# A New Method for the Examination of Textile Oils

## *An Original Procedure for Measuring Oxidizability to Predetermine Desirability of Oils for Textile Purposes*

*By* RALF B. TRUSLER[1]

PART I

RANCID odors, stickiness, and instances of spontaneous combustion — all of which are manifestations of oxidation —have led investigators to search for a means of predetermining the desirability of any fatty oil or fatty acid for textile purposes. The determination of the usual constants of fatty oils and acids has little bearing upon their behavior after they have been spread out in thin films upon either vegetable or animal fiber. Some method for measuring their oxidizability was obviously needed.

### *Types of Apparatus Requiring an Absorbent for the Oil*

ONE of the earliest methods for testing a textile oil was proposed by Mackey, who devised the Mackey Cloth Oil Tester (*Fig.* 1). It consists of a jacketed chamber into which is inserted a basket made of wire screen or other porous material. Fourteen grams of the oil to be tested is absorbed in 7 grams of cotton waste and placed in the basket. A thermometer with bulb placed in the center of the sample provides a means for observing the rise in temperature of the specimen. The container is first heated to approximately 100° C., the basket with the sample is put in place, and heating is continued. An arbitrary method states that a satisfactory oil should not exceed 100° on the thermometer in 30 minutes nor exceed 200° in one hour. Many arguments for and against this method have been given. The chief complaint seems to be the inability of different laboratories to obtain check results. Its simplicity is its chief advantage. One investigator[2] has demonstrated that check results in close agreement can be obtained on the same apparatus when due precautions are taken, and Aspegren[3] used a modified Mackey tester in making excellent comparisons between cottonseed oils containing variable amounts of free fatty acids. The Mackey method does not permit the examination of oils below 100°; this is a disadvantage because experience has shown that some fatty oils contain natural antioxidants which decompose at this elevated temperature. Factory conditions rarely require stability at 100°. More often, freedom from the effects of oxidation at 20° to 50° C. would be entirely satisfactory. Furthermore, this or any other method involving the recording of heat by means of a temperature registering device placed in a more or less insulating body like oiled cotton fiber is subject to peculiar errors, which will be described later.

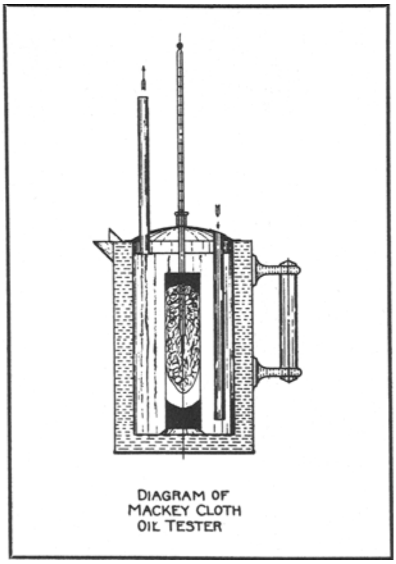

*Fig. 1*

In order to reduce radiation losses, Thompson[4] devised a tubular heater provided with an oil

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[2] R. E. Healy, Harkness & Cowing Co., Cincinnati, Ohio.

[3] H. Aspegren, Oil and Fat Industries, *6,* 19 (1929).

[4] N. J. Thompson, Industrial and Engineering Chemistry, *19,* 394 (1927); Oil and Fat Industries, *5,* 317 (1928).

