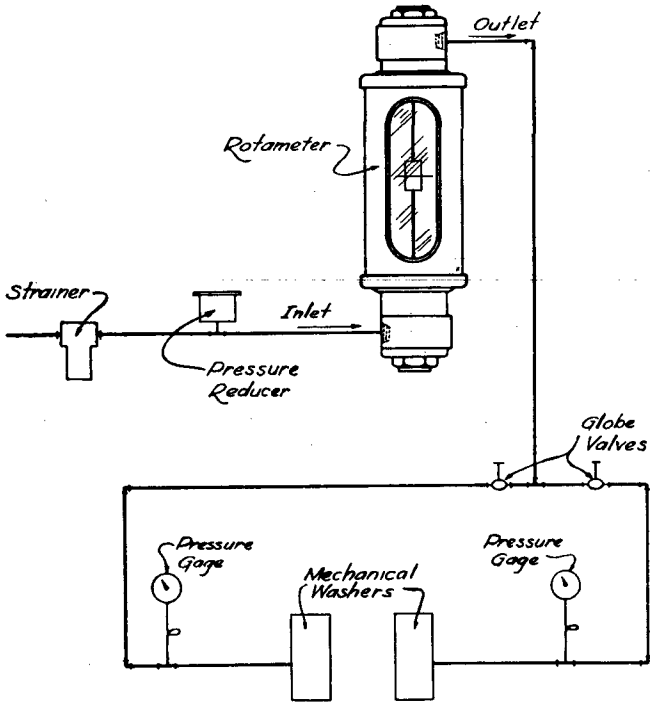

(Courtesy of Virginia Cellulose Division, Hercules Powder Company)

Installation of Rotameter on Mechanical Washers

It is seen from the above results that the wetting agent does not affect the yield of the lint. One-half c.c. red oil is added to each 525 c.c. of 1% caustic cooking solution.

Improvement 2—It was also suggested that we use a rotameter to measure exactly the amount of water used in washing the sample. The committee thought this was a good suggestion and we found that no work was required to approve the recommendation of the installation of the Fischer & Porter, No. 6 Master Enclosed Rotameter, Catalog Style Figure 735-P.

Recommendations

It is recommended:

1. That samples be sent out during the next year for the yield check analyses at least five times during the season.
2. That the method be changed to include the option of the use of red oil in wetting out the lint before digesting. These changes have been made in the Standard Analytical procedure which is attached.
3. That the Fischer & Porter Rotameter be installed as given in the attached sketch.

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C. H. COX
W. S. HUDE
E. H. TENENT
L. N. ROGERS, Chairman

Constant Pressure Oxygen Absorption Fat Stability Test

(General Foods Method)

R. GILMONT, H. S. LEVENSON and L. W. ELDER
General Foods Corporation, Hoboken, N. J.

Introduction

TESTS for measuring fat stability depend upon two factors, namely, one which imposes the accelerating conditions and the other which measures development of rancidity. In the oxygen absorption method the fat is subjected to an elevated temperature in the presence of an atmosphere of oxygen and the development of rancidity is determined by the volume of oxygen absorbed. The oxygen absorption method was used as early as 1924 (1).

References to subsequent modifications in the method were summarized in 1937 by one of the authors (2). A popular adaptation of this method to conventional equipment (Barcroft-Warburg apparatus) appeared in 1941 (3). Further adaptation of this apparatus was made in 1944 in which an emulsion of the fat is used as the sample (4).

The method to be described in the present paper is similar in principle to that which was used in studying the oxygen absorption of coffee oil (loc. cit. 2) and it differs from that published by Johnston and Frey (loc. cit. 3) in the following respects:

a) oxygen is absorbed under constant pressure and recorded volumetrically on a macro scale;
b) induction periods can be evaluated graphically from the direct plot of the experimental data without further calculation.

Method of Operation

Details of the individual burette are shown in Figure 1 and the manner in which the unit is mounted on the conventional Barcroft-Warburg stand for filling the apparatus with oxygen is shown in the photograph, Figure 2. Each unit carries its own mercury reservoir at a substantially constant level and the volume of oxygen absorbed is followed by measuring the equivalent volume of mercury accumulated in the bottom of the burette as a function of time.

