

Plant Results

Sludge. During the drossing of tin stacks, sludge was removed and weighed from stacks on palm oil and on low polyunsaturated tallow. The results are shown in the following Table IV.

Oil	Sludge, lbs.	Original polyunsaturated acids (%)
Palm.....	253	9.5
Low polyunsaturated tallow.....	35	1.3
Ratio.....	7.23	7.31

It appears significant that the sludge is directly proportional to the polyunsaturated acid content of the oils.

Consumption. Figure 2 shows the consumption of tinning oil per base box at two different tinning mills. It is to be noted that consumption increases with increasing polyunsaturation and that the curves for the two mills are parallel. The reason for the higher consumption in the second mill is due to a different mode of operation.

Factors that contribute to different consumptions are higher rate of formation of free fatty acids, maintenance of a lower level of viscosity, and greater speed of plate travel through the stack.

Ference and Johnson (5) report results which are similar to three of the points shown above for the first mill.

Prime Plate Yield. One of the mills kept accurate records of the prime plate produced during the experiments. The low polyunsaturated tallow resulted in an increase of over 5% in prime plate yield over the results with palm oil. Both mills stated that the tallow (low polyunsaturates) plate was definitely brighter.

Conjugation. In regard to conjugation it was found that reclaimed or spent oil which appeared to have a large conjugated diene content according to the official spectrophotometric method would not make good plate because of oil staining. However it was found that color which had been formed was interfering with the conjugated diene determination. Therefore the true conjugated diene content was unknown.

Summary

1. A theory was outlined, which predicts that low polyunsaturation should result in better tin plate at lower oil consumption.

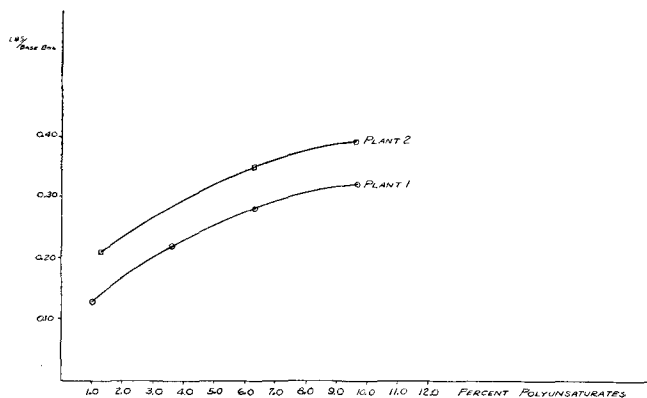


Fig. 2. Consumption of tinning oil per base box at two different tinning mills.

2. It has been shown that low polyunsaturation results in lower oil consumption in actual mill tests.

3. The percentage of prime plate is higher for lower polyunsaturation.

4. It has been demonstrated that percentage of polyunsaturation is lower in spent oils than in the original, indicating preferential reactivity of this fraction.

5. By actual mill test it has been shown that the percentage of sludge increases with the percentage of polyunsaturation in the original oil.

Acknowledgment

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Color Characteristics and Chemical Analyses of Oil from Frost- and Weather-Damaged Soybeans¹

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IN an earlier paper (1) some spectrophotometric methods for grading green soybean oil were presented. These methods were based on measurements made on oil which had been extracted from

soybeans of two varieties, grown in different fields and artificially frozen at several stages of ripeness. To make the methods more generally applicable, naturally frost-damaged soybeans from commercial sources were sought. Inquiries to several producers brought suitable samples of frost-damaged soybeans, and two cans of green oil. Localities represented in this group

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TABLE I
Analytical Data on Oil Samples

