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 II

Method of Applying the Test

TO examine an oil for its behavior toward oxidation by means of this apparatus, the first step is to place the specimen of oil in the reaction bulb. The bulb should be clean and dry and the cocks greased with a heavy stopcock grease. The tare of the empty bulb is determined, and to it is added 25 grams. This total gross weight will be constant for all experiments. The bulb is then partly exhausted by applying a vacuum, and then by dipping the inlet tube (the capillary tube extending to the bottom of the bulb) into the oil to be examined and opening the cock, the correct weight of oil can be drawn in. A convenient way to determine the weight of the bulb and contents is to suspend it from the hook of a sturdy balance by means of a wire hanger. If too much oil has been drawn in, the bulb can be filled with air under slight pressure, and then by opening the cock the excess oil will drop out while the bulb is still suspended from the balance. The bulb is next connected to a vacuum pump, at the short capillary tube, and exhausted to 2 mm. or less. Air amounting to 2 mm. pressure does not cause an objectionable error for most work. The bulb can be pumped out while the 100 ml. of oxygen are being measured.

The burette of the gas measuring apparatus is lowered to the position shown in Figure 10, filled with mercury, and then elevated (Fig. 8) so that the 100 ml. mark is on the same level as the calibrated mark "M" on the manometer. This level can be indicated with a pencil mark on the wood support as it will be constant for the same calibration of the manometer. The leveling flask is dropped to about the same level as mark M. Oxygen supplied through rubber tubing under slight pressure is then admitted through the stop cock until the mercury level is somewhat below the 100 cc. mark on the burette. Then by adjusting the leveling bulb and letting out a little oxygen the mercury level can be exactly adjusted at 100 ml. With the stop cock firmly closed, the burette is again lowered so that the zero mark is level with M (or line L). A short piece of pressure tubing, G, (Figure 9) must be tightly fitted on the burette. The reaction bulb, which has now been thoroughly exhausted and the stop-cocks securely closed, is connected to the burette through the short piece of pressure tubing. This connection with the bulb is made with the short capillary that goes directly to the top of the bulb. By opening the stop-cock on the bulb and that on the burette, the oxygen is quickly admitted. It is a good plan to twist a piece of wire around the rubber connection at both ends as precaution against leakage. After the oxygen has been transferred to the bulb, the stop-cocks are closed and made tight by rubber bands, and then the bulb is fastened in the clamps of the shaker. In mounting the bulb in the shaker, the inlet and outlet tubes carrying stop-cocks are upright and always out of contact with the oil.

Oxidation in the bulb at room temperature goes on so slowly that no appreciable error is introduced during the periods of loading or unloading. The time the specimen is subjected to oxidation is counted from the instant the motor is started until it is stopped. Of course, unnecessary delay in starting the motor and in removing the bulb after the reaction must be avoided.

After the bulb has been shaken for an optimum time of one hour and at the desired temperature, it is removed from the oil bath, wiped dry, and again attached to the burette which has been somewhat elevated (*Figure 7*). The connection with the burette is made with the same capillary through which the oxygen was

---

[1] Industrial Fellow, Mellon Institute of Industrial Research, Pittsburgh, Pa.

introduced into the bulb. As a matter of precaution against oil being drawn into the burette, a small cotton plug should be placed in the rubber connection, and renewed after each determination. The problem now is to transfer the unused oxygen from the bulb back into the burette so that it can be measured. This is done by filling the bulb with oil[7] as the residual oxygen is drawn into the burette. Oil for filling the bulb is supplied from a 250 cc. leveling bottle, through rubber tubing. Care must be taken to exclude bubbles. The cock on the oil inlet side is opened to allow oil to replace most of the absorbed oxygen, and then the balance of the gas is drawn into the burette by opening the cocks and lowering the leveling flask. When all of the oxygen has been drawn into the burette and the bulb is full of oil, the cock on the burette is closed and the bulb is removed.

