oil can be produced only when the many individual factors are controlled, each exhibiting small effects by themselves but in summation having an appreciable effect on quality and stability of the oil.

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Solvent Winterization of Partially Hydrogenated Soybean Oils[1]

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Abstract

Among the important advantages of solvent as compared with conventional winterization of soybean oil are the speed of operation and increased yields up to 25%. Easier and faster filtration results with the solvent system despite the high yields of solids when low iodine value (IV) oils are winterized at low temperatures. Hydrogenated stocks with IV as low as 90 can be winterized easily at temperatures of −16C. The time of winterization can be reduced from several days to a few hours. With all the variations possible in IV, temperature, and solvent selectivity, liquid soybean oil can be produced with specified characteristics and with a minimum linolenate content. Acetone was the best solvent tested for winterization.

Introduction

PARTIALLY HYDROGENATED SOYBEAN oils contain high melting constituents that must be removed to obtain clear, stable salad oils. It has been reported that partially hydrogenated soybean oil can be winterized with considerable success in the same manner as cottonseed oil (6). Some of the problems in the winterization process are low yields of liquid oils, long holding times required for crystallization, and difficulty of filtration. These problems become acute when the fat has been hydrogenated to low levels (IV. 90). Solvents lower the viscosity, and a lower cooling temperature allows formation of hard crystals that are easily filtered and washed. Solvent winterizations have been reported for cottonseed oil (2,4,11) and other edible fatty materials (1,8,15), but for soybean oil most of the fractionations recorded in the literature were done to improve drying oil properties (3,7,9,10,16). The results of extensive solvent winterization of partially hydrogenated soybean oils are reported here.

Materials and Methods

Soybean Oil. Commercially refined and bleached soybean oils (IV. 128) were used in this study.

Catalysts. Two nickel catalysts widely employed by industry for the selective hydrogenation of soybean oil were used. Catalyst A contained 24.4% nickel dispersed in hydrogenated cottonseed oil flakes. Catalyst B contained 65% nickel on kieselguhr.

Hydrogenation. Soybean oil was hydrogenated under selective conditions in a 3-gal stainless-steel convertor at 170C with a hydrogen pressure of 5 lb (6).

Winterization. Conventional and solvent winterization techniques were compared. For the conventional method hydrogenated fats were cooled slowly in Dewar flasks for a minimum of 3 days in a +6C constant temperature room then filtered under vacuum. Solvent winterization was conducted at temperatures ranging from −16C to +6C. The solutions were cooled rapidly and left for a minimum of $3\frac{1}{2}$ hr then filtered under vacuum. The filter cakes were washed with enough solvent at the proper temperature to cover the cakes, and washings were combined with the filtrates. Each winterization fraction was stripped of solvent on rotating vacuum evaporators.

Analysis. Fatty acid content of each fraction was determined as methyl esters by gas-liquid chromatography on a $\frac{1}{4}$ in. × 3 ft aluminum column containing 25% diethylene glycol succinate on Chromosorb W (17), with a flame ionization detector. Percent isolated *trans* was determined by infrared spectroscopy and calculated as methyl elaidate. The IV of the frac-

TABLE I

Hydrogenated-Winterized Soybean Oil Solvent Concentration

Fractions obtained at 6C	Percent acetone	Yield, %	IV.	Percent *trans*
Hydrogenated SBO	—	—	87.2	31.0
Hydrogenated-winterized SBO				
Liquid	10	60.6	95.6	29.8
Solid	10	39.4	74.8	35.3
Liquid	25	73.4	93.7	29.8
Solid	25	26.6	71.8	34.0
Liquid	80	85.2	93.1	27.2
Solid	80	14.8	56.4	34.7

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[1] Presented at AOCS meeting in New Orleans, La., 1964.

[2] A laboratory of the No. Utiliz. Res. and Dev. Div., ARS, USDA.

