for determining bacteria on plates in testing bacterial removal by dishwashing detergents is based on transferring agar from a petri dish to the plate, incubation, and observing bacterial growth (Flett & Guiteras—*Soap, Sanit. Chemicals 28,* No. 10, 48).

Sewage processing engineers are concerned with the increase in use of synthetic detergents because they may affect conventional sewage processing. In Germany, considerable foaming in aeration basins due to household and textile-industry usage of the synthetic is encountered in recent years (Imhoff—*Gas- u. Wasserfach 93,* 512). Spraying the surface with clarified effluent has aided in the control of this foaming. In England sewage processing difficulties have arisen from use of synthetic detergents for scouring wool (various authors—*Inst. Sewage Purif. J. and Proc. 1948,* Pt. 1, 100, 102, 105, 109, 113; *1950,* 276). Manganelli's (*Sewage and Ind. Wastes 24,* 1057) work on the problem indicates that anionic and nonionic detergents do not interfere with oxidation of sewage; cationic types retard oxidation; anionics and nonionic types may interfere with coagulation; cationic compounds aid coagulation; all three types improve dewatering of sewage sludge, and that any surface-active compound may impair aeration in activated sludge units. Some investigators found no evidence that household detergents, even in concentrations above those expected, cause adverse effects during treatment of the sewage (Wells & Scherer —*Sewage & Ind. Wastes 24,* 670; Fuller—*Ibid.* 844).

ERRATUM: U. S. Patent No. 2,598,469 listed on page 202 of the first part of this Review should have read No. 2,598,468.

Iodine Values of Acidulated Coconut Oil Soapstock

S. R. KUBER and WALES H. NEWBY, Opelousas Oil Refinery, Division of Cotton Products Company Inc., Opelousas, Louisiana

SOAPSTOCK is the by-product of the alkali refining of glyceride oils. It consists largely of soap, formed by reaction of the refining alkali with the free fatty acids present in all crude oils, and moisture, together with lesser quantities of entrained neutral oil, unsaponifiable material, and extraneous foreign matter. Soapstock can be used directly in the manufacture of soap, and formerly this was the major method of utilization. Today, however, most of the soapstock produced is eventually treated with sulfuric acid to hydrolyze the soap present and dissolve out as much non-fatty material as possible; it is then known as acidulated soapstock. Black grease or black acids are analogous terms sometimes applied to acidulated soapstock. The commercial value of this acidulated soapstock lies in its content of fatty acids which are normally purified by distillation. Each type of soapstock is designated by the name of the parent crude oil source, as acidulated coconut soapstock, acidulated cottonseed soapstock, etc.

Although the total production of various soapstocks is quite large (1) and they have been produced and utilized for many years, very little has been published regarding their composition or characteristics. A few references can be found (1, 2, 3, 4, 5), but they deal only with processing methods or determination of total fatty acid content, moisture, etc. No comprehensive study of fatty acid composition or iodine value of authentic samples can be found in any U. S. publication. In the absence of any published information to the contrary, it might be assumed that soapstocks have the same iodine value as the parent oil, but it will be shown that such an assumption is not warranted.

Prior to about 1940 the dearth of information on soapstock characteristics was of little importance because the end-users of distilled fatty acids were not too critical. In recent years however the increased use of fatty acids as raw materials for the synthetic chemical industry has called for more exacting specifications. This is especially true in the case of acidulated coconut oil soapstock, for coconut oil contains a high proportion of valuable acids not found in any other common oil. Accordingly in an effort to obtain pure coconut oil soapstocks, some processors have set up maximum iodine value specifications on the assumption that anything above some arbitrary value indicates contamination. In the absence of any extensive list of iodine values of authentic acidulated coconut oil soapstock samples it was difficult to say what the maximum iodine value of an authentic pure product should be.

