TABLE 7

Effect of Foreign Material

Sample	% FM	%H_2O	RB Color	Deodorized Oil			
				Flavor		Color	
				Fresh	Aged	Fresh	Aged
1. a. Illini	0.1	12.2	2.7	Fair+	Fair+	0.7	.....
b. Illini	3 (added)	12.0	2.9	Fair+	Fair	0.9	.....
c. Illini	6 (added)	11.5	3.7	Fair	Fair—	1.1	.....
d. Illini	9 (added)	11.2	3.1	Fair—	Fair—	1.3	.....
2. a. W—trashy, poor quality beans	15	12.2	12.9	Fair—	Poor	9.2	11.3
b. W—screened	0	12.7	9.3	Fair—	Fair—	3.3	6.3
3. a. X	11.3	10.0	4.3	Fair	Fair—	0.6	1.8
b. X—screened	0	10.4	3.2	Fair	Fair	0.5	1.2
4. a. Y	2.1	10.6	2.2	Fair	Fair	0.4	1.1
b. Y—screened	0	9.9	2.2	Fair	Fair	0.5	1.0

beans. The results in Table 6 show no significant variation.

Effect of Foreign Matter

A great difference can be expected to exist in the quality of the foreign matter in soybeans. The first test was made by separating the foreign matter from a quantity of soybeans by screening and adding 3, 6, and 9% to the Illini seed beans. The results in Table 7, Part 1, show a marked deterioration in quality with increased foreign material. A second series of tests was made by milling several samples that were high in foreign material and comparing the oil to that from the same beans after the foreign material had been removed by screening. The results show the same general trend of quality improvement by foreign material removal. Considerable quantitative variance in results should be expected in this type of test because of the non-uniformity of the material being removed.

Conclusions

The moisture of soybeans at the time of milling is a most important factor in obtaining good oil quality. It has been known that high moisture would cause soybeans to deteriorate in storage (2), (3), but the great effect of moisture at the time of milling whether on fresh or stored beans has not been published previously as far as is known.

The effect of splits and of damaged beans has not been established in any quantitative measure with the available data.

Foreign material is shown to be damaging to oil quality and a quantitative measure is shown by one test, but the unit effect of such material undoubtedly varies widely with its own characteristics.

In order to improve soybean oil quality, a hydraulic oil mill should dry all beans to the mill to below 12-13% and clean the beans of foreign material.

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Modification of Vegetable Oils

III. Fractional Crystallization of Fatty Acids From Solvents—Separation of the Solid and Liquid Acids of Cottonseed Oil

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VARIOUS investigators, including Brown and coworkers (4, 5, 6), Earle and Milner (8), and DeGray and DeMoise(7), have demonstrated the feasibility of separating saturated and unsaturated fatty acids by fractionally crystallizing mixtures of the acids from solvents at low temperatures. In published work in this field interest has centered on solvent crystallization as an analytical tool or as a method for the preparation of fatty acids of high purity. The object of the work reported here was to determine practicable conditions for carrying out the less exacting separations involved in the preparation of industrially useful products. Attention was given not only to the separation of cottonseed oil fatty acids into solid (saturated) and liquid (unsaturated) fractions, but also to the similar fractionation of the fatty acids of hydrogenated cottonseed oil. In the case of the hydrogenated acids, the solid acids include iso-oleic acids produced during the course of hydrogenation.

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Experimental Procedure

The fatty acids used were obtained from two different lots of raw cottonseed oil and from a single batch of hydrogenated cottonseed oil. The latter was hydrogenated under conditions deliberately chosen to produce a rather high content of iso-oleic acid (3). Analyses of the fatty acids are listed in Table 1.

TABLE 1

Analyses of cottonseed oil fatty acids used in solvent crystallization experiments.

	Unhyd. No. 1	Unhyd. No. 2	Hydrog.
Iodine value	104.7	106.6	69.7
Thiocyanogen value	67.0	67.2	64.3
Composition, per cent:			
Saturated	28.7	28.6	28.5
Normal oleic	26.8	24.9	49.7
Iso-oleic	.....	.....	15.9
Linoleic	44.5	46.5	5.9
Titer, °C.	36.7	.....	36.0

Crystallization of the acids from the unhydrogenated oil was in all cases carried out at a solvent-fatty acid ratio of 4 to 1 by weight. Crystallization of the acids from the hydrogenated oil was conducted at a solvent-fatty acid ratio of 6 to 1. The operations of chilling and filtering were carried out in the combined chilling and filtering apparatus described previously (2). Chilling times varied from about 1.5 to 4 hours, according to the crystallization temperature. A period of one hour was uniformly allowed for crystallization to take place, this period being measured from the time the minimum temperature was reached to the time at which filtration of the batch was started.

The filtrate- and in most cases the precipitate-portions of the fatty acid-solvent mixture were weighed before and after removal of the solvent to determine the amount of fatty acids in each portion and the proportion of the original charge of solvent associated with each of the two fatty acid fractions.