All glassware is scrupulously cleaned by the following treatment:

a) degreasing with carbon tetrachloride;
b) soaking in boiling hot alkaline detergent solution and rinsing;
c) soaking in chromic-sulfuric acid cleaning solution overnight;
d) rinsing three times with tap water, twice with distilled water, and drying in a vacuum oven.

This cleaning procedure is applied regularly to the 50 cc. round-bottom oxidation flasks and transfer

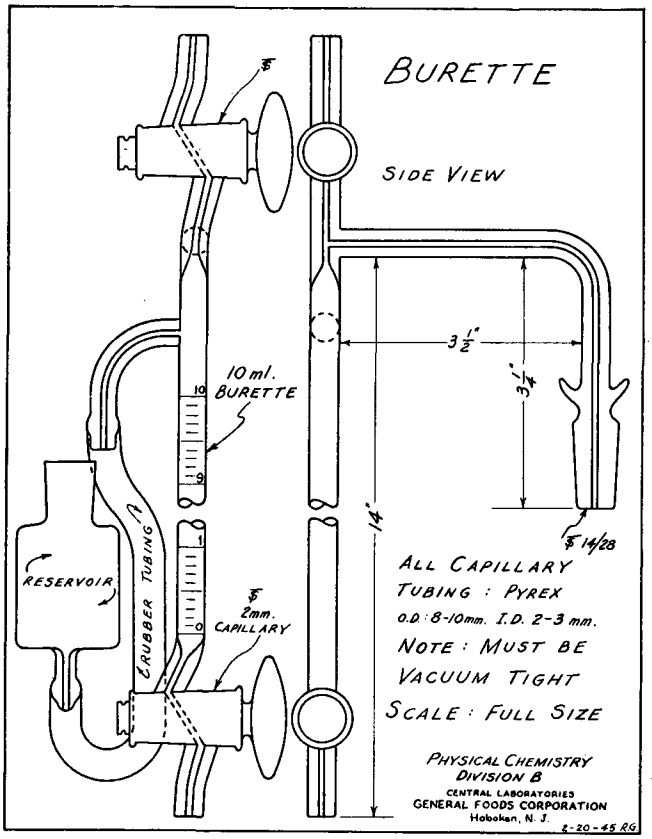

FIG. 1

pipettes. Facilities are also provided for periodically applying the same cleaning procedure to the entire burette assembly. It has also been found advantageous to add a small drop of trimethylene glycol to the mercury burette; this surface active agent increases the period of time for the fouling of the mercury to occur (5).

The method has been standardized to employ a 2 ml. sample which is pipetted directly into the round-bottom flasks. The flask is attached to the burette by means of spring clamps using a suitable grease

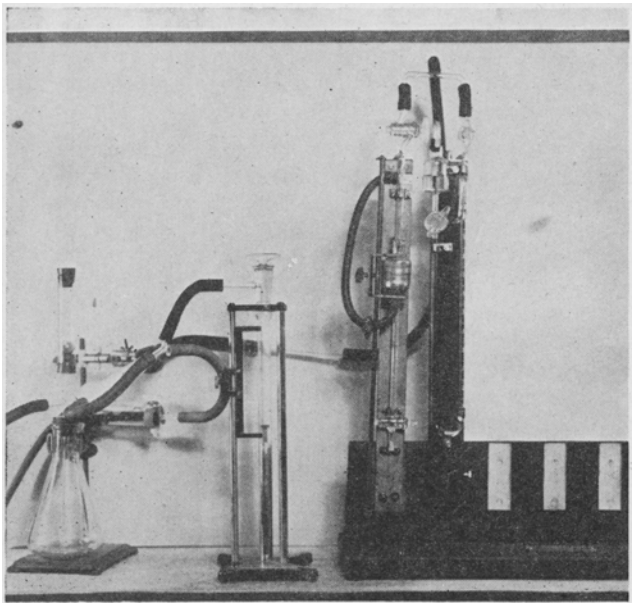

FIG. 2

(Dow-Corning Silicone has been found to be very useful in this respect; it is readily removed by using a 50-50 mixture of carbon tetrachloride and ethyl ether) and connected to the assembly for filling with oxygen as shown in Figure 3 and in the photograph,

