

advantages and disadvantages of these methods and comparing them with the proposed method. Results from some of the collaborators have been received, and there still seems to be some disagreement so that further thought will be necessary.

## 2. *The Determination of Phosphorous on Lecithin.*

When the proposed method for the phosphorous determination on lecithin was submitted, there was some discussion as to the correct temperature at which the phosphorous should be precipitated. After the chairman had investigated the objections to this method, it was thought that a slight revision in the wording would be all that would be necessary in order to complete the method. The members of the committee from whom the chairman has heard concerning this suggestion are not in entire agreement so that further discussion and possible further experimental work will be necessary before this method can be submitted. As to future plans, the incomplete work mentioned above will keep subcommittee busy for some time. It is also hoped that the spectrophotometric method for the determination of color in oils may be applied to the determination of the color of lecithin.

SUBCOMMITTEE ON DETERMINATION OF FLASH POINT, D. S. Bolley, chairman: A round robin test has been conducted among the subcommittee members, using linseed oil containing varying percentages of hexane and mineral spirits. The oils were tested according to a modified A. O. C. S. method, using a Pensky-Martens closed cup flash point apparatus. The results obtained by the collaborators were correlated and distributed with comments by the subcommittee chairman. Re-

sults to date indicate the proposed modified method gave good results.

A second similar round robin is now being prepared employing degummed soybean oil. When this series of tests has been completed, the effects of small amounts of moisture and other variables will be considered.

SUBCOMMITTEE ON DETERMINATION OF THIOCYANOGEN VALUES, F. R. Earle, chairman: The subcommittee has nothing to report this year. However, during this coming year, I should like to get a better idea of the precision of the method. I believe it would be worthwhile to send out a sample of linseed oil (to give maximum variations) and ask that it be run in quadruplicate every two months, using at least two batches of lead thiocyanate. The thiocyanogen method is being used as a control method, but I believe that the variation in results obtained at different times is much greater than is realized. Duplicates ordinarily agree well, but the level may shift with different batches of reagent or under different conditions.

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# Refining Fatty Oils With Liquid Propane \*

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THE purpose of this paper is to present a resumé of a preliminary study of the Ewing (1) process of degumming fatty oils with propane. Gums, including phosphatides and other so-called minor constituents, are precipitated from liquefied normally gaseous hydrocarbons, of which propane is the most common example. This means that the process is carried out under pressure.

Liquid propane is an intriguing solvent which has been extensively employed as a selective solvent in the refining of petroleum oils. Large commercial installations for de-waxing and for de-asphalting these oils have been in operation for the past decade. Liquid propane is also one of the two immiscible solvents employed in the Duo-Sol process of refining hydrocarbon oils. The propane dissolves the paraffinic hydrocarbons, and cresylic acid, the other solvent, takes out the naphthenic hydrocarbons. Liquid propane is cheap and very fluid at low temperatures, has a low boiling point, and can supply refrigeration through evaporation. All these properties have attracted investigators to the study of industrial applications of it. An excellent account of the use of liquid propane in the refining of lubricating oils may be found in the article by Wilson, Keith, and Haylett (2).

The solvent properties of liquid propane are unique. Unlike most common solvents which dissolve more solute as the temperature is raised, liquid propane dissolves less solute as the temperature is increased from room temperature to higher temperatures. Such anomalous behavior has prompted investigators to refer to it as an anti-solvent. As the temperature is lowered to 0°F., and below, liquid propane exhibits "normal" solubility characteristics, that is to say, the solutes become more insoluble.

Liquid propane boils at -44°F., under one atmosphere pressure; at 70°F., the vapor pressure is 126 lb./sq. in.; at 100°F., it is 190 lb./sq. in.; and at 140°F., the pressure is about 310 lb./sq. in.

Hixson and Miller (3) proposed treating tall oil with liquid propane to fractionate the rosin acids from the fatty acids. Hixson and his associates (4) have made several valuable, fundamental contributions to the knowledge of the solubility of known mixtures of pure fatty acids, abietic acid, and refined or synthetic triglycerides in the region of the critical temperature of liquid propane. Drew and Hixson (5), continuing the researches along these lines, established the limitations of the use of liquid propane as a selective solvent.

Ewing (1) was the first to advocate the refining of fatty oils with liquid propane. His process en-

\* Presented at the Fall Meeting of the American Oil Chemists' Society, Oct. 20-22, 1947, in Chicago.

compassed degumming, neutralizing with alkali, clay treatment, and winterizing or de-stearinizing. In this paper data relating solely to degumming will be presented.

Crude fatty oils, the triglyceride oils, such as vegetable and animal oils, offer an interesting field for exploring the possibilities of the selective solvent action of liquid propane. In view of the differences in chemical nature and molecular weight between the minor constituents, among which the phosphatides predominate, and the triglycerides, the singular anti-solvent properties of liquid propane become manifest as the temperature is raised. Phosphatides and other minor constituents are found concentrated in the lower layer.