C. P. grades of the different solvents were used, without further purification. All analyses of the samples were made by official methods of the American Oil Chemists' Society. For calculation of the composition of samples from iodine and thiocyanogen values, in terms of saturated, oleic, and linoleic[2] acids, use was made of the empirical equations suggested by the Committee on Analysis of Commercial Fats and Oils of this society (1).

[2]The linoleic acid, so calculated, included, of course, any isomeric octadecadienoic acids produced in the hydrogenated oil during hydrogenation.

Experimental Data

Acetone and Skellysolve B (petroleum naphtha) were selected as typical examples, respectively, of highly polar and nonpolar solvents, and were accordingly used in the most extensive of the various series of experiments. Yield and analytical data on the fractions obtained from these solvents are given in detail in Tables 2 and 3.

At certain temperatures comparative crystallizations were carried out also in methyl ethyl ketone, ethyl acetate, and methyl acetate. With respect to yields and composition of the fractions the results of these experiments were in general within the ranges obtained at comparable temperatures with acetone and petroleum naphtha. The results are, therefore, not given in detail but are simply reported in terms of the yields and analyses of the filtrate fractions in Table 4.

Calculations from the Experimental Data

The yields of fatty acids in the filtrate and the precipitate depended to a large extent upon the degree to which the precipitates were contaminated with entrained liquid consisting of dissolved fatty acids and solvent. It was not feasible, under the experimental conditions, to attempt to eliminate or minimize entrainment by pressing or washing the precipitated fatty acid crystals. However, it was possible, from the relative proportions of solvent found in precipitate and filtrate, to make allowances for entrainment, and thus to calculate the amounts of fatty acids actually crystallizing and remaining uncrystallized in the course of each experiment. The yields of material, as corrected for entrained fatty acids in the precipitate and hereafter referred to as "corrected yields." The yields obtainable in commercial operation of the process would obviously lie somewhere between the "actual" and "corrected" yields. It is believed,

TABLE 2

Fractional crystallization from acetone and Skellysolve B of fatty acids from unhydrogenated cottonseed oil[a]: Actual yields, analysis, and composition of the fractions. (150 g. fatty acids plus 600 g. solvent.)

Solvent	Temp., °F.	Fraction	Yields			Analysis of fraction			Composition of fraction, percentage[b]		
			Fatty acids, g.	Solvent g.	Fatty acids, %	I value	TC value	Titer, °C.	Sat.	Oleic	Linoleic
Acetone	35	Filt.	108.5	530.7	72.3	128.0	81.7	20.8	13.1	32.3	54.6
		Ppt.	.....	.....	.....	37.9	23.5	.....	75.1	7.9	17.0
Acetone	25	Filt.	98.6	512.1	65.8	134.6	86.1	11.5	8.4	34.4	57.2
		Ppt.	.....	.....	.....	42.2	26.5	.....	71.9	9.6	18.5
Acetone	15	Filt.	84.9	453.2	56.6	139.7	89.2	3.8	5.1	35.3	59.6
		Ppt.	.....	.....	.....	50.6	32.2	.....	65.8	12.5	21.7
Acetone	5	Filt.	65.5	357.0	43.7	144.3	91.0	<−2.0	3.3	33.8	62.9
		Ppt.	75.6	199.5	50.4	72.9	46.1	.....	51.0	17.4	31.6
Acetone	−5	Filt.	70.3	389.2	46.9	146.1	92.1	<−2.0	2.1	34.2	63.7
		Ppt.	70.8	171.6	47.2	66.9	42.2	.....	55.2	15.7	29.1
Skellysolve B	35	Filt.	105.8	498.7	70.5	125.0	80.0	22.3	14.8	32.1	53.1
		Ppt.	.....	.....	.....	49.8	31.9	.....	66.1	12.8	21.1
Skellysolve B	25	Filt.	103.3	505.1	68.8	127.6	81.6	18.4	13.1	32.6	54.3
		Ppt.	.....	.....	.....	43.8	27.5	.....	70.8	10.0	19.2
Skellysolve B	15	Filt.	84.9	453.2	56.6	134.3	85.9	12.0	8.6	34.3	57.1
		Ppt.	.....	.....	.....	45.1	28.4	.....	69.8	10.5	19.7
Skellysolve B	5	Filt.	87.3	451.6	58.2	138.8	87.4	5.4	7.2	32.1	60.7
		Ppt.	55.8	113.2	37.4	56.4	35.7	.....	62.1	13.5	24.4
Skellysolve B	−5	Filt.	89.8	477.6	59.8	144.2	91.0	<−2.0	3.3	33.9	62.8
		Ppt.	55.4	94.7	36.9	46.7	29.5	.....	68.7	11.0	20.3

[a]Acids from Lot No. 1 used for crystallizations at 35°, 25°, and 15° F.; acids from Lot No. 2 used for others.
[b]Calculated from iodine and thiocyanogen values.

TABLE 3

Fractional crystallization from acetone and Skellysolve B of fatty acids from hydrogenated cottonseed oil: Actual yields, analysis, and composition of the fractions. (100 g. fatty acids plus 600 g. solvent.)