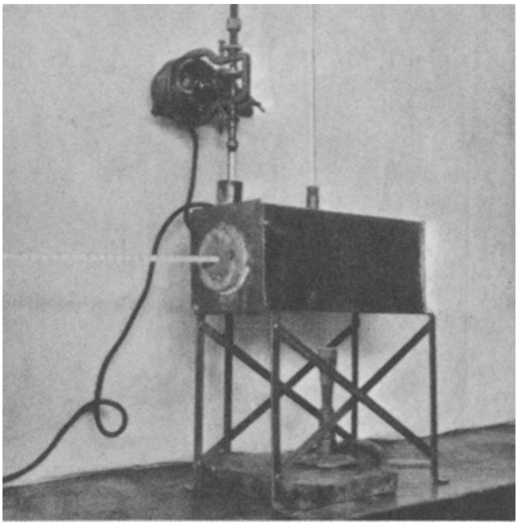

*Fig. 2*

jacket. The method was found to have advantages over the Mackey tester in that greater differences could be measured between different oils. A somewhat similar device of sheet copper (*Fig.* 2) was constructed in this laboratory for further study of the procedure. The heating compartment was 2½ inches in diameter and 12 inches long, surrounded by a jacket filled with oil. The temperature of the oil was maintained uniform throughout by means of a motor stirrer. It was hoped that this modification of the principle of the Mackey tester would provide a means for studying accurately the rate of oxidation of an oil at any temperature and for comparing oils in regard to their resistance to oxidation. It has been reported that, in using the Mackey tester, the results obtained vary with the type of fiber employed to absorb the oil sample and also vary with the amount of oil. Thompson observed these effects in his oil tester, and selected for convenient operation cotton waste as the absorbing medium and an optimum weight of oil.

If oxidation of an oil spread upon fiber of any sort is to proceed at a maximum rate, the reaction should be facilitated by providing a given sample of oil with a large surface of contact with the oxidizing medium. When oxidation takes place in air and in a device such as the Mackey tester or any modification, the greatest convenient surface is provided by wool, cotton, glass wool, or some other fine fiber. Experience has shown that wool and cotton fiber are most conveniently handled, and for economy and accessibility cotton fiber has the advantage. Furthermore, pure, greaseless, absorbent cotton is readily obtainable. Wool fiber has one advantage over cotton fiber in that it is more easily wetted with fatty oils.

It was found that considerable care was required to distribute the oil evenly upon the cotton fiber, and it should be mentioned here that unless the oil is evenly spread out upon the entire sample of cotton, ridiculous deviations in similar tests result. Thirty grams of absorbent cotton was unrolled into thin strips so that its area when spread out amounted to about 20 sq. ft. It was then sprayed with 15 grams[5] of oil and was rolled up into a bundle eight inches long to fit the tubular heating chamber. A thermometer was inserted in the center of the roll, and the outside was covered with a single piece of thin paper so that the roll might be easily slipped into the heating tube of the testing device.

After the oiled specimen of cotton had been placed in the heater, each end of the tube was partly closed by inserting a transite plug or stopper, through which were drilled four holes ¼ inch in diameter near the circumference and one ¼ inch hole in the center. The thermometer protruded through one of the center holes. Oxidation of the oiled cotton was brought by heating the oil jacket. In accordance with the recommendation previously made for this type of apparatus[6], the procedure consisted in keeping the oil bath 2° hotter than the temperature indicated by the thermometer in the specimen, and in making comparative readings upon the thermometer in the bath and that in the cotton. During the early part of the heating this is easily done, but during the last stages of the test the rapid rise of the temperature of the sample makes the control difficult. However, owing to a long heat lag through the cotton, very little error is caused from this source during the last twenty minutes of the experiment. By plotting the readings of temperature inside the roll of oiled cotton against time of heating, curves were obtained, some of which are shown in *Fig.* 3.

Peculiarities in the results made this method for examining oils inapplicable to the problem

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[5] Fifteen grams of oil was chosen as an optimum quantity because larger amounts had a tendency to drain off the cotton fiber and collect in the bottom of the heating tube.

[6] N. J. Thompson, loc. cit.