Oil	Green grade	NiSO ₄ equiv.	D _{700mμ}	A.O.C.S. color		Ref. loss	F.F.A.	I.V.
				Photo-metric	Wesson			
		<i>mm.</i>				<i>%</i>	<i>%</i>	
1	1	13.2	0.380	23.5	22.0	23.6	0.7	123.8
2	1	15.0	0.428	121.3
3	1	16.2	0.492	8.1	6.6	6.2	0.6	130.4
4	1	16.0	0.412	8.0	7.6	10.4	0.6	122.8
5	2	19.8	0.440	12.2	10.6	9.4	1.2	126.2
6	2	20.1	0.395	2.3	2.1	6.7	0.6	119.6
7	2	22.1	0.480	3.2	2.2	6.9	0.6	120.8
8	2	23.1	0.480	38.7	1.2	118.0
9	3	31.6	0.79	6.9	6.9	10.0	0.7	127.4
11	3	59.1	1.30	106.6

of samples were Oklahoma, Mississippi, Iowa, and Illinois. In addition to samples sent from elevators and producers, other soybeans were obtained from a late planting on a farm in Peoria County which, fortunately for the present work, were frosted before they had matured. To study the progressive effect of weather damage on frosted soybeans, the local planting was harvested at three intervals after the frost. A patch of soybeans on another farm was frosted in the field with solid carbon dioxide. Soybean plants were covered with tarpaulins, and carbon dioxide was thrown on the ground and lower parts of the plants. The air temperature did not fall below 28°F. (-2°C.). Only oils which were either dark, grade-1 oils, or were actually in the green grades, were considered in this program.

Experimental

After the soybeans were cracked and flaked, the oil was extracted in a 2-gallon Soxhlet extractor, using trichloroethylene as solvent. One early batch was extracted with hexane, but the remaining samples were extracted with trichloroethylene because it removed pigments more thoroughly than hexane. Admittedly extraction with trichloroethylene is not a prevailing practice, but the purpose was to obtain dark oils. That hexane and trichloroethylene extract pigments in the same ratio was shown by comparing oils from the same soybeans extracted with both solvents in a Duboseq colorimeter. By varying the depths, it was possible to obtain an exact color match between the two oils.

Diethyl ether also was tried as a solvent, and although it produced dark oil, the assortment of pigments extracted was so different from those extracted with either of the other solvents that no match could be made in the colorimeter.

Each extracted oil was compared with nickel sulphate solution B (2) (9% nickel sulphate in water) in a Duboseq colorimeter, with the specified red-glass filter, to establish the green grade and to determine the depth of solution required to match one inch of oil. The matching provided a continuous scale for comparison with optical density (1).

Absorption spectra of the crude oils were measured with a Coleman Model 6B³ spectrophotometer, and 20% solutions of them in carbon tetrachloride were measured with a Cary recording spectrophotometer.

The oils available in sufficient quantities were refined and bleached with both natural and activated earths, and, as a characterization of the samples, free fatty acids and iodine values of the crude oils were determined. Wesson colors and A.O.C.S. photomet-

ric colors were measured for refined, bleached oils. All methods used were official N.S.P.A. or A.O.C.S. procedures.

Discussion

Data presented in Table I show characteristics of the oils. The heading "Nickel Sulphate Equivalent" means the depth of solution B required to match 1 in. of oil. Samples 1, 3, and 9 were from the local farm. Number 9 was harvested immediately after frost; Number 3, 2 weeks later; and Number 1, 2 months later. It is evident that weathering destroyed the porphyrins originally present and produced other changes which brought about a high refining loss. It had been expected that weather damage would produce darker oils. Sample 8 was from commercial soybeans which showed a large amount of weather damage.

Inspection of the data presented in Table I of the earlier publication (1) shows that a steady increase in iodine value occurs as the soybeans ripen and a decrease occurs in free fatty acid and refining loss. The samples described in this paper were procured at random so that the soybeans are of different varieties and from several localities. It is not surprising, then, that the correlation shown in Table I between green grade and these properties is less regular than in the 1952 series. Sample 11, the darkest ever encountered at this laboratory, was extracted from soybeans sent in by a cooperative elevator. They showed