Solvent	Temp., °F.	Fraction	Yields			Analysis of fraction			Composition of fraction, percentage[a]		
			Fatty acids, g.	Solvent, g.	Fatty acids, %	I value	TC value	Titer, °C.	Sat.	Oleic	Linoleic
Acetone	35	Filt.	71.6	533.1	71.6	86.8	78.4	25.6	13.0	77.6	9.4
		Ppt.	27.5	47.6	27.5	29.4	27.6	.....	69.4	28.6	2.0
Acetone	25	Filt.	57.5	463.9	57.5	91.2	83.1	20.8	7.7	83.3	9.0
		Ppt.	38.7	108.0	38.7	41.3	38.2	.....	57.5	39.1	3.4
Acetone	15	Filt.	49.2	420.4	49.2	95.1	86.5	16.2	3.9	86.5	9.6
		Ppt.	46.3	153.9	46.3	45.9	42.3	.....	52.9	43.1	4.0
Acetone	5	Filt.	54.1	481.9	54.1	98.0	88.6	12.7	1.7	87.8	10.5
		Ppt.	41.1	81.2	41.1	37.2	35.1	.....	60.9	36.9	2.2
Acetone	—5	Filt.	35.8	390.4	35.8	99.0	88.8	1.2	1.5	87.0	11.5
		Ppt.	58.3	174.3	58.3	50.7	48.5	.....	45.9	51.9	2.2
Acetone	−15	Filt.	24.3	283.8	24.3	102.2	90.7	<−2.0	−0.4	87.4	13.0
		Ppt.	67.4	262.4	67.4	58.6	55.4	.....	38.3	58.4	3.4
Skellysolve B	35	Filt.	69.7	467.7	69.7	79.6	72.4	30.1	19.6	72.4	8.0
		Ppt.	26.8	100.8	26.8	50.3	46.2	.....	48.7	46.8	4.5
Skellysolve B	25	Filt.	65.9	494.1	65.9	85.7	77.9	26.4	13.5	77.8	8.7
		Ppt.	30.1	83.1	30.1	40.0	36.9	.....	59.0	37.6	3.4
Skellysolve B	15	Filt.	58.8	470.7	58.8	92.7	83.8	19.6	7.1	83.0	9.9
		Ppt.	37.9	102.6	37.9	39.0	36.0	.....	60.0	36.7	3.3
Skellysolve B	5	Filt.	55.8	478.0	55.8	96.2	86.5	16.1	4.1	85.0	10.9
		Ppt.	41.0	101.8	41.0	37.6	34.7	.....	61.4	35.4	3.2
Skellysolve B	−5	Filt.	47.6	424.1	47.6	97.6	88.7	10.2	1.6	88.5	9.9
		Ppt.	45.9	128.4	48.1	42.7	41.0	.....	54.3	44.0	1.7
Skellysolve B	−15	Filt.	42.4	462.7	42.4	100.5	90.4	3.6	−0.2	88.9	11.3
		Ppt.	52.6	112.7	57.6	44.8	43.5	.....	38.3	58.4	3.3

[a]Calculated from iodine and thiocyanogen values.

however, that they would correspond more closely to the corrected yields, as with properly designed filtering equipment it should be possible to press or wash out most of the liquid entrained in the precipitated crystals.

Recovery of the original charge of fatty acids and solvent in the precipitate and the filtrate was never complete; the loss of material through unavoidable volatilization of solvent and retention of fatty acids on portions of the apparatus amounted generally to 2 to 5 per cent in the case of the fatty acids and 3 to 7 per cent in the case of the solvent. Obviously, most of the loss was from the precipitate-fraction since this fraction had to be scraped by hand from the exposed surfaces of the chiller and filter, whereas the liquid filtrate-fraction drained cleanly into a closed flask. For purposes of calculation, all losses of both fatty acids and solvent were accordingly charged to the precipitate-portion of the fatty acid-solvent mixture. It was assumed that the liquid material entrained in the precipitated acids had the same composition as the filtrate and that the small proportion of unrecovered fatty acids was identical with the portion of fatty acids actually recovered from the precipitate-fraction.

The formulas applied in making the calculations were specifically as follows, all quantities being expressed in terms of 100 grams of fatty acids and the

TABLE 4

Crystallization of cottonseed oil fatty acids from methyl ethyl ketone, ethyl acetate, and methyl acetate: Yields and analyses of the filtrate fatty acids. (Solvent-fatty acid ratio, by weight: 4:1 for unhydrogenated acids; 6:1 for hydrogenated fatty acids.)