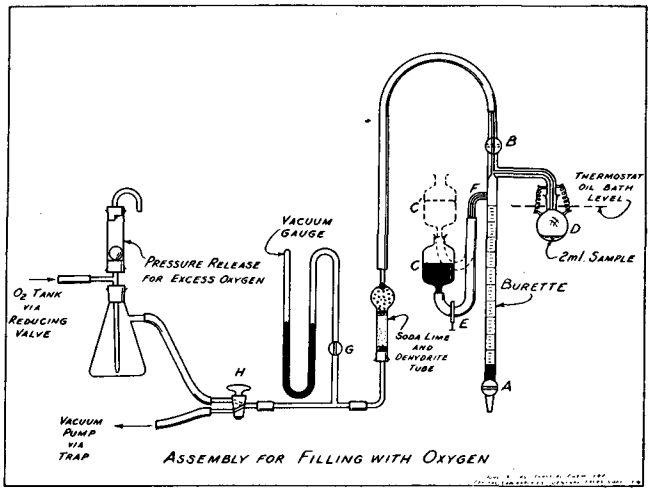

FIG. 3

Figure 2. Before connecting the rubber tubing from the oxygen filling assembly, mercury is drawn from the burette through stop-cock A to give a zero reading

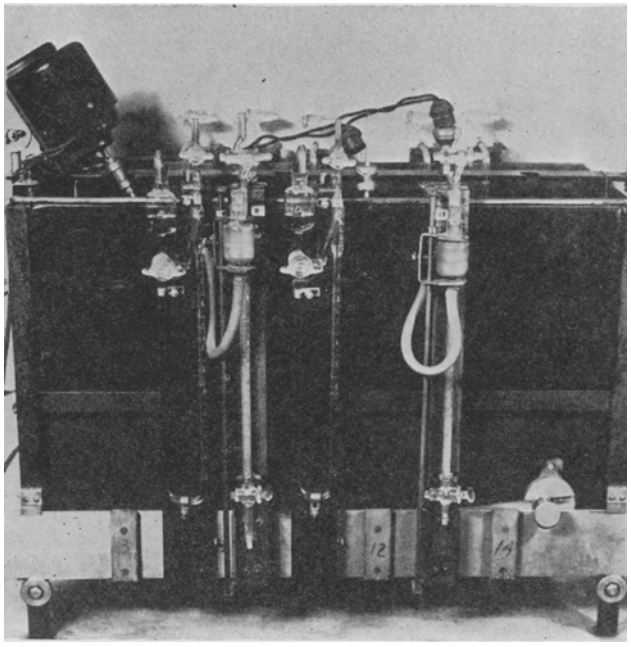

FIG. 4

and returned to reservoir C. After connection with the filling assembly, the reservoir is adjusted to position C, pinch clamp E is closed below the mercury level and stop-cock B opened to connect with the vacuum pump through stop-cock H. When the vacuum gauge indicates a minimum of residual gas in the system, oxygen is admitted through the three-way stop-cock H. The oxygen filling procedure is repeated with intermittent evacuation three times. Stop-cock B is closed and the burette assembly disconnected. It may be necessary to warm the sample in order to keep it in the liquid state so that dissolved gases are readily removed.