The amount of oxygen taken up by oil can be measured by leveling the mercury in the burette with mark "M" on the manometer. Although the volume of oxygen now in the burette may be considerably less than the original, it can be accurately measured in terms of the original volume, for again in both systems $P_1 = P_2$ and temperature is the same for both volumes of gas.

The bulb is made ready for a new determination by washing it out three times with a little benzene and drying by suction.

A little discussion should be devoted to the selection of the rate of shaking (140 per minute) and the time of heating the reactants in the oil bath (one hour). The rate of oxidation of an oil in this apparatus depends upon the susceptibility of the oil to oxidation and upon how intimately the oil and oxygen are brought into contact. The former condition we cannot control, but the latter is variable and is the one with which we are concerned mechanically. It was mentioned before that oxygen would be absorbed slowly if the bulb remained still, but oxidation in this type of container under static conditions would involve a long time and much inaccuracy. On the other hand, reaction is facilitated by shaking, as greater surface contact is obtained.

Experimentation showed that an optimum rate of shaking could be selected, such that a small increase or decrease would not seriously affect the results. Too rapid shaking involves the danger of breaking the reaction bulb and also causes too much splashing of oil from the bath. To remedy this, consideration was given to heating and shaking the bulb in a hot air oven, but too much time was required to bring the bulb and contents to the desired temperature, compared to oil bath immersion where the bulb and contents can be heated in about one minute. A short period for reaching the proper temperatures is an essential feature in reducing unconformity between different tests, and this is best accomplished by immersion in a heated liquid.

One hundred forty shakes per minute is an arbitrary value, based upon the conditions just described. Other speeds might have served as well, but the nature of the experiment requires that all of the mechanical ratios and the speed of shaking must be constant during a series of tests if comparable results are required, and that the specifications must be adhered to if similar results are expected from two or more individual outfits.

Temperature and Time Considerations

In applying the technique just described to the examination of oils, it was necessary to assume some fixed time for the period of shaking in the oil bath. Series of oxidation tests were run upon a technical oleic acid that was known to be moderately oxidizable. The first set of determinations was made for a period of 30 minutes each through the temperature range of 35° to 95° at intervals of from 2.5° to 5°. By plotting the volume of oxygen absorbed

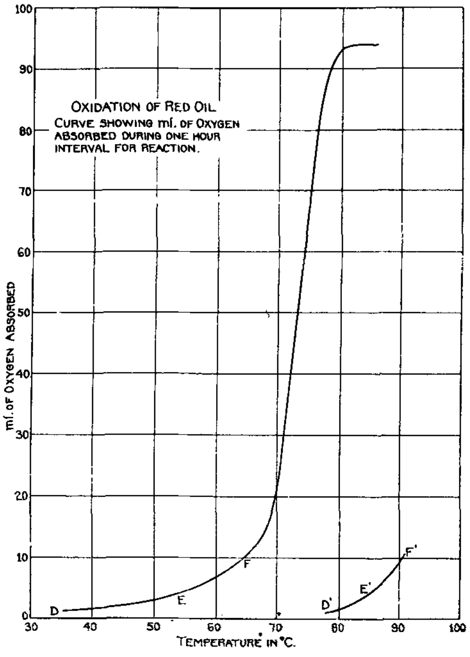

Fig. 15

---

[7] The same oil as used in the experiment, oil residues from oxidation tests, or any free running oil can be used for this purpose.

(as ordinates) against the temperature, curve A (*Figure* 15) was obtained. A set of determinations was similarly made for periods of one hour (Curve B) and for two hours (Curve C).

The resemblance of the curves is striking, as they follow the same general slope and are parallel for the greatest part of their length. It was found that determinations upon slightly oxidizable oils do not have a satisfactory degree of reaction in 30 minutes to permit representation by curves, while readily oxidizable oils deplete the supply of oxygen through a too long period of shaking. Since 30 minutes and 2 hours both appeared to be extremes, one hour was selected as the best time for reacting oxygen and an oil in the shaker.