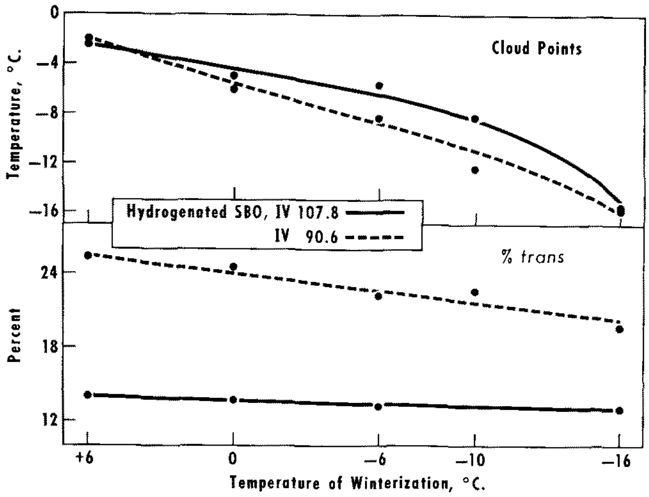

FIG. 1. Relationship of yield and iodine value to temperatures of solvent winterization for liquid fractions obtained from hydrogenated soybean oils.

tions was calculated from the percent unsaturated fatty acids and their respective molecular weights. Cloud point and cold test determinations were made by AOCS Official Methods, Cc6–25 and Cd–11–53 (14), respectively.

Organoleptic Evaluations. Flavor scores for deodorized oils were obtained by taste panel evaluation as described previously (12,13).

Results and Discussion

Various solvents were investigated for yield and selectivity of unsaturated glycerides at several winterization temperatures. Pure acetonitrile was immiscible with the fat at the boiling point of the solvent. However, at 27C, 85% yield of liquid oil was obtained from a 10% fat solution dissolved in a 3 to 1 acetone-acetonitrile solvent, but the fractionation was not very selective, particularly when compared with acetone at 0C and at comparable yields of liquid and solid fractions. Petroleum ether, mixtures with acetone, and mixtures of 5, 10, and 20% methanol in petroleum ether fractionated glyceride oils at temperatures of +6C or below. Pure acetone, however, gave equal or better separation with less cooling. Acetone was employed in these studies because of higher yields of liquid oils, better selectivity, ease of solvent removal, and its economical potential as a commercial solvent for large-scale operation.

Hydrogenated Oil from Hard Fat Suspended Catalyst. Solvent-to-fat ratio was compared to yield, IV, selectivity, and percent *trans* acids. Partially hydrogenated soybean oil, IV 87.2, was dissolved in acetone in solvent-to-fat ratios of 9:1, 3:1, and 1:4 and then winterized at 6C (Table I). Yield of liquid oil increases with the amount of acetone because there was less opportunity for the oil to be occluded in the crystals at higher solvent concentrations. The IV, percent isolated *trans*, and fatty acid composition were essentially unaffected by concentration. In the remaining winterization studies therefore, 25% fat in acetone was used.

Five temperatures from +6C to −16C were used to fractionate two hydrogenated soybean oils (IV 107.8 and 90.6) into higher IV liquid oils and lower IV solid fractions. Figure 1 shows the relationship of yield and IV of liquid oils to temperature of winterization. Yields decreased and IV increased nonlinearly with decreasing temperatures of winterization. Liquid fraction yields obtained from the lowest IV hydrogenated oil were lower than those from the highest IV oil.

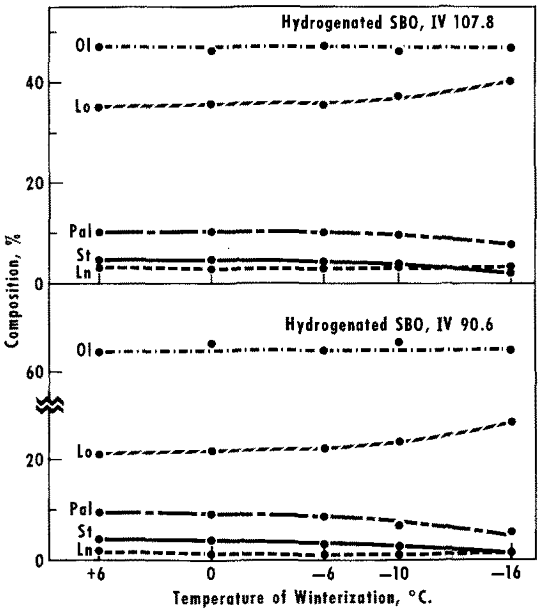

FIG. 2. Relationship of fatty acid composition to temperatures of solvent winterization for the liquid fractions from hydrogenated soybean oils.