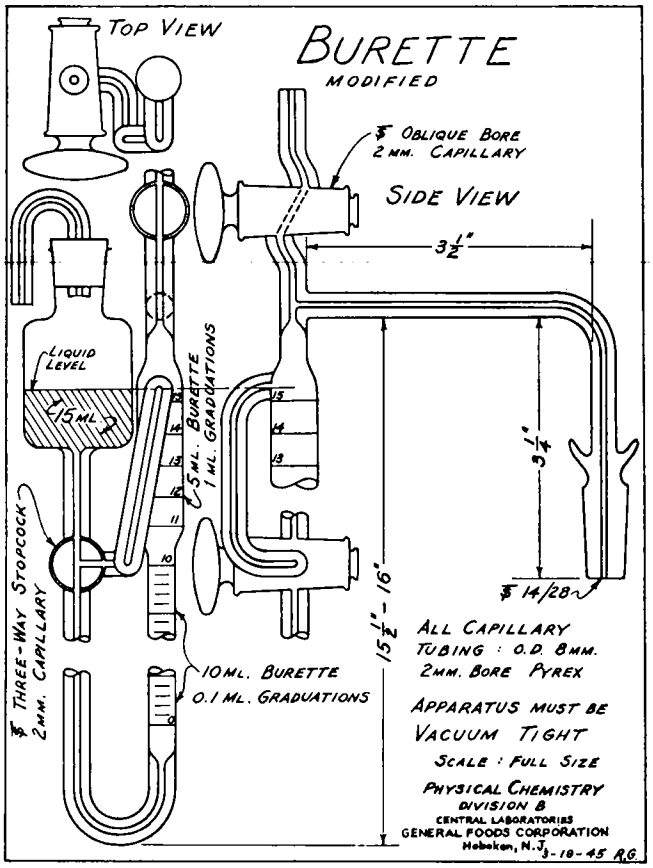

FIG. 5

Figure 4 is a photograph showing the individual units mounted on the shaking mechanism of the Barcroft-Warburg tank assembly. A bath temperature of 90° C. has been used in all our work on fats and oils although the same apparatus has been successfully used on more sensitive substrates at temperatures of 60 or 70° C. The oxygen filled burette is mounted on the shaking mechanism and allowed to shake at a rate of 100 cycles per minute and a 2 cm. stroke for 5 minutes when thermal equilibrium is usually reached. At this time stop-cock B is opened to bring the system to atmospheric pressure and then pinch clamp E is released. The reservoir is carefully raised to position C (a stop to mark this position has been found convenient) with stop-cock B opened until the mercury in capillary F is just at the point of spilling through the side tube into the burette. Stop-cock B is closed, a zero reading taken and subsequent readings taken on the burette at convenient intervals depending upon the stability of the sample.

It has been found that samples of unknown stability, if run more than one working day, can be carried over the following day by pinching the rubber tubing, removing from the thermostat and holding overnight at room temperature. Re-attainment of equilibrium at the bath temperature the following day indicates that negligible absorption has occurred during the overnight interval at room temperature.

Two methods have been found convenient in the preparation of samples containing added antioxidants. The first consists in carefully weighing out (on a micro or semimicro balance) the amount of antioxidant corresponding to the desired concentration in a given amount of substrate (usually 10 grams), then triturating to a homogeneous solution or suspension with the use of heat if necessary. When transferring the 2 ml. sample to the reaction flask, the mixture is thoroughly stirred, especially if the antioxidant is not completely dissolved. The effectiveness of relatively insoluble antioxidants has been amply verified in our experiments. The second method, which has recently been found to be preferable, involves weighing the corresponding amounts of ~~antioxidant and substrate directly into the flask. The~~ added difficulty in weighing such a small amount of antioxidant is more than compensated for by eliminating the triturating or homogenizing step; it also affords a more adequate check when duplicate runs are made. The use of molar concentration has been found expedient for theoretical studies.

Modified Burette Assembly *

Recently the absorption burette has been redesigned to avoid certain difficulties encountered with the units just described. The new design (Figure 5) makes possible the elimination of rubber tubing and reduces the weight of mercury carried. This makes for smoother operation of the shaking apparatus and extends the time interval during which the glassware remains free from fouling by impurities picked up by the mercury. We have found that the mercury may be replaced by di-butylphthalate containing a slight amount of dye resulting in the following advantages:

a) the length of time between cleaning is vastly increased;

b) the slight change in pressure due to change in level is made even more insignificant;

c) the weight of the entire assembly is considerably reduced. The new burette is also provided with an enlargement at the top which makes possible the location of additional points on the portion of the absorption curves following the end of the induction period (Cf. Figs. 7 and 8). For those samples which are permitted to run overnight, certain ones may unexpectedly complete their induction period before the next morning; this results in the mercury being carried over into the flask of the older designed unit. In the modified burette when all the liquid is sucked over by the completion of the induction period, air can be sucked into the system so that the above difficulty is eliminated.