Accordingly samples have been taken from a number of regular tank car receipts of crude coconut oil, received from three separate producers over a period of two years. These samples have been laboratory-refined and the resultant soapstocks acidulated. Iodine values were then determined on both the refined oils and the corresponding acidulated soapstock. Iodine values have also been determined on laboratory acidulated samples of commercially produced coconut oil soapstocks for comparison to the laboratory refining results. And some data concerning the role of entrained neutral oil was obtained by a study of neutral oil free soapstocks. Similar studies on soapstocks from other oils are under way, and although they were not sufficiently advanced to include in this report, they will be referred to wherever necessary to prevent misunderstanding.

The data accumulated disclosed some interesting relations, which it is felt may be of general interest, not only to producers and processors of coconut soapstock, but also to fat-splitters or students of fatty acid behavior.

Analytical Methods

All the laboratory refinings were made by Method Ca9a41 from the Official Methods of Analysis of the American Oil Chemists' Society, and the resulting soapstocks were acidulated with sulfuric acid. After acidulation the samples were allowed to stand in tall thin cylinders at 90°C. for some time to remove excess moisture. They were then stirred with a little dry sodium chloride to remove the remaining moisture and filtered through qualitative filter paper. Iodine values were determined by the standard Wijs method, using a 30-minute reaction time.

In some cases the soapstocks are referred to as having been freed of neutral oil before acidulation. This was accomplished by dissolving a 10-g. sample in 50% ethyl alcohol and extracting repeatedly with Skellysolve F. The alcohol was then evaporated, the soap solution acidified with hydrochloric acid, and the fatty acids extracted with Skellysolve F. Obviously, this method extracted the unsaponifiable matter present along with the neutral oil so that soapstocks referred to as neutral oil-free were also assentially unsaponifiable matter-free.

Nitrogen blanketing was used in the preparation of some of the samples. No difference was noted between results obtained with or without nitrogen blanketing. In some similar work on acidulated cottonseed soapstock it was found that exposure of a small sample to air at 100°C. for 23 hours resulted in a change in iodine value of only 1.2 units.

Experimental Results and Discussion

A total of 13 samples were laboratory-refined and acidulated with the results shown in Table I. It is apparent that in every case the iodine value of the acidulated soapstock was higher than that of the refined oil by an amount much greater than could be accounted for by loss of glycerol. Coconut oil contains approximately 94.3% fatty acids (6), which means that the whole fatty acids should have an iodine value about 6% above that of neutral oil (7), whereas the minimum spread between any oil and soapstock recorded in Table I is over 40%, and the lowest free fatty acid content crudes produced soapstocks having iodine values nearly twice that of the corresponding refined oil. Furthermore the spread in iodine value between acidulated soapstock and refined oil was not constant but varied inversely as the free fatty acid of the parent crude oil. Reference to Figure 1, where these two variables have been plotted, will show that the correlation is quite good. The average relation is expressed by the equation, I.V. Spread = 9.5 − .759 FFA.

TABLE I

Iodine Values of Acidulated Coconut Oil Soapstock and the Corresponding Refined Oil

Sample identification			% FFA[a] crude oil	Iodine value	
Sample	Mill	Crop year[b]		Refined oil	Acidulated soapstock
1	2	1952	8.0	9.2	13.2
2	2	1952	7.5	8.7	12.4
3	2	1951	7.5	8.4	11.9
4	?	1951	7.3	8.3	12.6
5	2	1951	5.7	8.2	13.2
6[c]	3	1951	5.5	8.4	13.8
7[c]	3	1951	4.5	8.4	14.7
8[c]	1	1951	3.7	8.3	14.8
9	1	1952	3.5	9.0	15.7
10	1	1951	3.4	8.3	15.5
11[c]	1	1951	2.9	8.4	15.7
12	1	1952	2.9	9.5	17.0
13[c]	1	1951	2.7	8.4	15.8

[a] Calculated as oleic acid.