Solvent	Fatty acids	Temp., °F.	Yields, %		Analysis		
			Actual	Corrected[a]	I value	TC value	Titer, °C.
Met Et ketone	Unhyd.	35	67.4	83.5	123.9	78.8	24.9
		25	60.9	77.4	129.1	83.0	18.2
		15	54.3	75.5	134.7	86.5	7.9
Et Ac	Unhyd.	35	72.8	79.5	129.8	83.3	17.8
		25	62.2	77.4	134.7	86.2	11.4
		15	58.0	72.4	137.8	87.8	−1.0
Met Ac	Unhyd.	35	62.5	80.5	131.3	84.0	17.5
		25	54.0	77.5	136.8	86.4	10.3
		15	55.3	72.8	139.8	89.9	−0.5
Met Et ketone	Hyd.	35	76.6	86.8	80.3	72.9	29.7
		25	66.3	79.2	86.6	78.8	25.3
		15	55.4	73.1	92.3	84.0	19.2
		5	47.1	69.3	95.4	86.4	15.3
Et Ac	Hyd.	35	68.4	81.0	85.8	78.0	26.2
		25	61.0	77.6	89.9	81.9	22.2
		15	59.6	71.1	94.5	85.8	17.3
		5	48.1	68.7	97.4	87.9	14.1
Met Ac	Hyd.	35	70.6	80.4	86.6	78.8	25.6
		25	57.4	73.6	91.5	83.2	20.9
		15	48.4	69.1	95.6	86.6	16.3
		5	46.2	66.8	98.0	88.4	13.6

[a]See succeeding explanation of calculation of corrected yields.

TABLE 5

Corrected yields and compositions of fractions crystallized from mixtures of solvents and unhydrogenated cottonseed oil fatty acids. (Calculated on basis of perfect separation of solid and liquid portions.)

Solvent	Temp. °F.	Fraction	Cor. Yield, %	Distribution of acids in fractions[a]			Composition of the fractions, per cent[b]		
				Sat.	Oleic	Linol.	Sat.	Oleic	Linol.
Acetone	35	Filt.	81.8	10.7	26.4	44.7	13.1	32.3	54.6
		Ppt.	18.2	19.6	−0.9	−0.5	100.0	0.0	0.0
	25	Filt.	77.0	6.4	26.5	44.1	8.4	34.4	57.2
		Ppt.	23.0	23.7	−0.6	−0.1	100.0	0.0	0.0
	15	Filt.	74.9	3.8	26.5	44.6	5.1	35.3	59.6
		Ppt.	25.1	27.7	−1.1	−1.5	100.0	0.0	0.0
	5	Filt.	73.4	2.4	24.8	46.2	3.3	33.8	62.9
		Ppt.	26.6	27.7	−0.2	−0.9	100.0	0.0	0.0
	−5	Filt.	72.3	1.5	24.7	46.1	2.2	34.1	63.7
		Ppt.	27.7	28.8	−0.4	−0.7	100.0	0.0	0.0
Skellysolve B	35	Filt.	84.9	12.5	27.2	45.2	14.8	32.1	53.1
		Ppt.	15.1	17.4	−0.8	−1.5	100.0	0.0	0.0
	25	Filt.	81.8	10.7	26.6	44.5	13.1	32.6	54.3
		Ppt.	18.2	20.4	−1.1	−1.1	100.0	0.0	0.0
	15	Filt.	77.4	6.7	26.8	44.5	8.6	34.3	57.1
		Ppt.	22.6	25.3	−1.6	−1.7	100.0	0.0	0.0
	5	Filt.	77.3	5.6	24.8	46.9	7.2	32.1	60.7
		Ppt.	22.7	24.6	−0.5	−1.4	100.0	0.0	0.0
	−5	Filt.	75.2	2.5	25.5	47.2	3.3	33.9	62.8
		Ppt.	24.8	27.1	−0.8	−1.5	100.0	0.0	0.0

[a]On basis of corrected yields, and 100 g. of original acids.
[b]Precipitate corrected for entrained filtrate.

corresponding amount of solvent in the original fatty acid-solvent mixture:

$$AF_c = (S)\ (AF_a)/S_f \quad (1)$$
$$AP_c = 100\text{-}AF_c \quad (2)$$
$$OF_c = (OF)\ (AF_c)/100 \quad (3)$$
$$OP_c = [(100\text{-}AF_a)\ (OP_a)/100] - [(AF_c\text{-}AF_a)\ (OF)/100] \quad (4)$$

where, S_f = solvent in filtrate fraction, g.
S = solvent in original charge, g.
AF_a = actual yield of filtrate-acids, g.
SF_a = solvent actually appearing in filtrate, g.
OF = oleic acid in filtrate, per cent
OP_a = oleic acid in actual precipitate, per cent
AF_c = corrected yield of filtrate-acids, g.
AP_c = corrected yield of precipitate-acids, g.
OF_c = oleic acid in filtrate, corrected basis, g.
OP_c = oleic acid in precipitate, corrected basis, g.

Calculations with respect to the distribution of saturated acids or linoleic acid were, of course, analogous to those for oleic acid, as outlined above.

In Tables 5 and 6 are the calculated data on the crystallizations carried out in acetone and in Skellysolve B, including corrected yields of the fractions, distribution of the three classes of acids (saturated, oleic, and linoleic) in the fractions as corrected, and compositions of the corrected fractions.

In view of the slight degree of uncertainty at present involved in the thiocyanometric method, and the necessity for determining yields of the fractions indirectly, precise materials balances were hardly to be expected. There were, however, no large inconsistencies in the results. Negative calculated values for the content of unsaturated fatty acids in the precipitates (*cf.* Tables 5 and 6) occasioned by experimental errors were in no case greater than 1.7 per cent on the basis of the original fatty acids. The general validity of the calculated results is attested by the regular and consistent variation of derived values with values and characteristics experimentally determined, as shown graphically in Figures 1 to 5.