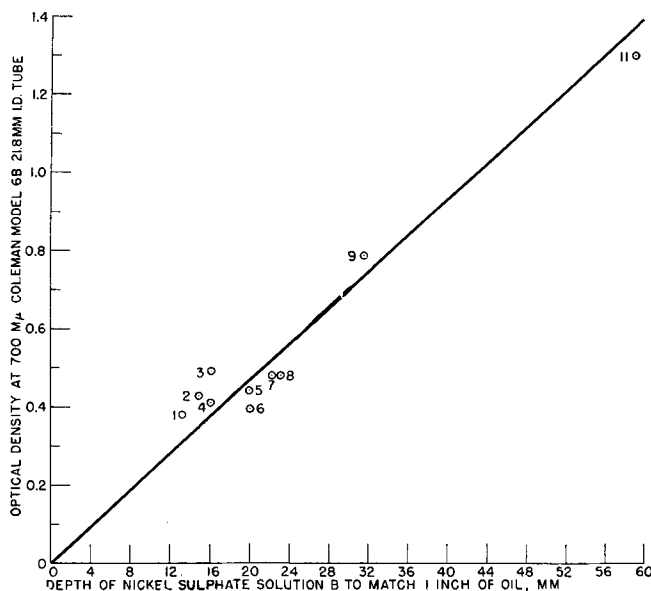


FIG. 1. Depth of nickel sulphate solution B required to match 1 in. of oil versus optical density of oil at 700 mμ.

³The mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

some weather damage but, in general, looked no worse than some lots of soybeans which produced better oil.

A difference was noticed in response to natural and active earths when refined oils were bleached. In some cases, reported in Table II, the difference was marked, but in others it was slight.

In the graph (Figure 1) which shows optical density at 700 m μ versus nickel sulphate equivalent, there is less regularity than was found in the maturity series. In the graph presented in the earlier paper (Figure 2) the points fell on a smooth curve. The scatter of the points in the present work was such that a straight line was the best representation of the new data. Since there were no naturally frosted soybeans in 1952, it was suggested that it might be necessary to move the limits between grades 1 and 2 (optical density 0.5 at 700 m μ) and grades 2 and 3 (optical density 0.7). The optical density at 700 m μ for the lower limit of grade 2 becomes 0.45 whereas that for grade 3 becomes 0.58.

The scatter in Figure 1 can be accounted for by the greater background present in the absorption spectra of some of the samples. Figure 3 shows absorption curves obtained with the Cary spectrophotometer for oils in all 3 grades. Backgrounds in the

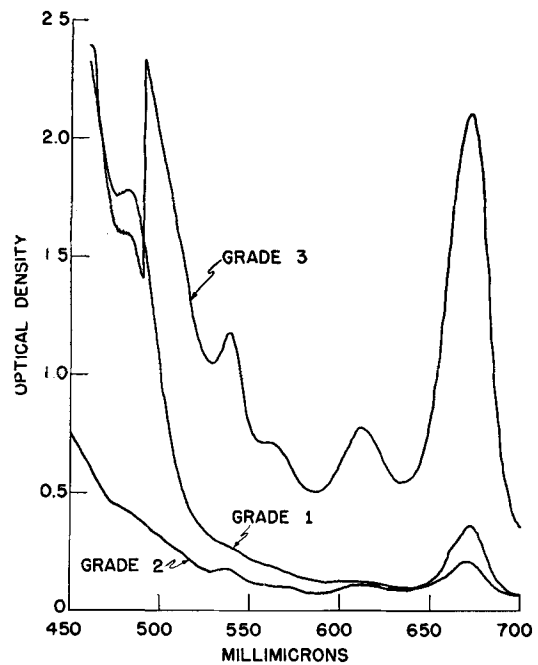


FIG. 3. Absorption spectra of 20% solutions of oils in carbon tetrachloride.