[b] This was actually calendar year in which received, not necessarily the year of production, but 51 and 52 samples were received 12 months apart.

[c] Yield of actual fatty acid in acidulated soapstock equaled 94-97% of refining loss from oil on these samples.

It is necessary at this point to inject a word of caution and to note that these results, obtained on coconut oils, cannot be used as a basis for determining the iodine value of soapstock from other oils. Similar data obtained on cottonseed and peanut oils have shown that they do not behave at all like coconut oil. Their soapstocks are almost invariably lower in iodine value than the corresponding refined oil, often by several units. This work on other oils is not complete, but sufficient data are available to warrant these statements.

After obtaining the results shown in Table I and Figure 1, on laboratory produced soapstock, it was desirable to have similar data on soapstocks from regular commercial refinings. Accordingly, samples of soapstock and refined oil were taken from a number of plant refinings, in which every effort to prevent contamination had been taken. The soapstocks were laboratory-acidulated and iodine values were determined. Results are shown in Table II and Figure 2.

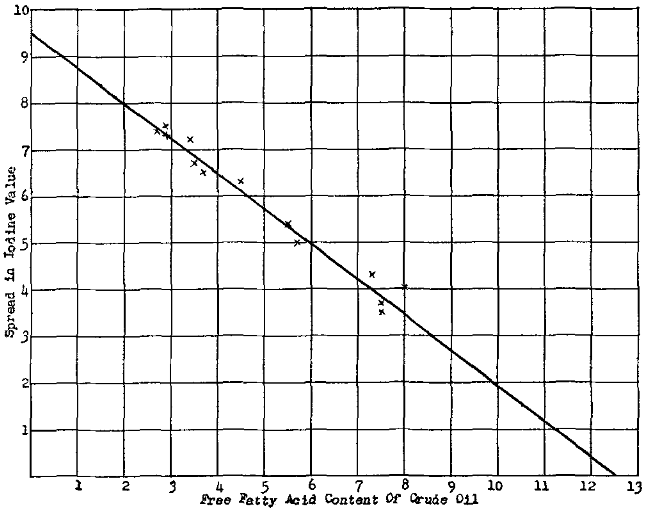

FIG. 1. Iodine value spread between acidulated coconut oil soapstock and the corresponding refined oil as a function of the free fatty acid content of the original crude oil.

Unfortunately the free acid range of the crude oil available for the plant study was not as great as that of the oils used in the laboratory refinings so that trends are not as clearly defined. However if the results are plotted on Figure 1, as has been done in Figure 2, it will be seen that 10 of the 15 points lie either on the average line or within 0.3 unit of it. From this it appears that regular commercial refinings usually follow the same trends as were found in laboratory experiments.

TABLE II

Iodine Values of Plant Produced Coconut Oil Soapstock Laboratory Acidulated

Tank number	% FFA[a] crude oil	Iodine value	
		Refined oil	Acidulated soapstock
P1	7.3	8.3	13.8
P2	6.4	8.2	14.4
P3	6.2	8.5	13.1
P4	6.0	8.4	13.4
P5	6.0	8.6	13.6
P6	6.0	8.8	13.8
P7	5.5	8.8	14.8
P8	5.0	8.9	14.3
P9	4.9	8.7	14.3
P10	4.8	8.2	14.1
P11	4.8	8.8	15.0
P12	4.8	8.4	14.3
P13	4.5	8.7	14.1
P14	4.1	8.4	15.1
P15	4.1	9.0	15.2

[a] Calculated as oleic acid.