Separation of the Saturated Acids

The regular variation with crystallization temperature of the saturated fatty acid content of the liquid acid fractions is shown in Figure 1.

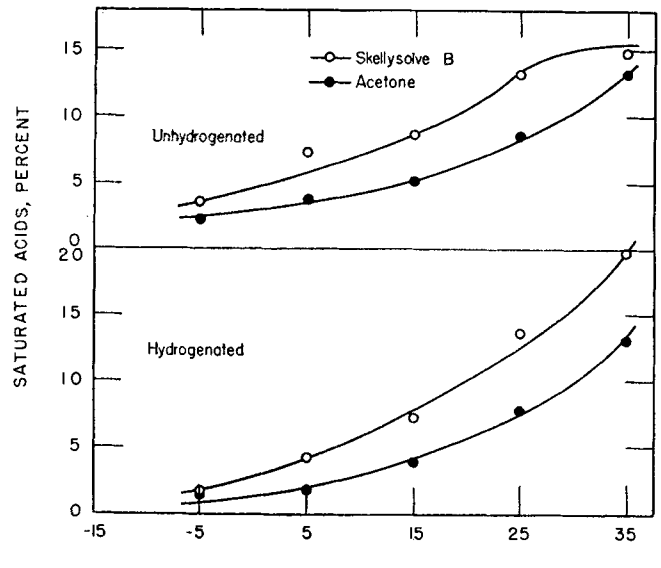

FIG. 1. Relationship between saturated content of the liquid acid fractions and crystallization temperature, in crystallizations from acetone and Skellysolve B.

The analytical data indicate that under the conditions outlined, the saturated acid content of the fatty acids from unhydrogenated cottonseed oil can be reduced to 2 to 3 per cent. According to calculations from the iodine and thiocyanogen values, the saturated acid content of the fatty acids from the hydrogenated oil was in some cases reduced to zero. It is apparent, however, from Twitchell separations carried out on certain fractions (Table 7) that in the case of the hydrogenated acids the calculations yield slightly low values for saturated acids and that actually all the liquid acid fractions contain at least a small proportion of saturated fatty acids.

Within the range of temperatures employed, there was no apparent difference in the action of the different solvents except with respect to the temperatures required to cause a given degree of separation of the

TABLE 6

Corrected yields and compositions of fractions crystallized from solvents and hydrogenated cottonseed oil fatty acids. (Calculated on basis of perfect separation of solid and liquid portions.)

Solvent	Temp. °F.	Fraction	Cor. Yield, %	Distribution of acids in fractions[a]			Composition of the fractions, per cent[b]		
				Sat.	Oleic	Linol.	Sat.	Oleic	Linol.
Acetone	35	Filt.	80.6	10.5	62.6	7.5	13.0	77.6	9.4
		Ppt.	19.4	18.5	1.1	−0.2	94.3	5.7	0.0
	25	Filt.	74.4	5.7	62.0	6.7	7.7	83.3	9.0
		Ppt.	25.6	23.1	2.5	0.0	90.2	9.8	0.0
	15	Filt.	70.2	2.7	60.8	6.7	3.9	86.5	9.6
		Ppt.	29.8	26.1	3.7	0.0	87.6	12.4	0.0
	5	Filt.	67.4	1.2	59.2	7.0	1.7	87.8	10.5
		Ppt.	32.6	27.7	5.2	−0.3	84.0	16.0	0.0
	−5	Filt.	55.0	0.8	47.9	6.3	1.5	87.0	11.5
		Ppt.	45.0	29.2	16.6	−0.8	63.1	36.9	0.0
	−15	Filt.	51.4	0.0	44.9	6.6	0.0	86.9	13.1
		Ppt.	48.6	29.0	20.6	−0.9	59.7	40.3	0.0
Skellysolve B	35	Filt.	89.5	17.5	64.8	7.2	19.6	72.4	8.0
		Ppt.	10.5	10.9	−0.2	−0.2	100.0	0.0	0.0
	25	Filt.	79.9	10.8	62.2	6.9	13.5	77.8	8.7
		Ppt.	20.1	18.3	1.9	−0.1	94.1	5.9	0.0
	15	Filt.	75.0	5.4	62.2	7.4	7.1	83.0	9.9
		Ppt.	25.0	23.5	1.7	−0.2	95.3	4.7	0.0
	5	Filt.	70.1	2.9	59.6	7.6	4.1	85.0	10.9
		Ppt.	29.9	26.5	3.6	−0.2	88.0	12.0	0.0
	−5	Filt.	67.3	1.1	59.5	6.7	1.6	88.5	9.9
		Ppt.	32.7	28.1	5.7	−1.1	82.6	17.4	0.0
	−15	Filt.	55.0	0.0	48.9	6.2	0.0	88.7	11.3
		Ppt.	45.0	29.6	16.1	−0.7	65.8	34.2	0.0