This modified burette is now being adapted for automatic recording, the latest design of which is shown in Figure 6. A fine Nichrome wire of suitable resistance contained in the burette is connected to a multi-point resistance recording instrument. As the conducting liquid (mercury) fills the burette a proportional length of wire is shorted out of the circuit so that the volume of oxygen absorbed is proportional to the drop in resistance. As soon as more information concerning the experimental characteristics on this device is available, it will be published in a subsequent paper. The operation of the modified burette follows directly from that of the older design; however, a few pointers should be mentioned. To set the burette for a zero reading the three-way stop-cock is turned to connect only the two vertical tubes and

* These units may be obtained from E. Machlett & Son, 220 E. 23rd St., New York, N. Y.

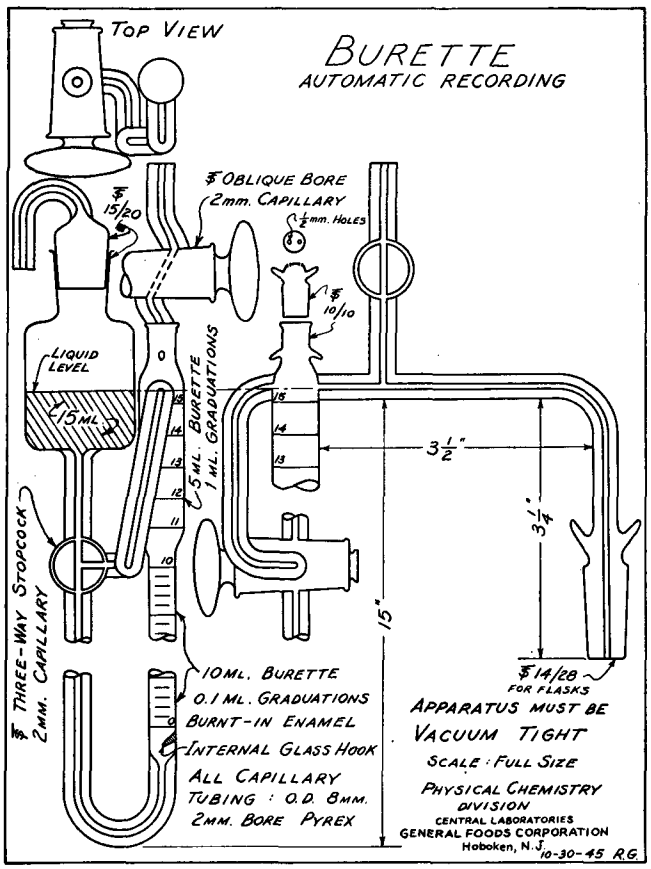

FIG. 6

slight suction is applied to the reservoir to bring the liquid in the burette to the zero graduation. For filling the burette with oxygen the three-way stop-cock is closed by turning to a 45° position. In this connection the U-tube serves as a closed end manometer and indicates when the unit is evacuated. The burette is equilibrated in the same manner as the older design except that the operation is considerably simplified. First, the excess pressure is released through the upper stop-cock after equilibration; then the three-way stop-cock is turned to connect only the upper tube and side arm; and finally, the upper stop-cock is opened to the air again, and when the liquid in the side arm is on the verge of spilling over into the burette the stop-cock is closed.