There were however three commercial soapstocks (P1, P2, and P7) which evidenced higher iodine values than would be predicted from Figure 1, although the iodine value of the refined oils did not indicate any contamination. In fact, the refined oils corresponding to soapstock samples P1 and P2, which were the farthest out of line, were lower than aver-

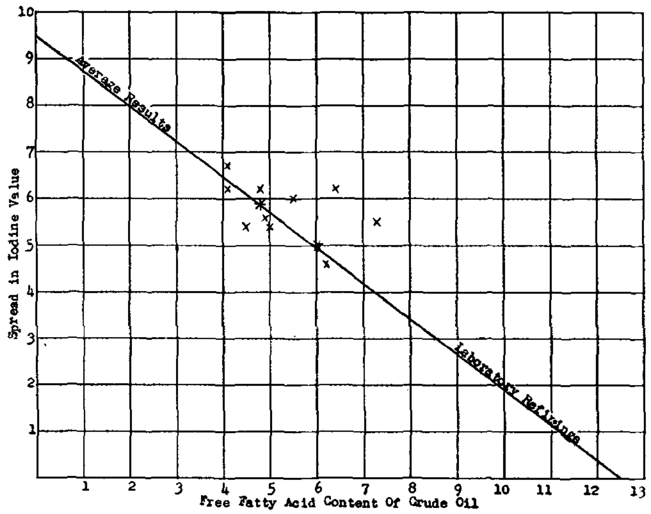

FIG. 2. Comparison of data obtained on commercially produced coconut oil soapstock to average results obtained from laboratory refinings.

age for coconut oil. It was suggested that the reason for these anomalous results might lie in variations in the amount of entrained neutral oil in the different soapstocks.

Accordingly four samples of laboratory produced soapstock were freed of neutral oil prior to acidulation as described under analytical methods. Results on the neutral oil free soapstocks compared to untreated samples are shown in Table III.

In every case the removal of the entrained neutral oil prior to acidulation resulted in a higher iodine value for the acidulated soapstock, and the difference is consistently close to two iodine value units. From this it appears that soapstocks from refining processes, which leave less neutral oil in the soapstocks than does the standard laboratory refining test, may have iodine values up to two units higher than is indicated in Table I and Figure 1. Since it is well known that commercial refining procedures often leave considerably less neutral oil in the soapstocks, it is believed that the high iodine value of soapstocks P1 and P2 in Table II was due partly, at least, to a very low entrained neutral oil content. Unfortunately the samples were discarded before this point could be checked.

TABLE III

Effect of Removing Neutral Oil Prior to Acidulation on Iodine Value of Acidulated Coconut Soapstock

Sample	Iodine Value			Iodine value difference
	Results from Table I		Same stocks neut. oil removed before acid.	
	Refined oil	Acidulated soapstock		
1	9.2	13.2	14.6	1.4
2	8.7	12.4	14.4	2.0
9	9.0	15.7	17.9	2.2
12	9.5	17.0	19.2	2.2

Theoretical Considerations

A detailed explanation of the phenomena brought out by the data in Table I and Figure 1 is outside the scope of this study, but a brief discussion is indicated. Preferential saponification, as used by Nicholsen and Formo (11) or Shuraev and Vasil'eau (12), might be suggested as an explanation, but it is not apparent how preferential saponification would account for the free fatty acid relations found. It seems more probable that, under the conditions existing in copra or crude coconut oil, there is a tendency for oleic acid to hydrolyze preferentially, so that crude coconut oils, which have undergone but little hydrolysis, will contain free fatty acids of higher iodine value than the average for the whole oil. Naturally as the relative proportion of fatty acids hydrolyzed is increased, the preponderance of short-chain acids present would reduce the effect of any such preferential hydrolysis proportionately, with a resulting correlation, between free fatty acid content of crude oil and iodine value of soapstocks, as is found in Table I.

That such a difference in the tendency toward hydrolysis of different fatty acids in coconut oil should exist is consistent with the known ability of low molecular weight acids to displace higher molecular weight acids from glycerides (8). And there are several references in the literature (9, 10, 11) from which it is possible to infer that such differences might be found, not only in coconut oil, but in other oils, although possibly to a lesser extent. Additional work to confirm this explanation would have been highly desirable, but the program, under which the data presented here was obtained, was directed only at the more practical aspects of the problem.