[a]On basis of corrected yields, and 100 g. of original acids.
[b]Precipitate corrected for entrained filtrate.

fatty acids. Polar and nonpolar solvents are exemplified respectively by acetone and Skellysolve B. Although at any fixed temperature more efficient separation of the saturated fatty acids was obtained in acetone than in Skellysolve B, it was possible in every case to make Skellysolve B fully equivalent to acetone by merely reducing the crystallization temperature, usually about 10° F. (5.6° C.). The equivalence between results obtained in acetone and those obtained 10° F. lower in Skellysolve B is readily apparent from the curves of Figures 1 and 3. Since Skellysolve B is cheaper than acetone or other polar solvents and has other advantages such as relative immiscibility with water, it would appear that it may be generally the most desirable solvent for commercial use in the fractional crystallization of fatty acids.

At any given temperature methyl ethyl ketone was very nearly equivalent to Skellysolve B and methyl acetate was practically equivalent to acetone, whereas ethyl acetate appeared to occupy a position of intermediate effectiveness. There was no apparent tendency for the saturated acids to form mixed crystals with normal oleic or with linoleic acid in any of the solvents.

Solubility of the Saturated Acids

The most soluble saturated fatty acids present in cottonseed oil are myristic and palmitic acids. It is of interest to compare the solubilities of these acids in the pure form, as reported approximately by Foreman and Brown (9) with the solubilities of the saturated acids of cottonseed oil as found under the conditions of the present investigation and calculated according to the following equation:

Solubility of sat. fatty acids, g. per 100 g. solvent= (g. mixed acids in filtrate) (% sat. acids in mixed acids)÷(g. solvent in filtrate).

This comparison is presented in Figure 2.

It is apparent that in acetone the solubility of the saturated acids is not greatly influenced by the presence of the unsaturated acids in the mixture but that in Skellysolve B the solubilizing effect of the unsaturated acids is considerable.

The Separation of Iso-oleic Acids

The term "iso-oleic acids" is used here according to its customary sense in oil and fat technology, i.e., as applying to the monothenoid acids produced by hydro-

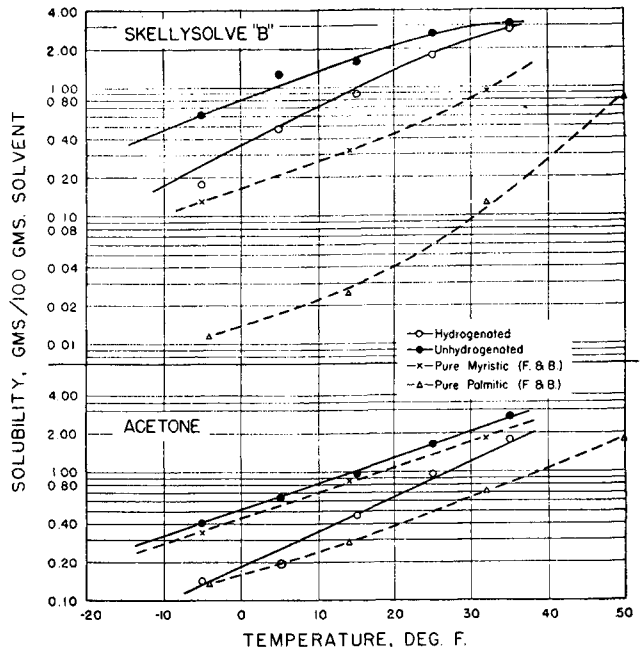

FIG. 2. Solubilities of the saturated fatty acid content of cottonseed oil fatty acids at various temperatures, in comparison with the solubilities of myristic and palmitic acids as reported by Foreman and Brown.

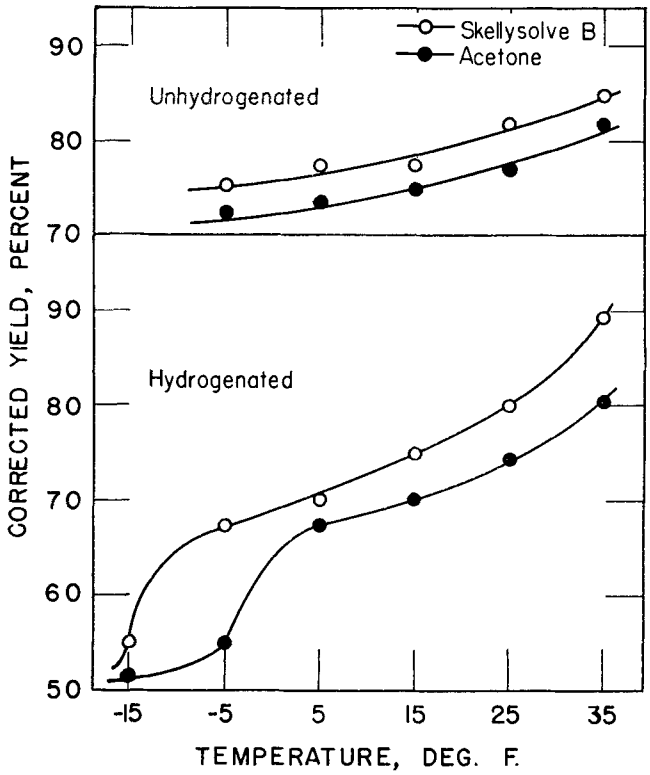

FIG. 3. Corrected yields of the liquid acid fraction of cottonseed oil fatty acids from Skellysolve B and acetone, as a function of crystallization temperature.

genation which are higher melting than normal oleic acid and which consequently are inclined to separate with the saturated acid fraction during the course of fractional crystallization.