In Figure 2 fatty acid composition of liquid oils, obtained by winterization of hydrogenated soybean oils, IV 107.8 and 96.6, was plotted against winterization temperature. Above −6C the composition remained relatively constant. Below this temperature linoleate increased, palmitate and stearate decreased, and oleate and linolenate remained constant. The greatest difference between fatty acid composition of the original hydrogenated oil and that in winterized liquid oils was obtained at −16C. Saturated fatty acids in the −16C liquid oils, obtained from hydrogenated oil with an IV of 107.8, decreased 40% from the original oil. Linoleate content increased 20%. A

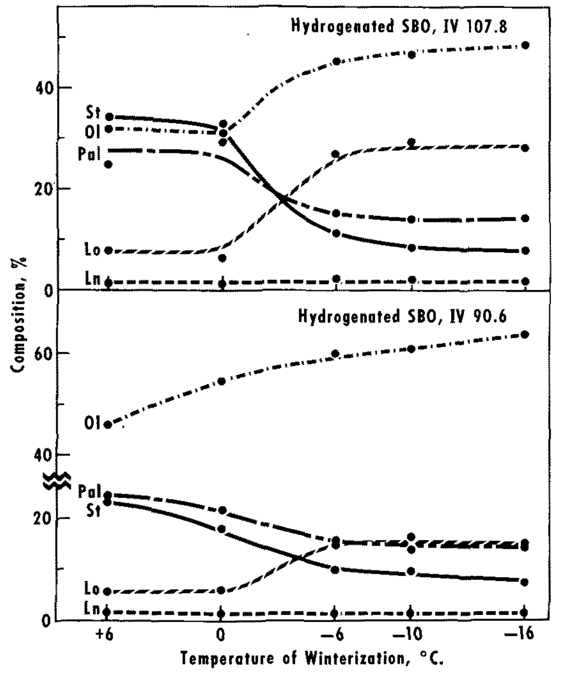

FIG. 3. Relationship of fatty acid composition to temperatures of solvent winterization for the solid fractions from hydrogenated soybean oils.

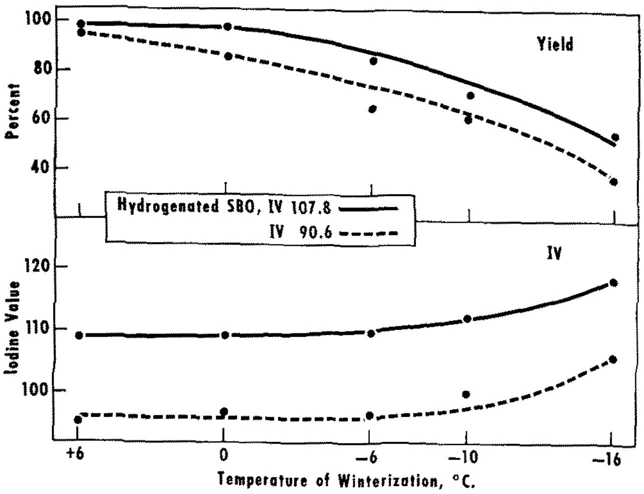

FIG. 4. Relationship of cloud points and percent isolated *trans* to temperatures of solvent winterization for the liquid fractions from hydrogenated soybean oils.

greater compositional difference was exhibited by the liquid oils obtained from the more highly hydrogenated fat. Saturates decreased 68% while linoleate increased 35% in the liquid fractions obtained from a 90.6 IV oil.

Figure 3 shows the fatty acid composition of the solid fractions, which differ a great deal from the composition of liquid fractions. When yield of solids was low, at +6C and 0C, the saturate content of the solid fraction was high and linoleate was only 7%. An increase in linoleate and a decrease in saturates occurred between winterization temperatures of 0C and −6C. Below −6C, composition was quite uniform although yield of solids continued to increase. Compositional changes of the solid fractions are markedly less between 0C and −6C for the more heavily hydrogenated oils.

For consumer acceptance the temperature at which a salad oil becomes cloudy is considered quite important. Hydrogenation raises cloud points to unacceptable levels, but they can be reduced by winterizing the oil. Cloud points of liquid oils obtained by solvent fractionation were within a few degrees of the temperatures of crystallization (Fig. 4).