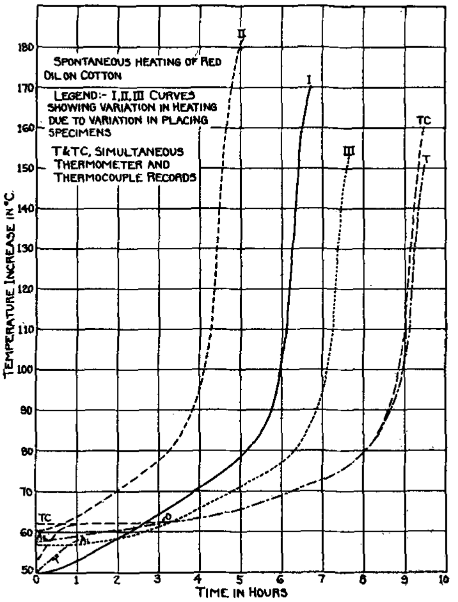


*Fig. 3*

at hand, as is illustrated by the curves, I, II, III, TC and T in *Fig.* 3. As was stated before, in most industrial work one is concerned with the stability of an oil at ordinary temperatures, for if an oil resists oxidation at temperatures of 25° to about 50°, there is very little opportunity for it to heat up spontaneously to accelerating temperatures. Hence, a suitable method for studying the resistance of an oil to oxidation must be one that permits an accurate history of its behavior at any temperature, a condition practically impossible with the Mackey tester or any modification of it.

Referring to the curves I, II and III, it will be observed that from 80° upward the curves are nearly identical, and that almost three hours difference in time was required to reach 80° for the specimen in the heater, represented by curve III, as compared with curve I, while the oil and cotton were identical in cases I, II, and III. If the time displacement upon this chart indicated a difference in three different oils—and, for example, it could be said that the oil represented by curve II became heated to 70° in two hours, while the oil represented by curve III required about five hours—it could then be stated that oil III showed a marked resistance to oxidation and therefore was much safer to use than oil II. However, the specimens are identical and the great deviation in the curves is due simply to the manner in which the specimens were placed in the heating compartment. An ideal sample (seldom equalled) gave the results shown by curve I, but if the cotton fiber were somewhat fluffier and slightly elongated in the heating tube, more rapid oxidation was obtained (curve II) while if the specimen was just slightly more compact, oxidation took place more slowly (curve III). Numerous experiments were made in an attempt to secure duplicate results, but these were obtained only occasionally.

An interesting experiment was conducted in order to determine the nature of the curve during its early, gradual slope. A specimen of oiled cotton was prepared in the usual manner. The thermometer was placed near the center of the roll as usual, and a thermocouple was placed one inch from the thermometer bulb and led off through the opposite end of the tube so that it did not come in contact with the thermometer. The jacket was quickly heated to 62° and maintained at constant temperature. A period of one hour was required for the thermocouple to reach the temperature of the bath, while the thermometer required about four hours. Although oxidation of the oil was progressing constantly during the three hour period represented by the portion of the curve TC to 0, not the slightest difference could be detected between the temperature of the oil bath and the cotton, as indicated by two similar thermocouples. This and other experiments demonstrated that temperature indicating devices have little opportunity for successful application to a problem of this kind, except where sufficient heat is evolved from rapid oxidation, as shown by the steep part of the curve.

A frequent lack of uniformity in degree of oxidation throughout the mass of cotton fiber is another reason why this type of apparatus gives inconsistent results. In some instances, after 150° to 160° was indicated by the thermometer in the cotton, the reaction was stopped as quickly as possible by pouring out the hot oil in the jacket and refilling with cold oil in order to arrest the reaction. When an inside temperature of 70° to 75° was indicated, the specimen could be moved without danger of catching fire. Specimens removed in this fashion demonstrated how diversely the oxidation can take place. Although great care was always taken in distributing the oil evenly upon the fiber and in rolling up the oiled cotton into a parcel of uniform density, in some of the experiments oxidation proceeded uniformly throughout (*Fig.* 4), while in others it was so