It has been the practice of this laboratory to follow the course and efficiency of degumming through the phosphatides content of the oil before and after the removal of the gums. The per cent phosphorus multiplied by 26 is taken to represent the phosphatides. The measure of extent of degumming with liquid propane was likewise based on the phosphorus of the crude oil and the oil recovered from the upper layer, as will be explained later.

The apparatus employed was similar to that the Hixsons (6) used in their study of the extraction of fatty acids from rosin acid. It consisted of a stainless steel Jerguson gage of about 600-c.c. capacity. The approximate outside dimensions were  $3\frac{1}{4} \times 3\frac{1}{4} \times 11$  inches. Gage glass windows, held in position by flanges, on two opposite sides permitted visual observation. The gage was mounted on a special support.

Liquid propane (C. P. grade) from an inverted steel cylinder was introduced into the gage. There were two stainless steel sampling chambers of about 15-c.c. capacity. One was connected by a pipe leading to the bottom of the gage, the other to a pipe that entered the gage at a point about one-third down from the top. Samples of the bottom and top layers could thus be obtained. Valves were in the connecting lines which were used to regulate the flow of materials from the propane cylinder to the gage, from the gage to the sampling chambers, from the sampling chambers to the atmosphere, and from the gage to the atmosphere. Specially constructed couplings allowed the dismantling of parts of the unit without disturbing the rest.

In the first few experiments the gage was charged with a known volume of the fatty material under observation by pulling a vacuum and sucking the material into the gage. When all the material was in the gage, the vacuum was taken off. Liquid propane from an inverted steel cylinder was then led into the chamber of the gage. The total volume of the gage was known so the ratio of the volume of liquid propane to the fatty material was established with a fair degree of accuracy. Later a chamber lock comprising two "tees" and a nipple was interposed between the propane cylinder and the gage. By manipulation of valves the material could be introduced into and held in the lock and then the liquid propane from the cylinder allowed to flow into the lock, the valve leading to the gage having been opened. By following this procedure, the oil and propane were mixed to some extent before they entered the gage.

The gage was immersed in a large Pyrex glass jar filled with water. Two electric heaters supplied the heat to the water bath. Temperature was controlled

through thermo-regulators. After the gage was filled with the charge, the heat was turned on. The gage was fitted with a hand-operated stirrer. An electric light, placed on the outside of the far side of the bath, illuminated the bath and the glass of the gage. The physical condition of the materials in the gage, what was happening inside it, could readily be observed. The log of a typical experiment is given in Table I.

TABLE I

Materials: 50 c.c. Crude Cottonseed Oil; 550 c.c. Liquid Propane

Time	Temp.	Pressure	Remarks
	°C.	lbs./sq. in.	
Start.....	17	125	Clear yellow solution
20 minutes.....	38	150	Clear yellow solution
40 minutes.....	43	200	Clear yellow solution
60 minutes.....	55	250	Clear yellow solution
80 minutes.....	63	300	Clouding
85 minutes.....	67	325	Two layers; ratio vol. upper — 20 lower — 1
90 minutes.....	70	350	Both layers clear
150 minutes.....	70	350	Sampled

Oil from the upper layer, from which the solvent was removed, assayed 0.286% phosphatides. The original crude oil before the propane treatment had 1.40%. The color of the oil from the upper layer was lighter than the starting oil. The propane degummed oil had a 35Y-2.38R Lovibond reading in a one-inch column while the crude oil was too dark to read. The F.F.A. of the propane degummed oil was lower than the crude oil, 0.6% and 0.9% respectively. In these respects propane degumming is similar to water degumming. The acidity and color are reduced. The decrease in F.F.A. from propane degumming appears to be somewhat greater than from water degumming.

An extracted crude soya oil, diluted with eight volumes of liquid propane, was degummed. The details of the run are given in Table II.

TABLE II

Materials: 70 c.c. Crude Soya Oil; 550 c.c. Liquid Propane

Time	Temp.	Pressure	Remarks
	°C.	lbs./sq. in.	
Start.....	18	115	Clear solution
45 minutes.....	44	190	Clear solution
110 minutes.....	73	370	Two layers; ratio vol. upper — 5 lower — 1
125 minutes.....	70	350	Sampled

There were 0.3% phosphatides left in the propane degummed oil. The crude oil had 1.35% before propane degumming. Other propane degumming of crude soya oil resulted in degummed oil with less than 0.1% phosphatides.

The next common oil investigated was a crude corn oil. The separation point at which the gums precipitated as a separate lower layer was about 68°C. The degummed corn oil had 0.10% phosphatides and the undegummed oil 1.25%. Color was reduced to 35Y-2.50R in a one-inch column and acidity from 2.45% F.F.A. to 2.20%. Details of the test are shown in Table III.