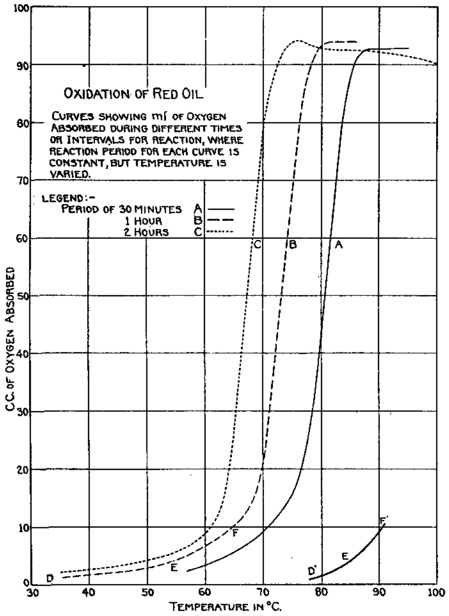

Fig. 16

Important information bearing upon this method for examining oils is revealed by the curves. A difference in the rate of oxidation at ordinary temperatures can be measured with ease and accuracy without first heating the oil to 100° (as in the Mackey tester) or higher with the consequent destruction of any naturally occurring, low temperature anti-oxidants. It also demonstrates that oxidation is accelerated by increased temperature. The reliability of this method over a wide temperature range for indicating the susceptibility of an oil to oxidation is shown by the nearly straight curves from the point where oxidation becomes rapid up to where less than 20 per cent of the original volume of oxygen remains in the bulb, and even more strikingly by only moderate deviation in the rate of absorption until scarcely more than 2 cc. of gas is left and the pressure of the gas in the bulb has dropped to about 4 centimeters.

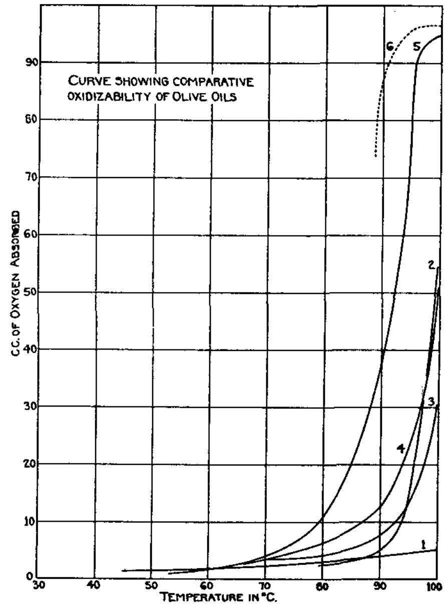

Fig. 17

Fatty oils appear to pass through three stages of oxidation. At low or ordinary temperatures, oxidation produces temporary peroxide combinations[8], which are associated with the subsequent occurrence of rancidity. Increased temperature during oxidation causes stable oxygenated compounds to be formed. At high-

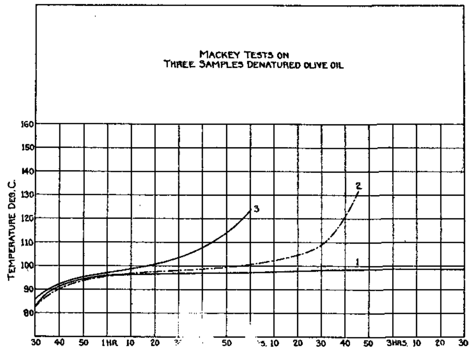

Fig. 18

---

[8] G. E. Holm, G. R. Greenbank and E. F. Deysher, Industrial and Engineering Chemistry, *19*, 156-8 (1927).
W. L. Davies, Chemistry and Industry, *47*, 185 T (1928).

er temperatures, oxidation resembles combustion in that carbon dioxide is evolved. This last reaction is most common with unsaturated fatty acids. The downward dip in Curve C, *Fig.* 15, was found to be due to the generation of carbon dioxide which gave an increase in the volume of gas in the tube. Determinations of the temperature or temperature-time factors which are responsible for the production of CO_2 have not yet been made.