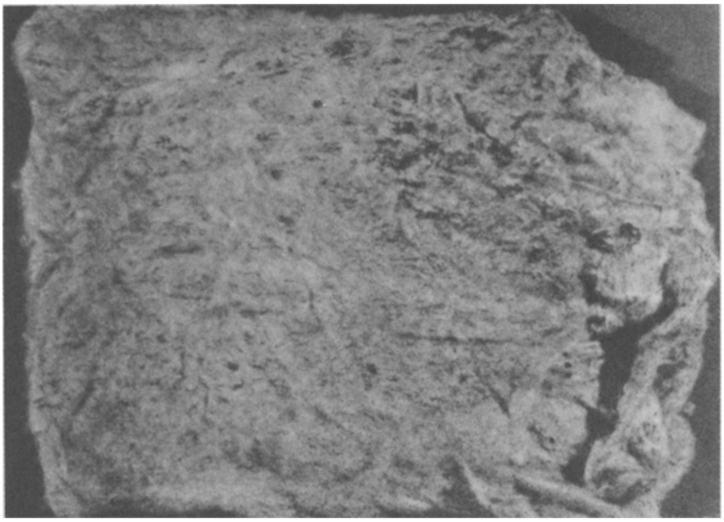


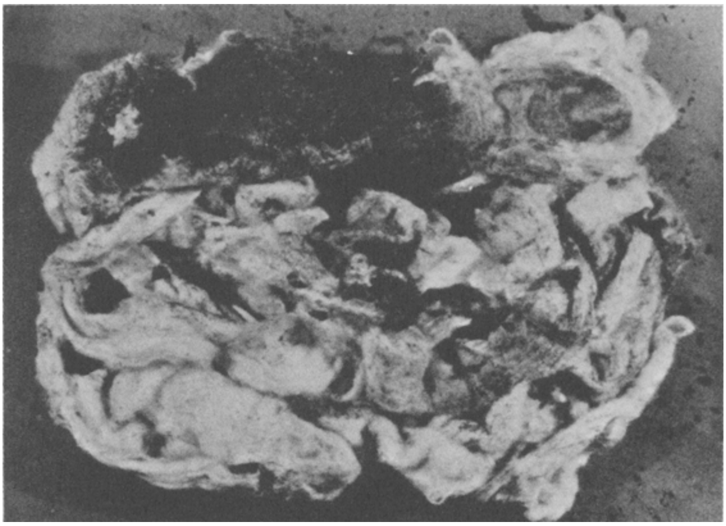
**Fig. 4**

**Showing appearance of cotton fiber after being subjected to uniform oxidation in Mackey testing apparatus**

intense in localized portions that the cotton actually charred (*Fig.* 5). Thus, in the latter case, nothing but irregular results could be indicated by the thermometer. Upon reviewing these experiments, it was obvious that any method dependent upon measurement of heat of combustion could not conveniently assist in the solution of the present problem. Although special calorimeters were considered, no attempt was made to utilize them because it was suspected that erroneous results might also be obtained from another source, namely, the entropy change due to polymerization, which takes place to a high degree with some types of fatty oils.

**Fig. 5**

**Cotton fibre after undergoing oxidation in Mackey testing apparatus under conditions resulting in lack of uniformity, with partial charring**

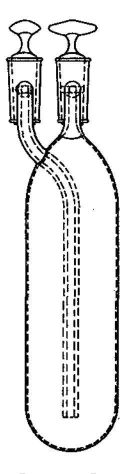


## *Apparatus for New Method of Testing Oils*

THE problem of measuring the susceptibility of an oil to oxidation involves only two materials, oxygen and oil, and it would therefore be most desirable not to introduce any other ingredient. Various types of apparatus were constructed in order to arrive at a satisfactory means for measuring the amount of oxidation at any temperature and for comparing the values of anti-oxidants. The experimental work demonstrated that quantitative oxidation of an oil wholly or only in regard to a double bond is not necessary, nor even an exactly desirable accomplishment, owing to the wide variations in composition of oils, which would thus require a complete knowledge of their constitution before an examination was made. Partial oxidation under uniform conditions permits a satisfactory examination since the susceptibility of an oil to oxidation is the important factor.