The behavior of a crude tallow was studied. The tallow, a low grade, was introduced as a slurry in petroleum ether into the gage. The petroleum ether was evaporated in vacuo with heat on the bath. After cooling the system to room temperature, liquid

TABLE III

Materials: 70 c.c. Crude Corn Oil; 550 c.c. Liquid Propane

Time	Temp.	Pressure	Remarks
	°C.	lbs./sq. in.	
Start.....	22	125	Clear solution
50 minutes.....	57	250	Cloudy
75 minutes.....	66	325	Very cloudy
85 minutes.....	68	350	Two layers; ratio vol. upper — 5 lower — 1
100 minutes.....	73	375	Two layers; ratio vol. upper — 5 lower — 1
115 minutes.....	70	350	Sampled

propane was added and the contents of the gage stirred. A separation into two layers, with the lower layer considerably darker than the upper layer, occurred when the temperature was 76°C. The propane treated tallow, that is the fat in the upper layer, had 0.048% phosphatides, which was approximately one-third that in the crude tallow at the start. The fat from the upper layer was lighter than the starting material. The log of the experiment is shown in Table IV.

TABLE IV

Materials: 70 c.c. Crude Tallow; 550 c.c. Liquid Propane

Time	Temp.	Pressure	Remarks
	°C.	lbs./sq. in.	
Start.....	20	125	Very cloudy
15 minutes.....	30	.....	Clear
95 minutes.....	70	350	Cloudy
120 minutes.....	76	390	Two layers; ratio vol. upper — 5 lower — 1
135 minutes.....	78	405	Sampled

The extent of dilution of the starting fatty material with liquid propane determines the per cent of the fatty material that remains in the upper layer when the gums precipitate. As the dilution with liquid propane increased, the per cent of fatty material based on the weight of charge recoverable from the upper layer increased. When the ratio of the volume of liquid propane to oil was 2 to 1, 5 to 10% of the oil was in the upper layer. As the liquid propane was increased to 5 and 11 volumes, the oil recovered from the upper layer rose to 35% and higher of the weight of crude oil charged into the gage. These values of the per cent of oil recovered are approximations. The gum separation or precipitation point at the elevated temperatures was affected very little by the ratio of the volume of liquid propane to crude fatty oil under the conditions of the experiments.

Soya black grease was subjected to treatment with liquid propane. The course of the experiment is described in Table V.

TABLE V

Material: 65 c.c. Soya Black Grease; 550 c.c. Liquid Propane

Time	Temp.	Pressure	Remarks
	°C.	lbs./sq. in.	
Start.....	17	125	Black; opaque
60 minutes.....	55	245	.....
100 minutes.....	71	355	Clearing
115 minutes.....	75	380	Two layers; ratio vol. upper — 20 lower — 1
125 minutes.....	77	425	Sampled

The lower layer was very dark. The fatty material from the upper layer was much cleaner and lighter in color than the soya black grease. The phosphorus was reduced from 0.0127% in the black grease to 0.0019% in the material from the upper layer. Approximately six-sevenths of the phosphorus compounds were thus removed. They are not phosphatides but are decomposition products of them. A summary and resumé of the data are shown in Table VI.

In general it may be said that treatment of crude oils with liquid propane resulted in the precipitation of the gums, the extent of which was followed by the phosphorus content of the oils before and after precipitation as a separate layer when the temperature was raised to about 70°C. As in the present practice of degumming crude oils with water, the acidity is lowered and some of the color bodies, part of the minor constituents, come along with the gums and phosphatides. The fact that color bodies accompany the gums when the phosphatides are precipitated from crude oils would lend support to the hypothesis that in the crude oils the phosphatides are linked in some manner to the color bodies. The connection may not be stronger than an adsorption complex. Because the phosphatides are acidic, their precipitation and removal result in degummed oils of lower acidity than undegummed oils. The propane degummed oils were less acidic than the undegummed oils. A comparison of a water and propane degumming of a crude oil is made in Table VII.

TABLE VII

	Crude corn oil	Degummed corn oil	
		Water	Propane
	%	%	%
F.F.A.....	2.45	2.11	2.05
Phosphatides (% P × 26).....	1.25	0.18	0.10

The author wishes to express his appreciation to W. L. Kubie for experimental assistance in this work.