TABLE II
Effect of Natural and Active Earths on Bleached Color of Soybean Oil

Oil	A.O.C.S. photometric color		Wesson color			
	Natural	Active	Natural		Active	
1.....	23.5	19.7	70Y	22.0R	70Y	18.7R
3.....	8.1	5.7		6.6R		5.7R
4.....	8.0	4.0		7.6R		4.7R
5.....	12.0	12.2		5.7R		10.6R
6.....	4.7	2.3		4.8R	20Y	2.1R
7.....	3.8	3.2		5.2R	20Y	2.2R
9.....	10.7	6.9		9.0R	70Y	6.9R

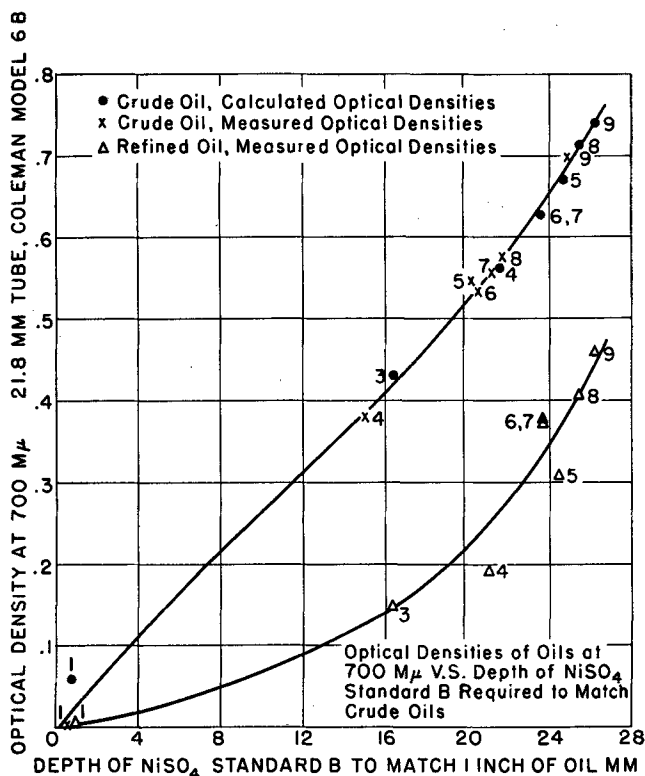


FIG. 2. Depth of nickel sulphate solution B required to match 1 in. of oil in 1952 series.

grade-3 oils are far greater than that of any oil encountered in the 1952 series, and a porphyrin absorption is superimposed on this background. Varying amounts of background were found in the several oils which scatter around the line. Two samples, Numbers 3 and 8, had the same optical densities at 700 m μ measured in the Coleman instrument but had different nickel sulphate equivalents. When a comparison of the Cary curves was made, it was found that, although the 670 m μ peaks were of the same density, the peak positions and the shape of the bands were different, with more absorption in the region between the short wavelength limit of the filter, 630 m μ , and 670 m μ in the oil of higher nickel sulphate reading. Another pair of oils, Numbers 3 and 4, had the same nickel sulphate equivalents and different Coleman optical densities; and, again, inspection of the Cary curves showed that a difference in sharpness of the absorption bands permitted like quantities of light to pass in the region beyond 630 m μ although the density at the peak is greater in one than in the other.

Refining losses were unduly high, iodine values were lower than normal, and free fatty acid was slightly higher than normal for all oils. Most oils were difficult to refine, one produced foots which required five remelts.

Discounts or premiums (2) which would be applied to the green soybean oils are shown in Table III. All but two oils would have been subject to heavy penalties. These two oils would have taken a penalty for green grade and were the only screw-pressed oils available for this study. When the visual, crude, green-grading method was adopted in 1942, screw-pressing was the prevailing practice and accounted for about 75% of the oil produced. In recent years 75% or more of the soybean oil has been produced by solvent extraction. The method or scale of penalties may need revision if the differences in bleaching response presented here can be substantiated on a larger number of samples. The common practice of

TABLE III

Percent Discount or Premium for Green Grade, Refining Loss, and Refined Bleached Color of Green Soybean Oils