The apparatus that was designed for this investigation is shown in *Figures* 6, 7, 8, 9, 10, and 11 and consists of three parts: (1) the reaction bulb, (2) the gas measuring device, and (3) the shaker. The recation bulb (*Fig.* 6) in which the sample of oil and oxygen is contained, is made of pyrex glass and is approximately 138 mm. long and 40 mm. in diameter; it contains approximately 130 cc. This capacity accommodates 25 grams of oil and 100 ml. of oxygen. An inlet for oxygen is provided by a capillary tube, with a stop-cock attached to the top of the bulb. The sample of oil is admitted through a separate capillary tube (with cock) with an inlet near the bottom of the bulb.

The gas measuring device (*Figs.* 7 to 10) consists of a leveling flask A, containing mercury, a balancing manometer B, and a gas burette C. The leveling flask, of 300 ml. capacity, contains sufficient mercury to fill the tubing, to maintain a column in the stem S of the balancing manometer, and to fill the gas burette C. The flask is adjustable to any level by means of the ring clamp which moves along the iron support.



REACTION BULB

*Fig. 6*

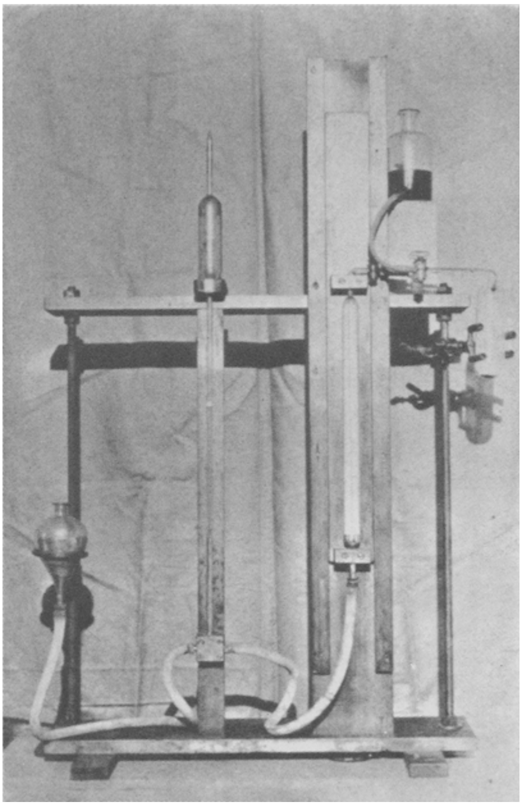


*Fig. 7*

The balancing manometer, B, serves as a means for attaining a standard pressure in the gas burette C when a volume of oxygen is to be determined. When the gas burette is at any given level. (*Fig.* 8) and the mercury column in the stem of the balancing manometer is at the same level as the mercury in the burette (indicated by the line L L), obviously the gas pressures in the two systems are equal. The proper level of the mercury in the stem of the manometer is determined in the manner described below, and is indicated by a mark M on the stem. If a volume of gas is admitted into the burette and the positions of the burette and leveling flask are adjusted so that the levels of the mercury in the stem of the manometer and the burette are identical at M, then the volume of a gas in the burette can be accurately measured in respect to the gas in the mano-