The oleic acid calculated as appearing in the precipitate-fractions of the hydrogenated acids (Table 6) may be considered iso-oleic acid. The separation of iso-oleic acids did not proceed uniformly as the crystallization temperature was decreased but was sharply augmented as this temperature approached —5° F. (—20.6° C.) in the case of the crystallizations carried out in acetone and —15° F. (—26.1° C.) in those carried out in Skellysolve B. This effect is very evident from the relationship between crystallization temperature and corrected yields of the liquid acid fractions, as shown in Figure 3, and from the relationship between crystallization temperature and calculated iso-oleic acid content of the precipitates after correcting for filtrate entrainment, as shown in Figure 4.

The acetone filtrate fractions and the corresponding fraction obtained from Skellysolve B at —15° F. were analyzed for iso-oleic acid content by the official A.O.C.S. Twitchell lead soap-alcohol method. The analytical results are shown in Table 7.

The various analytical and operational data yield very poor materials balances with respect to the iso-oleic acids. Thus, for example, analysis indicated that there were 15.9 g. of iso-oleic acids in each 100 g. of the original acids (Table 1). Crystallization from acetone at —5° F. removed 16.6 g. of oleic acids (Table 6), and yet further analysis (Table 7) indicates 12.8 per cent of iso-oleic acids in the filtrate, which corresponds to an additional 7.0 g. of these acids, or a total of 23.6 g. calculated to be present in precipitate and filtrate combined. However, it is to

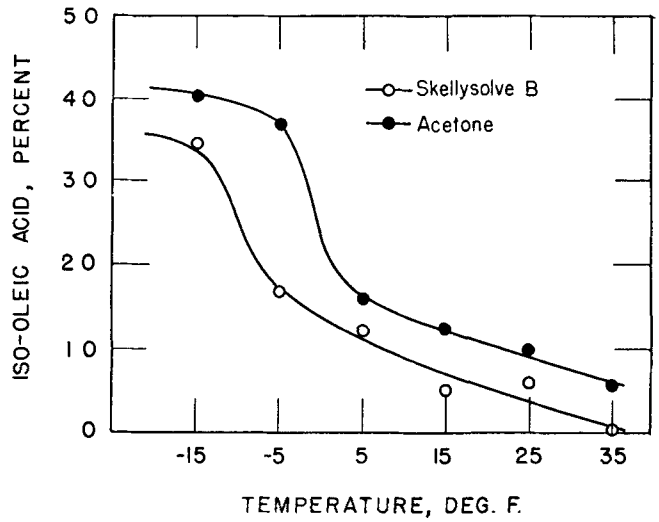

FIG. 4. Relationship between crystallization temperature and iso-oleic content of the precipitate-acids. (Precipitates corrected for entrainment of filtrate).

be remembered that the official method for determination of iso-oleic acids is empirical and that it includes only such iso-acids as appear with the lead soaps of the saturated acids when the latter are crystallized under arbitrarily chosen conditions. The "iso-oleic" acids precipitated in the form of lead soaps from the filtrate acids are not necessarily identical with those which precipitate from the much different original fatty acid mixture.

TABLE 7

Yields and analyses of solid acid fractions separated by the Twitchell method from fractionally crystallized hydrogenated cottonseed oil fatty acids.

Fraction analyzed			Yield solid acids, %	Distribution of the solid acids[a]		
Solvent	Fraction	Temp. of crystn., °F.		Sat.	Oleic (iso-oleic)	Linoleic
Acetone	Filtrate	35	34.1	13.1	21.0	0.0
Acetone	Filtrate	25	30.8	7.9	22.9	0.0
Acetone	Filtrate	15	27.6	5.1	22.5	0.0
Acetone	Filtrate	5	27.9	2.9	24.8	0.2
Acetone	Filtrate	−5	14.5	1.4	12.8	0.3
Acetone	Filtrate	−15	11.6	0.8	10.2	0.6
Skellysolve B	Filtrate	−15	13.9	1.3	12.3	0.3
Original hydrogenated fatty acids	.....	.....	43.5	27.6	15.9	0.0

[a]On basis of total solid acids, as shown in column 4; calculated from iodine and thiocyanogen values.

Titers of the Liquid Acid Fractions

From a practical standpoint, the content of saturated acids in a liquid fatty acid product is of importance chiefly with respect to the influence of these acids on the solidification point or titer of the product. Titers of all of the samples that solidified above —2° C. are plotted against the saturated fatty acid content of the samples in Figure 5.