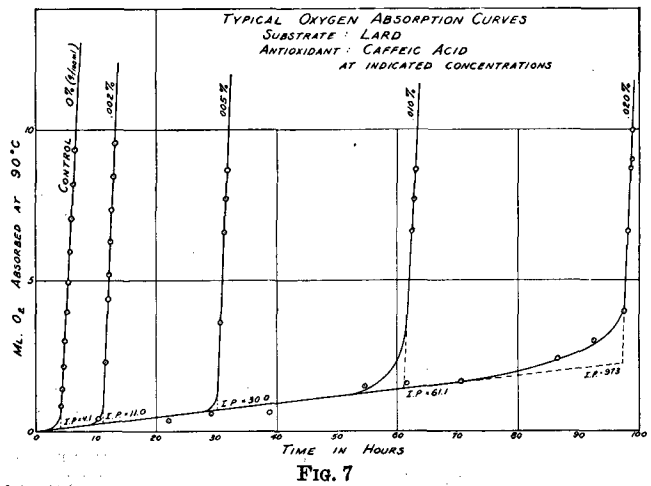

FIG. 7

Graphic Representation of Results

Figures 7 and 8 show the types of curves resulting from direct plots of the experimental data—ml. 0_2 absorbed vs. time elapsed—for an animal fat (lard) containing different amounts of added antioxidant and similarly for a vegetable oil (corn oil), respectively. The curve for each sample has two nearly linear branches, whose intersection locates the end of the induction period on the time axis. It will be noted that increasing amounts of antioxidant increase the length of the initial flat linear branch, so that pure lard, which is relatively free of naturally contained antioxidants, has hardly any such branch; whereas, corn oil, with no added antioxidants, shows a definite initial linear branch, from which it may be concluded that corn oil contains a considerable amount of natural antioxidants. Thus, in expressing the effectiveness of an added antioxidant care should be exercised in accounting for antioxidants already present in the substrate. In our laboratories the use of a standard substrate, such as methyl oleate, free of material antioxidants or other interfering substances has been considered as a preferable way of evaluating antioxidants.

Particular attention should be called to the fact that the induction period cannot be located reliably by observing the time required to absorb a definite volume of 0_2 nor by the initial slopes of the absorption

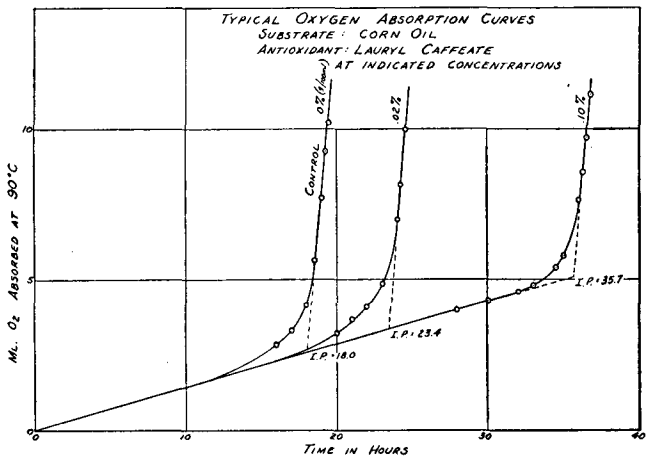

FIG. 8

curves unless prior calibration tests can be set up to show the validity of such procedure. For the samples represented, values of the induction period so obtained could be misleading. For example, in the case of corn oil, if the level of 2.5 ml. of 0_2 per 2 ml. of fat were used as a criterion, the added antioxidant would appear to have little effect in inhibiting oxidation. Likewise, the use of the initial slope, which appears to be independent of concentration for the above substrates and antioxidants, would fail to indicate the true antioxidant effectiveness of these compounds.

Variables Affecting the Procedure

(a) *Temperature control*

An error of 0.2° C. in bath temperature control, which is normally encountered with the bimetallic regulators supplied with the tank, is estimated to introduce an error of about 1½% in reaction rate. This is based on Mehlenbacher's reported temperature coefficient of the reaction rate (6).

A temperature change of 10° C. in the gas contained in the burette will cause an error of about 0.3 ml. when the burette is full of oxygen. The effect of this variation cannot be detected in locating the induction period.