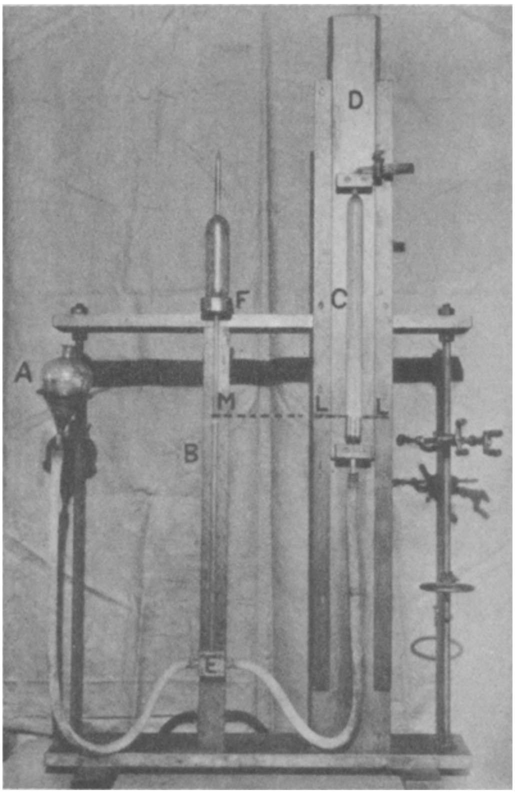


*Fig. 8*

meter and can also be compared with any other volume at any time, since in the two systems $P_1 = P_2$ and $T_1 = T_2$.

The balancing manometer B is constructed from a 100 ml. pipette. The tip should first be drawn out to facilitate its final sealing, and a stop-cock is sealed at the long end to aid in standardization. The problem now is to standardize the pipette at 20° (same as burette) and 760 mm. pressure. To find the volume occupied by 100 ml. at 20°, it is necessary only to draw up into the pipette 99.82 to 99.84 grams of water from a beaker upon a balance. The correct amount is easily obtained by means of the stop-cock, and the fine tip at the end of the pipette. The stop-cock is then closed and the pipette is inverted so that the water will drain out of the capillary tip, which now can be gently sealed on the end with a flame. The pipette is then inverted, tip down, and bubbles of air are displaced by careful manipulation. It is then immersed in a deep container of water at 20°, and, when sufficient time has elapsed to reach uniform temperature, the position of the meniscus should be recorded on the stem. One other mark should be established in the same way for 105 ml. The distance between the marks indicates the volume occupied by 5 ml. and can be divided into milliliters by marking off the divisions on a narrow strip of paper pasted on the stem. Any position on the stem of the pipette, which is to be the manometer, may be taken as the point M for leveling, as shown in *Fig. 7*, but in order to have some standard for reference so that identical results may be had upon another similar apparatus, or if the manometer has to be replaced, it is necessary to select a point corresponding to a known pressure. For convenience, the point corresponding to 760 mm. pressure was selected. The position on the stem is calculated by the relation $V = \frac{76 \times 100}{P}$ where P is atmospheric pressure. Then $V - 100$ is the increase in the volume of the gas at the present atmospheric pressure. For ex-