Summary

Analyses and comparisons of a number of representative samples have shown that acidulated coconut oil soapstock may have an iodine value as much as 100% greater than that of the corresponding refined oil without any contamination being involved. Exactly what the spread between any given soapstock and oil will be apparently depends on the free fatty acid content of the original crude oil and the relative efficiency of the refining process. It was found that, for coconut soapstocks produced by standard laboratory refining tests, the relation between free fatty acid content and iodine value spread can be represented by the formula I.V. Spread = 9.5 — .759 FFA. The efficiency of the refining process affects results insofar as it reduces the entrainment of neutral oil. Removing all of the neutral oil from four laboratory-produced soapstocks prior to acidulation raised the iodine value approximately two units in all cases.

The practical significance of these results is obvious. A refiner processing high grade crude coconut oil of 9.5 iodine value by a highly efficient refining procedure cannot be expected to produce an acidulated soapstock of less than about 18.0 in iodine value. With higher free fatty acid crude oil and less efficient refining procedures lower iodine values are possible, but since soapstock is of minor economic value compared to refined oil, the trend will always be toward better grade crude oils and more efficient refining processes.

Acknowledgments

The authors are indebted to E. D. Gile, superintendent of the Opelousas Oil Refinery, for assistance in obtaining samples and to Miss Audrey Gros of the S.R.R.L. for assistance with the literature search.

REFERENCES

1. Peterson, W. A., "Proceedings of a Six-Day Short Course in Vegetable Oils," A.O.C.S., Univ. of Ill., August, 1948.
2. Wurster, O. H., Govan, W. J. Jr., and Stockmann, G. J., "Cottonseed and Cottonseed Products," A. E. Bailey, editor, Interscience, New York, 1948, p. 812.
3. Jamieson, G. S., "Vegetable Fats and Oils," Reinhold, New York, 2nd ed., 1943, p. 155 and p. 206.
4. Bailey, A. E., "Industrial Oil and Fat Products," Interscience, New York, 2nd ed., 1951, pp. 646-49.
5. U. S. Patent 2,319,929.
6. Tomssen, E. G., and McCutcheon, J. W., "Soaps and Detergents," Macnair-Dorland, New York, 1949, p. 497.
7. Bailey, A. E., "Industrial Oil and Fat Products," Interscience, New York, 2nd ed., 1951, p. 136.
8. Same as 7, p. 40.
9. Gulino, E. A., and Newby, W., J. Am. Oil Chem. Soc., *26*, 418 (1949).
10. Arenson, S. W., and Heyl, E. G., J. Am. Oil Chem. Soc., *20*, 150 (1943).
11. Nicholsen, R., and Formo, M. W., J. Am. Oil Chem. Soc., *26*, 329 (1949).
12. Shuraev, G. I., and Vasil'eau, V., Chem. Abs. *35*, 6471.

[Received October 30, 1952]

Boiling Point-Vapor Pressure-Composition Relations for Trichloroethylene-Cottonseed Oil Miscellas

LIONEL K. ARNOLD, Professor of Chemical Engineering, and FU K. LIU, Formerly Graduate Assistant, Iowa Engineering Experiment Station, Iowa State College, Ames, Iowa

COLOR bodies are removed with the oil in the solvent extraction of cottonseed oil and must subsequently be removed from it in the production of an edible oil. If the miscella is heated to too high a temperature while removing the solvent, the color bodies may be "fixed" so that they cannot be removed by the usual refining and bleaching operations. It is desirable to have data on the boiling points of trichloroethylene-cottonseed oil miscellas at reduced pressures since in trichloroethylene extraction the solvent must be removed below atmospheric pressure to avoid overheating.