Accuracy of the Method

DUPLICATE tests upon oils and check runs at various temperatures were frequently made in order to note the accuracy and consistency of this method for examining oils for their tendency toward oxidation. It was found that with ordinary care taken in exhausting the bulb, protection against leaks and in leveling the burette, results can be easily duplicated to within 0.2 cc. (approximately 0.2%) deviation. In some cases moisture affects the results and it is therefore advisable to employ dry oils.

The question naturally arises whether or not one is justified in substituting oxygen for air in determinations upon the stability of oils, especially, since most instances of oxidation occur in air. In so far as the measurement of the degree of oxidation to which an oil is susceptible, is concerned, oxygen provides a more accurate means because the total volume shrinkage can approach 100%, while with air only approximately 20% is possible. Of course the method might be modified so that a larger volume of air could be used in respect to the weight of the oil sample, but the size of the apparatus soon becomes cumbersome. Oxygen provides a more energetic treatment without thermal decomposition, and if an oil can be shown to resist oxidation at temperatures above normal under such treatment, its safety and resistance to any form of oxidation in air is reasonably assumed.

Accepting the arbitrary period for shaking of one hour as a standard, B (*Fig.* 16) is a representative curve and is subject to certain interpretations. The portion D-E-F designates the conditions for moderate oxidation. Below 54° (at E) oxidation takes place at a comparatively slow rate. From E. to F, or from 54° to 65°, the oil is more reactive, while above 65° oxidation becomes rapid. If this oil were used in some technical process wherein it would be spread out in thin films and well insulated, as in the case of certain textile operations where considerable amounts of wool, for example, may be oiled for lubrication during the stages of processing, oxidation would be enhanced owing to the large surface contact with atmospheric oxygen. The susceptibility of the oil upon the fiber to oxidize would then be dependent upon the temperature. The fiber always entrains sufficient air to provide oxidation, and therefore penetration of air into the pile is not necessary for the reaction. In fact, good circulation of air through a pile of oiled fiber is one means for carrying away accumulated heat and provides a factor of safety against what is usually designated as spontaneous combustion. It may be said, then, that below 55° oxidation would not be particularly dangerous, providing that the heat of reaction can be led away.

Suppose that another textile oil was found to be more resistant to oxidation and could be represented by the hypothetical curve D'E'F'. In this case, only appreciable oxidation would occur at 85° (E). Owing to an increased dispersion of heat at higher temperatures, there is little probability of oiled fiber reaching this temperature with the meager amount of heat accumulated from such a slow rate of oxidation, and the possibility of reaching F becomes remote. Therefore, while the oil represented by the Curve B is a possible hazard[9], an oil whose susceptibility to oxidation might be shown by a curve similar to D'-E'-F' could scarcely be the source of any danger from any spontaneous and rapid combination with oxygen.

Comparison of Results of the Mackey Method and of the New Method of Examining Oils

INASMUCH as many commercial laboratories are accustomed to qualifying textile oils by the Mackey method and specifications, it became advisable to make a few determinations upon textile oils by this means in order to determine if the results of one method might be interpreted in terms of the other. At the present time it can be said only that the two methods are comparable to a reasonable degree, but that the Mackey test may produce some unexpected differences when the data are compared with those of the oil-oxygen method.

A comparison of the results of the two methods of examination is depicted by *Figures* 17 and 18.[10] In Figure 17 are shown curves representing the susceptibilities of oxidation of six different specimens of denatured olive oil. The oil represented by curve number one was the least affected by the treatment, while oils num-

(*Turn to page* 109)

---

[9] Depending upon factory conditions, as previously explained.