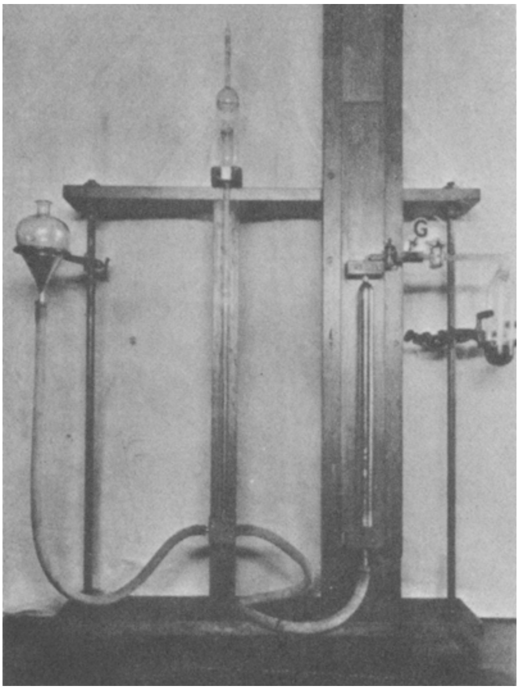


*Fig. 9*

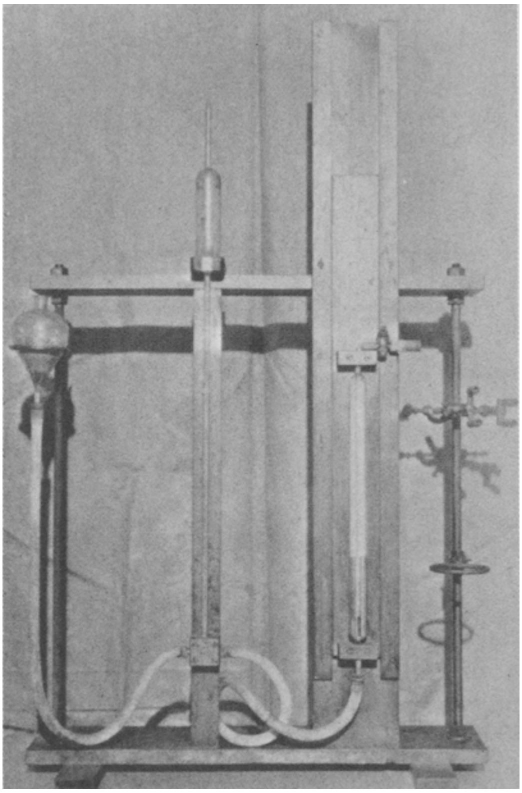


*Fig. 10*

ample, if the atmospheric pressure is 740 mm. while the pipette is being filled, 100 cc. at 760 mm. (assuming temperature constant at 20°) will occupy

$$\frac{760 \times 100}{740}$$

cc. or approximately 102.7 cc. This calculated point should be marked upon the stem of the pipette, and a correction is also indicated for room temperature over or below 20°. A small portion of the tip is now broken off and the water is drained out.

The stop-cock should be cut off and an extension with a "T" should be put in its place so that the entire length of the stem below the bulb is approximately 50 cm., as illustrated by *Fig.* 11. The pipette, which now constitutes the manometer, is mounted on the support (*Fig.* 9). The weight of the manometer is supported by the bracket F, and the glass "T" is protected by a wood block E, cut to fit. The manometer is connected to the leveling flask and to the burette with pressure tubing. Mercury is poured into the leveling flask until it overflows through the stop-cock, at the top of burette, which is closed to retain the mercury. A convenient elevation for the burette is shown in *Fig. 7*. Care must be taken to dislodge all bubbles of air in the rubber tubing. The next step is to raise the leveling flask high enough to send the mercury to the top of the manometer stem, thus displacing all the air. Then by lowering the flask and thus adjusting the level of the mercury in the manometer stem, dry air is drawn into the manometer until the meniscus stands at the mark (calculated for 100 ml. of gas at 760) at the atmospheric pressure and temperature at the time of filling (102.7 ml. in the case illustrated). The tip of the manometer is sealed with a blow torch. Although the mark first determined for 100 ml. at 20° is the one to be used( referred to as M— it would be well to preserve the milliliter calibration marks on the stem in case the manometer has to be opened and resealed at any time as this would do away with much unnecessary work.

The gas measuring burette, to which reference has frequently been made, is a standard 100 ml. gas burette provided with a stop-cock. The burette is held in place by wood cleats fastened to a support D, which slides in grooves and can be secured at any elevation by means of a thumbscrew on the back.

The shaking device (*Figures* 12, 13) provides the means for oxidizing oils under conditions that can be controlled and duplicated. This is accomplished by causing thorough contact between an oil and oxygen contained in the bulb while it is shaken in a heated oil bath. The reaction bulb is clamped at the end of a rocker (*Fig.* 12) by means of two screws, one in each circular metal band. The bands need to be tightened only sufficiently to prevent the

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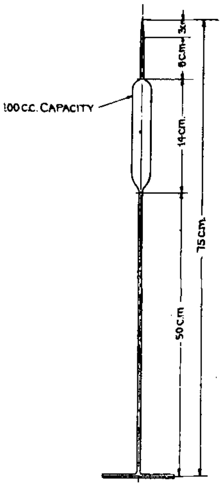