Oil	Green-grade discount	Discount for RBC ^a	Discount or premium for RL ^b	Net discount
1954 Beans				
5.....	1	Sample grade	1.80 (discount)	Sample grade
6.....	1	None ^c	0.22 (premium)	0.78
7.....	1	None ^c	0.07 (premium)	0.93
9.....	2	6.25 ^c	2.25 (discount)	8.50
1952 Beans				
5.....	1	Sample grade	0.22 (premium)	Sample grade
6.....	1	Sample grade	9.15 (discount)	Sample grade
7.....	1	Sample grade	6.45 (discount)	Sample grade
8.....	2	Sample grade	1.28 (discount)	Sample grade
9.....	2	Sample grade	12.00 (discount)	Sample grade

^a RBC—refined bleached color.^b RL—refining loss.^c Green-grade discount applies only if RBC discount is less than green-grade discount.

Summary

Frosted soybeans and oils from frost-damaged soybeans were obtained from the farm and commercial sources. All soybeans used were classed as inferior, according to the Handbook of Official Grain Standards of the United States, with respect to both green and weather damage. Localities represented were Oklahoma, Mississippi, Illinois, and Iowa. Spectrophotometric measurements and visual comparisons were made to establish the green grades. If the necessary quantities of oils were available, the samples were refined and bleached; otherwise only the chemical analyses, green grading, and spectrophotometric measurements were made on the crude oils. Iodine values and free fatty acid were determined also.

If a spectrophotometric method for the green grading of soybean oil were to be adopted, present indications are that the boundary between grades 1 and 2, comparable to the present N.S.P.A. grading system, should be at optical density 0.45 at 700 m μ , as measured in a 21.8 mm. I.D. tube in a Coleman Model 6B instrument, and that between grades 2 and 3 should be at optical density 0.58. It is recommended that duplicate systems of green grading be avoided.

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blending frost- or drought-damaged soybeans with sound soybeans before processing has made it extremely difficult to procure samples of damaged soybeans or oil from damaged soybeans. Extensive green damage would raise processing problems in which the present N.S.P.A. grading system would not give the real value of the oil.

The authors are not in a position to state what effect variety, locality, and weather during the growing season may have had on the refining and bleaching qualities of the oil in frosted soybeans. There were however some indications that variety and processing were involved. Some samples of soybeans did not look unusually bad, but they produced dark oil whereas other soybeans which were entirely green and badly shriveled produced better oil.

The Infrared Spectra of Mono-, Di-, and Triglycerides¹

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ARAPIDLY growing interest in various types of modified glycerides has been evidenced by an increasing number of publications describing their preparation, purification, physical and chemical properties, and their possible uses. These modified glycerides include products obtained by hydrogenation and fractionation, mixed glycerides of long- and short-chain fatty acids such as acetostearins, and mixtures of mono-, di-, and triglycerides.

While chemical methods for analyzing modified glycerides are generally satisfactory, some of them are tedious and others are not entirely adequate for investigational and control purposes. Physical methods which would provide rapid and convenient means of determining qualitatively and quantitatively specific glycerides present in admixtures as well as trans-isomer content would be extremely useful.

Infrared absorption appears to be a most promising physical tool for analytical purposes. However before development of any specific procedure can be attempted, the spectra of several pure glycerides, rep-

resentative of the various types, must be obtained and characterized. Availability of such compounds in this laboratory has afforded an unusual opportunity to obtain and examine the infrared spectra of several types of glycerides. The purpose of this paper is to report the infrared spectra of 21 pure glycerides, including various mono-, di-, and triglycerides of long-chain (C₁₄, C₁₆, and C₁₈) fatty acids, both saturated and unsaturated, and of mixed long- and short-chain fatty acids, such as diacetotriglycerides. With two or three exceptions, which are included for completeness, none of these spectra has heretofore been published. The infrared spectra of these compounds in the rock salt region, 2 to 12 microns, are presented. Conclusions which can be obtained from their examination and which are of possible importance to the development of analytical methods are discussed.

Experimental

Infrared absorption spectra were measured with a Model IR-2T Beckman Automatic Recording Infrared Spectrophotometer.³ The instrument was housed in a room maintained at approximately 23°C. and

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