(b) *Partial pressure of oxygen*

The effect of a slight variation in pressure due to the change of mercury level in the reservoir or to barometric fluctuations is expected to be negligible on the basis of the report by Henderson and Young to the effect that a five-fold variation in oxygen partial pressure is without effect on the magnitude of the induction period (7).

In the method here described pure oxygen is used in preference to air in order to maintain constant oxygen partial pressure and a high rate of absorption following the induction period, so that the break in the absorption curve can be easily distinguished under all circumstances.

(c) *Rate of shaking*

Preliminary experiments indicated that the induction period is independent of the rate of shaking, above a critical minimum. The rate employed (100 cycles/min.) is well in excess of this minimum.

(d) *Size of samples*

For sufficiently small samples, the induction period has been shown to be independent of the size of sample (8). A 2 ml. sample has been found to be quite adequate in the 50 ml. flasks employed.

Summarizing, the over-all effect of these minor variables makes it possible to reproduce the induction period of a given mixture with a precision of 1 to 2% in most cases or a maximum 5% variation in the most unfavorable cases.

Correlation with Organoleptic Test for Rancidity

Working with a wide variety of fats and oils we have to date encountered no exception to the observation that the samples are always free from rancid odor when observed prior to the break in the absorption curve and are unmistakably rancid at a reasonably short time interval following the break. We have also found excellent correlation between the oxygen absorption tests and storage tests at both elevated and room temperatures for polyphase as well as single phase systems, although, in the case of polyphase systems, several of the other factors such as rate of diffusion of antioxidant, mutual solubilities and interaction between the phases must be taken into account.

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Report of the Refining Committee 1945-1946

A resumé of the program of the Refining Committee for 1945-46, given in this report, includes comments on the following activities:

Report, Subcommittee—Glass Kettle Refining—June 8, 1945.
Report, Subcommittee—Centrifugal Method of Refining—October 30, 1945.
Report, Subcommittee—Modified Cup Method of Refining—October 10, 1945.
Meeting, Refining Committee—Chicago, Ill.—November 6, 1945.
Report, Subcommittee, Centrifugal Method of Refining—April 17, 1946.
Report, Subcommittee, Modified Cup Method of Refining—March 14, 1946.

Complete subcommittee reports and the minutes of the November 6 meeting as listed have been furnished the members of the Refining Committee. The considerable mass of data involved will make full publication in the journal this year inadvisable. A complete file will, however, be made available for the Society's records so that the information as to detailed results will be permanently available.

Glass Kettle Refining

A complete report of the work done by S. O. Sorensen's subcommittee (James, Milner, Kruse, Mitchell) was prepared by him under date of June 8, 1945. This report was furnished the main committee prior to the November 6 meeting and was discussed at the meeting. Procedure and results were said not to be promising, and at Mr. Sorensen's recommendation the committee agreed that the work on the glass kettle method for extracted soybean oil be discontinued as a subcommittee project.

Centrifugal Method of Refining

E. M. James presented to the November 6 meeting of the Refining Committee a report dated October 30, 1945, covering the latest results using the Centrifugal method. The following tentative conclusions were suggested from the program which had been carried out at the Lever Bros. and Sharples Laboratories:

1. When properly carried out the centrifugal method will give reproducible results.
2. It is probable that the time necessary to make a refining can be reduced to a considerable degree.
   [Note: First tests were made with 60 minutes' agitation cold (1200 R.P.M.) and 15 minutes hot (1200 R.P.M.). In later tests the times were one minute in the cold (700 R.P.M.) and 15 minutes hot (350 R.P.M.).]
3. In every case satisfactory foots were obtained, no trouble being encountered with soft or fluffy material.

The October 30 report indicated that if the Refining Committee thought it advisable to continue the Centrifugal method investigation, four major lines of study should be followed:

1. Collaborative work to test the reproducibility of the new method between laboratories (at least three collaborators will be available during the coming year).
2. The application of the method to expeller and hydraulic soybean oil as well as extracted.
3. A study of the possibility of reducing the amount of time now required for refining with the centrifuge.