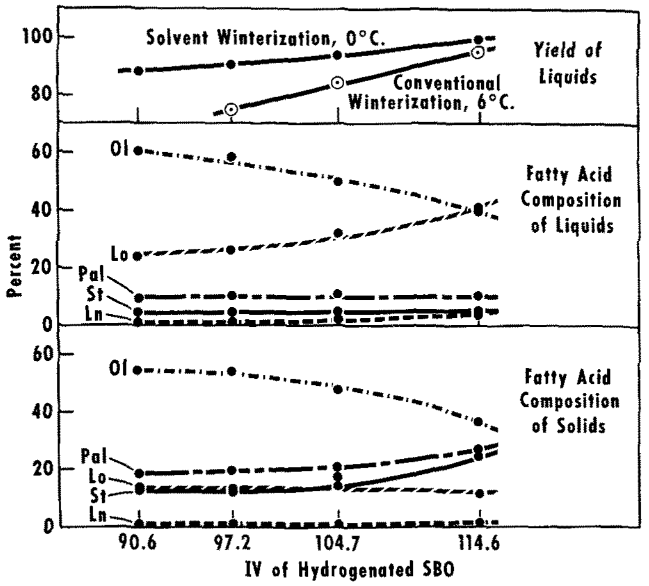

FIG. 5. Relationship of yield and fatty acid composition to degree of hydrogenation for liquid and solid fractions obtained by solvent winterizations conducted at 0C.

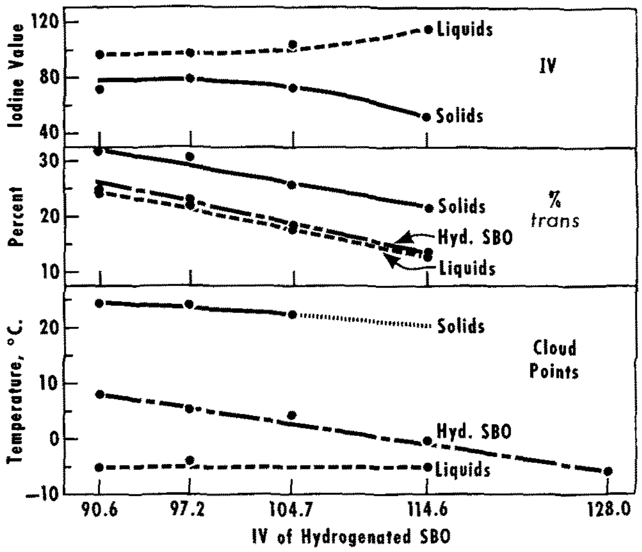

FIG. 6. Relationship of iodine value, percent isolated *trans*, and cloud point to degree of hydrogenation for liquid and solid fractions obtained by solvent winterizations conducted at 0C.

Formation of *trans* isomers is usually a reason for increased cloud points in hydrogenated oils. Solvent winterization did decrease *trans* acids in the liquid oils (Fig. 4) but only slightly. The *trans* value of the liquid oil fractionated at −16C was 17% lower than the *trans* in the original hydrogenated soybean oil, IV 107.8. From the lower IV oil *trans* acid values were 23% less in the liquid fraction obtained at −16C.

The AOCS cold test (14) was applied to liquid fractions from winterizations of hydrogenated soybean oils, IV 107.8 and 90.6. Results indicate that the hydrogenated oils must be winterized at −6C or below to produce a clear liquid oil stable to the conditions of the test.

Hydrogenated Oils from Ni-Kieselguhr Catalyst. Soybean oil (IV 128) was hydrogenated to four IV levels (90.6 to 114.6) by a 65% Ni-kieselguhr catalyst. Winterization was accomplished by solvent and conventional methods at 0C and 6C, respectively. Yields of liquid oil from both crystallization methods were plotted against IV of the hydrogenated oil (Fig. 5). Solvent winterization produced consistently higher yields, and as IV of the hydrogenated oil decreased, the difference between yields from the two methods became larger. Liquid oils from conventional and solvent fractionations had similar fatty acid compositions; however, the solids from the conventional method were much lower in saturates than the comparable solids from the solvent method. This difference indicates a considerable amount of occluded oil in the conventionally winterized solids.

Figure 5 also shows the change in fatty acid composition of liquid oils. Since their analysis is similar to that of hydrogenated soybean oils, plots of the fatty

TABLE II

Holding Time for Hydrogenated-Winterized Soybean Oil

IV of hydrogenated SBO	Carrier for Ni catalyst	Yield of liquid fraction, %						
		OC Winterized, hr			−16C Winterized, hr			
		3½	24	75	3½	6	12	75 or longer
107.8	Hardened CSO	98.0	97.5	96.7	51.8	—	—	55.5
90.6	Hardened CSO	86.1	88.0	87.1	38.4	—	—	37.7
114.6	Kieselguhr	99.8	99.0	99.0	92.5	73.7	51.9	52.2
104.7	Kieselguhr	99.5	94.2	—	67.8	—	—	35.4
97.2	Kieselguhr	91.0	94.5	93.3	53.3	35.4	25.7	25.9

TABLE III

Organoleptic and Oxidative Stability Evaluation of Hydrogenated-Winterized Soybean Oil