Harris (1) gives the distillation curves for separating and recovering solvents such as "Naphtha E" and ethylene dichloride from cottonseed oil. In the curves he compares the distillation ranges of mixtures containing 50% solvent and 50% cottonseed oil with the distillation ranges of the pure solvents at atmospheric pressure. Pollard, Vix, and Gastrock (3) reported the boiling point data at various concentrations of crude cottonseed oil and crude peanut oil over a range of pressures from 160 to 760 millimeters absolute in commercial hexane.

In the present investigation the boiling points of crude cottonseed oil-trichloroethylene miscellas of different compositions were determined. The trichloroethylene was of the commercial extraction grade having the following characteristics: boiling point at 760 mm., 188.4°F.; vapor pressure, 57.8 mm. Hg. at 68° F.; latent heat of vaporization (at boiling point), 103.0 B.t.u. per lb.; and specific gravity (liquid) at 68°/39°F. 1.464. The oil was a crude hydraulic oil.

Equipment and Procedure

A diagram of the apparatus used is shown in Figure 1. A 5-liter, 3-necked distilling flask equipped with a stainless steel stirrer operating at 250 r.p.m. served as a boiler. The shaft of the stirrer passed through a piece of glass tubing inserted in the cork stopper in the center neck of the flask. A short piece of tygon tubing was slipped over the upper end of the glass tubing with another piece of larger diameter tygon tubing over the upper end of the first piece. The space between the tygon tubing and the stirrer shaft was filled with silicone cock grease to act both as a lubricant for the shaft and as a vacuum seal. The mineral oil bath, 7, was heated by an electrical heating element inserted into the oil near the bottom. The bath was insulated with magnesia insulation. Vacuum was produced by an aspirator type of filter pump connected to the system through two ⅛-inch needle valves, 2, by means of which the pressure was controlled. A mercury manometer between flasks, 1 and 11, indicated the pressure in the system. Ice water was stored in a stainless steel container from which it was pumped to precooler, 5, and reflux condenser, 13, and then back to the container. Tygon and glass tubing were used to connect the various pieces of equipment.

In each run the composition of the miscella was kept constant while the pressure in the boiler was varied by adjusting the needle valve. Approximately 3 liters of miscella containing 10% oil by weight were fed into the boiler where it was heated from room temperature to boiling with the needle valve closed to give the lowest obtainable pressure. The miscella was stirred during heating below the boiling point. Stirring was stopped at the boiling point to prevent flooding into the condenser, 13. When the thermometer reading became constant, the temperature was recorded as the boiling temperature. During heating, ice water was circulated through the condensers to condense and return to the miscella any solvent which evaporated and thus keep the composition constant.

After the recording of the boiling point at the lowest pressure the needle valve was opened slightly to

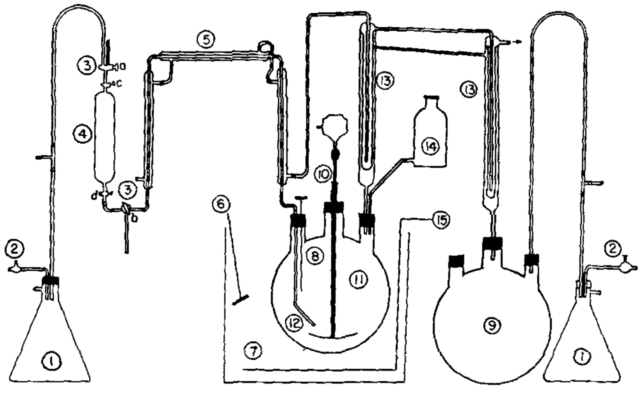

FIG. 1. Apparatus for determination of boiling point of oil-solvent mixture.

(1) 500-ml. flask; (2) ⅛-in. needle valve; (3) 3-way cock; (4) 200-ml. sampler; (5) precooler; (6) stirrer; (7) oil bath; (8) thermometer; (9) distillate receiver; (10) stirrer; (11) boiler; (12) sampling tube; (13) condenser; (14) feeding vessel; (15) heating element.