Recovery of the Saturated Acids

The experimental results indicate that in commercial practice it would probably be possible to obtain from unhydrogenated cottonseed oil fatty acids a saturated fraction reasonably free from unsaturated acids by washing the precipitated crystals on the filter with cold solvent. The efficacy of such a procedure would depend to a large extent upon the design of the filter used. Consequently, in the course of the present work no attempt was made systematically

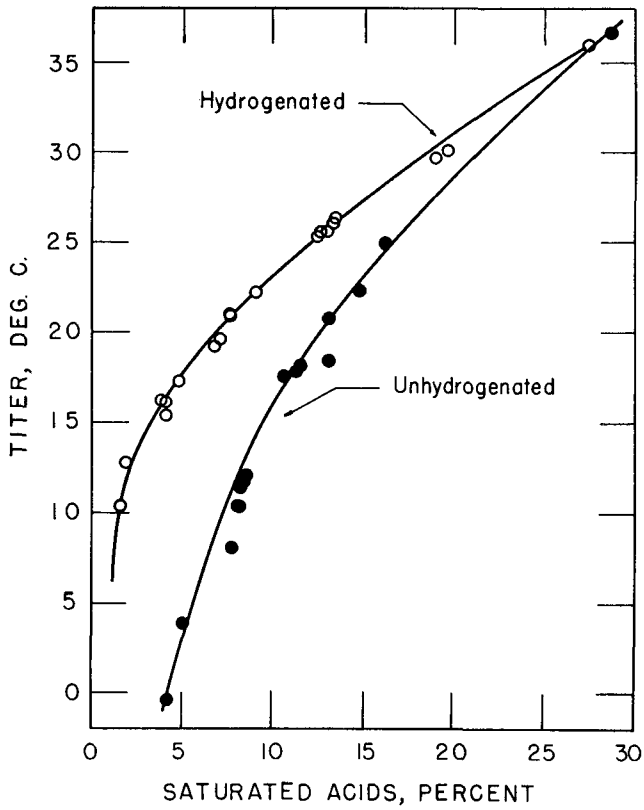

FIG. 5. Relationship between titer and saturated acid content of the liquid acid fractions.

to investigate this feature of the operation. In a single instance, however, involving crystallization of the unhydrogenated acids from Skellysolve B at 15° F., the precipitate from 150 g. of acids was washed on the filter with four successive 300 cc. portions of solvent at 15° F. There were obtained 35.2 g. of washed acids, which had an iodine value of 7.1, and, therefore, consisted of about 95 per cent saturated and 5 per cent unsaturated acids.

Summary

1. An investigation has been made of low-temperature crystallization from organic solvents as a means of effecting practical separations of the solid and liquid acids of unhydrogenated and hydrogenated cottonseed oils.

2. At any fixed temperature the most efficient separations were obtained in the highly polar solvents, acetone and methyl acetate. However, it was possible in any case to make nonpolar petroleum naphtha (Skellysolve B) fully equivalent to the polar solvents simply by conducting the crystallization at a temperature approximately 10° F. lower than that employed with the polar solvents. Ethyl acetate and methyl ethyl ketone were intermediate between petroleum naphtha and acetone or methyl acetate in their effectiveness.

3. By employing a solvent-fatty acid ratio of 4 to 1 by weight and conducting crystallizations at 5° F. or lower from acetone and —5° F. or lower from petroleum naphtha, the liquid fatty acids from unhydrogenated cottonseed oil could be reduced to below —2° C. in titer and to below about 3 per cent in saturated acid content. Under these conditions there was no appreciable crystallization of oleic acid.

4. At a solvent-fatty acid ratio of 6 to 1 and the same temperatures (5° F. for acetone and — 5° F. for petroleum naphtha) equally good separations could be made of the saturated fatty acids present in the mixed acids from hydrogenated cottonseed oil (I.V.=70). Separation of "iso-oleic" acids from the fatty acids of the hydrogenated oil took place over a wide range of temperatures, beginning at 35° F. in acetone and at 25° F. in petroleum naptha, and being incomplete (according to Twitchell analyses of the liquid acids) in either solvent at —15° F. However, the bulk of the higher melting iso-oleic acids was precipitated as the temperature approached —5° F. in acetone and —15° F. in petroleum naphtha.

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Stability Values Obtained by Different Rapid Methods as a Means of Evaluating Antioxidants for Fats and Oils

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THE most widely used rapid methods for determining stability of fats and oils are the active-oxygen (Swift stability test), oxygen-absorption, and oven incubation methods. These methods are also being extensively used to determine the relative effectiveness of antioxidants.

Little is known of the mechanism by which antioxidants inhibit oxidation. It is possible that some antioxidants cause the formation of products different from those normally formed during oxidative rancidification. In this case, use of a pre-established peroxide value or quantity of oxygen absorbed as an end point of the induction period, as commonly employed in rapid tests, might be invalid.

Surprisingly few data have been published that permit a comparison of stability values by different rapid methods for evaluating antioxidants. King, Roschen, and Irwin (1) reported results of a collaborative study in which the stabilities of four lards

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