Description	Laboratory processed [a]						Commercial	
	Hydrogenated-winterized SBO						SBO	HWSBO [c]
Iodine value	88.8	95.5	100.1	104.0	109.0	127.0	129.0	112.0
Initial flavor	7.8	6.8	7.8	7.7	8.4	7.6	7.8	8.4
Aged 60C, 4 days	6.3	6.4	6.2	5.6	6.2	6.6	5.1	6.9
Aged 60C, 6 days	5.9	5.6	—	—	—	5.4	5.1	6.4
Light exposure, 2 hr	6.4	5.8	—	—	—	6.7	5.6	7.2
Heat test at 200C	4.6	3.3	—	—	—	2.7	2.4	3.7
AOM peroxide value at 8 hr	2.0	2.0	1.2	1.5	3.4	8.2	17.4	0.7
Predominating Flavor Descriptions Samples aged 4 days								
Buttery	A[b]	A	A	A	A	D	D	A
Beany		D	D			A		B
Grassy	D	C		C	C	B	B	
Rancid	B		B	B	B	C	A	
Painty							C	
Tallowy	C	B	C	D	D			

[a] Treated with 0.01% citric acid.

[b] A > B > C > D order of predominance.

[c] Contains butylated hydroxytoluene, butylated hydroxyansiole and methyl silicone as preservatives.

acid composition look like typical selective hydrogenation curves. Linoleate and linolenate decreased, oleate increased, and saturates remained constant with an increase in the degree of hydrogenation. Effects of winterization are more evident from the compositional changes of the solid fractions. Percentages of linolenate and linoleate are relatively constant regardless of the degree of hydrogenation. Saturates decreased between hydrogenated IV 114.6 and 104.7 but became constant at an IV below 104.7.

The IV of the liquid fractions decreased nonlinearly with degree of hydrogenation (Fig. 6). Differences in IV between the liquid and solid fractions, when winterized at 0C, remained relatively constant at about 20 units for all oils hydrogenated to IV 105 or lower. This difference is expected to hold until the degree of hydrogenation causes an increase in the stearic acid content. The *trans* values were reduced slightly by winterization. Cloud points of the liquid oils, regardless of the degree of hydrogenation, are approximately 5C below the winterization temperature. Cloud points of the hydrogenated stocks show an inverse linear relationship with IV. The true cloud point of stocks hydrogenated with a Ni-kieselguhr catalyst and the solid fractions can be determined because the catalyst does not contain hardened cottonseed oil.

In nonagitated solutions, holding times for complete crystallization are longer than 3½ hr for oils hydrogenated with Ni-kieselguhr catalyst because no tristearin is present to act as crystallization nuclei. Twelve hours were required to give maximum fat crystallization. The difference in yields of liquids was insignificant for those oils winterized at 0C for 3½ and 12 hr (Table II). However, when the temperature of winterization was −16C, liquid oil yields at 12 hr or longer were approximately one-half those obtained at 3½ hr. Slow stirring at 80 rpm during solvent winterization at −16C did not reduce the holding time appreciably.

Taste Panel Study. Organoleptic evaluations were made on many of the hydrogenated winterized soybean oils, and initial flavor scores have been equal to, or better than, the control unmodified soybean oils. Oxidative stability as measured by AOM peroxide development on 0.01% citric acid-treated oils was excellent, and because of the low peroxide values obtained, no trend with IV of the oil was observed.

The flavor scores of the aged "laboratory-processed" oils were graded considerably lower than expected because of the tallowy and hydrogenated flavors that developed. Hydrogenation and winterization processing on a laboratory scale expose the oil to many unfavorable conditions where it cannot be protected from air and light. Trace oxidation promotes the development of the typical hydrogenation and tallowy flavors associated with hydrogenated stocks. Although these same flavors have not been particularly objectionable in margarine stocks, their appearance in a normally bland salad oil has focused attention on them because they are more readily observed. The flavor components have not been identified, although they are reported to be saturated carbonyls (5). Since the flavor is general for hydrogenated oils, its source could be the oxidation of the isomeric fatty acids formed during hydrogenation. Commercially prepared hydrogenated winterized oils have shown a high stability and, under comparable aging, less development of the hydrogenated-tallowy flavor than the laboratory-prepared samples. Typical flavor scores and predominant flavors developed upon aging are shown in Table III. Strong buttery flavors are characteristic of hydrogenated winterized oils in contrast to the beany, grassy flavors usually associated with unmodified soybean oils.

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