[10] From data contributed by Stanley Goranflo, Wilson-Martin Co., Philadelphia, Pennsylvania.

The science and technology of refining edible oils has been greatly enhanced during the past ten years since 1920-22, when Drummond and Zilva experimented with palm oil. By applying the accumulated experience in selecting good raw materials the American Refiner can produce at present an edible palm oil which is palatable and which contains an abundance of vitamin A, equal in potency to some butters and in some cases more potent than the average butter.

It is also known that vitamin D usually accompanies vitamin A. At the time Drummond made his feeding experiments in 1922 there was no differentiation made between these two vitamins. Spectrophotometric examination made on a good sample of palm oil indicates that it may also contain vitamin D to the extent of about five units per gram.

◆

Textile Oils

(From page 106)

bers 5 and 6 were rather easily oxidized. When oils numbers 1, 2 and 3 were tested by the Mackey method, they gave the results shown in *Figure* 18. By comparing the curves obtained by the two different methods it can be seen that the Mackey test bears an agreeable relation to the new method in the appearance of the curves, which of course indicate oxidation at considerably higher temperatures.

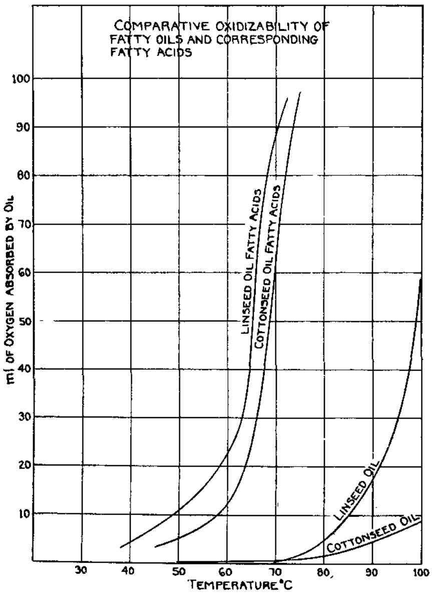

Fig. 19

Application of the New Method to the Study of Oils

THE new method for examining oils permits numerous applications to problems dealing with the behavior of oils toward oxidation. For example, the presence of unsaturated, free fatty acids in a glyceride were found to render an oil more sensitive to oxidation.[11] This effect is clearly presented in the curves of *Figure* 18.

The accuracy of this test permitted an extensive study of textile oils, in regard to their stability in the presence of oxygen, and also gave a means for evaluating numerous antioxidants and for measuring their effect upon oxidizable oils. The evaluation of antioxidants, untreated and stabilized oils is presented in another publication.[12]

---

[11] H. Aspergren, *loc.cit.*

[12] See Textile World, March 8, 1930.

◆

Cohune Nut Cracking

A new type of dekerneling machine for cracking babassu, cohune, coquita and similar tropical oil-bearing nuts has been perfected by a machine designer of Plainfield, New Jersey, according to reports. The machine is said to be capable of handling nuts of any size and of cracking them open regardless of the shell thickness. The equipment is more than six feet overall height and weighs about two tons. The nuts are dumped into a large hopper, thence being fed to ten dekerneling units through separate tubes. The mechanism of operation is said to be quite simple. As the operation is started, the nuts pass from the hopper through the feed tubes into correct position within the machine. Heavy plungers then descend, rapidly driving sets of tungsten steel cracking chisels into the shells. As the cracking chisels rise, the broken shells automatically spread out. Shells, husks and kernels are thrown onto a sieve which vibrates in a horizontal plane, instantly separating the kernels from the husks and the shells. It is claimed that the machine recovers the kernels entirely undamaged, seldom even scratched.

◆

The Department of Commerce requests all manufacturers of mayonnaise to return the questionnaires covering the department's survey of the mayonnaise industry for 1930, at the earliest possible date. The results of the department's previous survey of the industry were of tangible value to all mayonnaise manufacturers.