In summary, the data presented, although of a preliminary nature, show that the anti-solvent and selective solvent action of liquid propane can be em-

TABLE VI

Run	Material treated	Ratio of propane to material (by volume)	Conditions of degumming		Phosphatides	
			Temp.	Pressure	In starting material	In upper layer (solvent-free basis)
			°C.	lbs./sq. in.	%	%
3.....	Crude cottonseed oil	2 to 1	70	350	1.40	0.44
4.....	Crude cottonseed oil	5 to 1	70	370	1.40	0.23
5.....	Crude cottonseed oil	11 to 1	70	370	1.40	0.29
6.....	Soya black grease	8 to 1	75	410	0.33	0.05
8.....	Crude soya oil	8 to 1	70	350	1.25	0.10
9.....	Crude soya oil	8 to 1	70	350	1.35	0.32
10.....	Crude tallow	8 to 1	76	400	0.155	0.048

ployed to precipitate the gums from crude fatty oils. Precipitation of the gums from the liquid propane solution of the crude oils occurred at about 70°C. and 350 lb./sq. in. pressure.

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[Received August 8, 1949]

## Rice Bran Oil. V. The Stability and Processing Characteristics of Some Rice Bran Oils<sup>1</sup>

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DATA and information have been presented in the previous reports of this series on the extraction and processing (1), composition (2), and utilization (3), of rice bran oil produced from several varieties of Southwestern-grown rice brans and on the effect of storage of the bran on the free fatty acid content of the extracted oil (4). The present report is an extension of previous work to include data on nine different lots of rice bran as well as data with reference to the stability of unhydrogenated and hydrogenated oils.

### Extraction of Crude Oils

One sample each of freshly milled bran from Rexoro, Patna, and Magnolia varieties and two batches of bran from Zenith variety of rice were obtained from a local rice mill and subjected within a few hours to solvent extraction. Each lot of 360 pounds of bran was extracted with a total of 500 gallons of hexane at prevailing atmospheric temperature in a previously described extractor (5). The miscellas were concentrated by evaporation at approximately 65°C. After standing several days the separated solids were removed by filtration. Data and information with respect to the variety, lipid, and moisture content of the brans (A to E, inclusive) as well as the yield, color, and content of free fatty acids of the corresponding crude oils are given in Table I.

Three 10-pound batches of bran (F to H, inclusive) produced from "Converted" rice shipped from Houston, Texas, were extracted in a large glass Soxhlet-type extractor. A fourth 10-pound batch of bran

produced locally from Blue Rose variety of rice (I) was similarly extracted. The contents of free fatty acids of the rice bran oils, F to I, were 4.7, 2.1, 2.0, and 2.9%, respectively.

Extraction in the pilot plant of the five batches of bran containing from 13.8 to 17.0% hexane-soluble lipids yielded crude oils approximately equivalent to 91% of the hexane-soluble lipids present in the bran (Table I). Subsequent re-extraction of these brans with hot hexane yielded only semi-solid materials, indicating that the original extraction in the pilot plant had removed practically all of the glycerides. The crude oils obtained in pilot plant extractions contained 3.0 to 6.3% free fatty acids even though the freshly milled bran was extracted within a few hours after milling. By comparison the brans produced from "Converted" rice and shipped from Houston, Texas, to New Orleans gave crude oils (F to H) containing 4.7, 2.1, and 2.0%, respectively, thus indicating that the treatment (6) followed in the "Conversion" process markedly inhibits hydrolysis of the oil in the bran.

### Refining and Bleaching

The nine crude oils (A to I, inclusive) were refined according to the procedure of the Official and Tentative Methods of the American Oil Chemists' Society (7) prescribed for slow-break cottonseed oil (Method Ca 9a-41) except that the lye used was 0.5% excess of the quantity required to neutralize the free fatty acids. The refined oils were bleached according to the directions for bleaching refined cottonseed oil (Method Cc 8a-47). The content of neutral oil in crude oils (A to F, inclusive) was determined by the method described by Jamieson (8). Results of the refining and bleaching tests are shown in Table II.

TABLE I  
Characteristics of Rice Bran and Oils

Samples	Bran				Crude Oil					
	Variety of rice <sup>1</sup>	Locality grown	Hexane-soluble lipids, per cent	Moisture, per cent	Yield, <sup>2</sup> per cent	Free fatty acids, per cent	Lovibond color			
							1" column		5 ¼" column	
							Y	R	Y	R
A.....	Rexoro	Eunice, La.	13.8	10.8	90.5	3.0	....	....	70	13.1
B.....	Patna	Vinton, La.	14.9	10.6	92.6	3.1	70	5.6	....	....
C.....	Zenith	Knable, Ark.	17.0	11.6	91.0	3.0	....	....	70	12.7
D.....	Zenith	Rayne, La.	15.9	11.0	91.0	4.9	70	4.6	....	....
E.....	Magnolia	Eunice, La.	16.4	11.8	90.5	6.3	70	4.2	....	....

<sup>1</sup> Field dried. <sup>2</sup> Yield, per cent =  $\frac{\text{weight oil recovered from miscella}}{\text{weight bran extracted} \times \text{original content of hexane-soluble lipids (per cent)}} \times 100$ .