Manometer Tube

*Fig. 11*

## Textile Oils

*(From P. 57)*

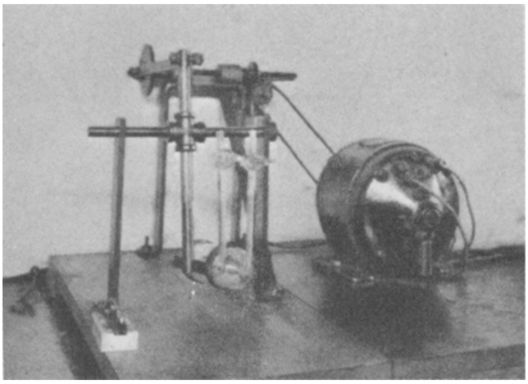


*Fig. 12*

bulb from slipping. The rocker arm is 14 mm. long from axis of shaft to the center of the bulb. The upper part of the rocker arm, from axis of shaft to the pivot of the rocker beam is 7.5 cm. The rocker beam is given a transverse motion by means of a rotating wheel, about which it travels in a circle of 36 mm. diameter at its point of attachment. The speed reduction to 140 r.p.m. on the driving pin is accomplished through a worm gear. Although the load is light, a substantial motor is recommended as a provision for constant speed. A ⅛ to ¼ h.p. motor, induction type, is preferable. The mechanical relations of the shaker are shown in the diagram of *Figure* 14. When in operation, the bulb is immersed in an oil bath (*Figure* 13) which is electrically heated by a coil of resistance wire along one side and at the bottom of the oil container. A glass plate cut to fit the bottom of the pan prevents the oil from shorting. The temperature of the oil bath is regulated by suitable resistances. A medium or heavy motor oil serves very well for the bath. It would be advisable to construct the pan with ends about three inches higher than the sides (not shown in the photographs) to reduce splashing.

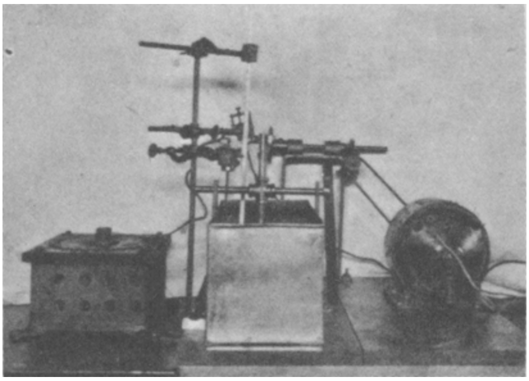
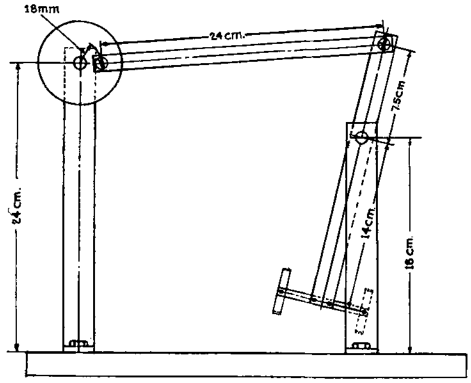


*Fig. 13*



LEVER RATIOS OF SHAKER

*Fig. 14*

*(To be continued)*

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## Margarine Legislation

*(From P. 65)*

margarine. N. F. O'Dea, of the Baltimore Butterine Company, testified that dairy interests had opposed the sale of margarine before foreign oils were used.

Mr. Pearsall testified further that, from records of the Department of Agriculture, there were 113 judgments against creameries for adulteration of butter in 1929 and 144 in 1930, whereas in ten years the only judgment against margarine was one instance of packages being overweight, this being a violation of the internal revenue laws.

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The Neuhoff Packing Company, Nashville, and its subsidiaries, the Nashville Cold Storage Company and the White Provision Company, Atlanta, have been purchased by Swift & Co., Chicago, for about $3,000,000 plus inventories at current prices.