

# Recording Apparatus for Measuring Oxygen Absorption<sup>1</sup>

E. B. LANCASTER, E. D. BITNER, and R. E. BEAL, Northern Utilization Research Branch,<sup>2</sup> Peoria, Ill.

SINCE THE ORIGIN of fat technology as a science there has been a continuing interest in the selection of a method for predicting the shelf life of edible fatty products. Tests range in complexity from statistically controlled studies of human sensory responses to determination of the time required for the product to absorb a given quantity of oxygen. Each method entails special problems in sample preparation, in manipulation of the testing apparatus, and in interpretation of the results.

In connection with studies on the hydrogenation of soybean oil a convenient method of determining the stability of the product was desired (1). An apparatus was devised therefore which measures and records the pressure of oxygen in a heated flask containing a small amount of a deodorized, hydrogenated oil. By the use of a simple open mercury manometer and an elementary electrical circuit, the induction time in hours to reach the break-point of the oxidation curve was determined. Other workers have also been of the opinion that the length of the induction period of an oil or fat when it is subjected to oxidation is the most meaningful simple criterion of stability (2).

More recently the oxidation apparatus has been used to study the stability of global spread, a mixed composition of vegetable oil, monostearins, salt, and other ingredients, since peroxide values of samples of this material oxidized by the Active Oxygen Method were not reproducible (3). The success of the investigation suggested that the absorption method of determining stability would be more applicable to a variety of food products than existing methods. Also, a good measuring and recording device should find general applicability in a wide variety of operations where changes in gas pressure over an extended period of time are to be measured.

The manometer and electrical circuit employed in measuring the stability of hydrogenated soybean oil is shown diagrammatically in Figure 1. For the test a 1-g. sample of hydrogenated oil was weighed into a 250-ml. flask, which was then placed in a heated bath. The flask was connected by a ground glass fit-

ting and rubber tubing to the 3-way stopcock on the manometer through which the system was evacuated and filled with oxygen. The connecting rubber tubing should not be exposed to elevated temperatures which cause it to react with the oxygen. The extension of the atmospheric leg of the manometer below the U-portion retains a pool of mercury under all conditions, thus preventing an open circuit between the electrical elements which would place too high a voltage on the recording potentiometer. The electrical circuit shown here was found to be fairly satisfactory in translating change in mercury level to the proper d.c. voltage necessary to drive a conventional recording potentiometer. It is the purpose of this paper to discuss this circuit and a newer one which incorporates important advantages.

## Resistance Circuit

The circuit of Figure 1 operates as follows. A low current passes through a rheostat and a milliammeter, through a resistance element which is inserted in the open leg of the manometer, and back to the power source. The mercury acts as a shorting conductor, and the resistance in this part of the circuit increases as the pressure drops on the system side of the manometer. The change in resistance produces a change in the voltage across the element, and a potentiometer connected to the leads of the element measures and records this voltage. In actual practice several elements are connected in series, and the individual voltages are recorded by a multi-point recorder. Thus it was possible to run as many as eight tests concurrently by using a 12-point recorder. The four remaining points measured bath temperature, room temperature, cold junction temperature, and, indirectly, the current in the circuit. The magnitude of the current was indicated by the drop in potential across a fixed resistor which had about half the resistance of an element. The instrument was one designed for use with iron constantan thermocouples at a range between 0° and 400°F. (-16° and 204°C.). About 10 mv. is sufficient to produce full-scale deflection of the indicator.

The value of the resistance of the control rheostat may be computed by Ohm's law from the expected battery voltage, full resistance of the element, and the e.m.f. required for full-scale meter reading. An essentially constant flow of current through each element is desired. Since the value of the current at any time is inversely proportional to the sum of the resistances of the control rheostat and the exposed element, it is advisable to design the circuit so that the resistance of the element is less than 0.1% of the resistance of the rheostat. This is especially true if several elements are to be connected in series.

The electrical principle involved in this circuit has been employed by others, who have found that nichrome wire was the most satisfactory material for constructing the sensitive element in their particular cases (2, 4, 5). The first elements which we employed were constructed of 18-gauge nichrome wire. These were found to be impractical because of their excessive drain on the current from the 1.5 v. dry cell

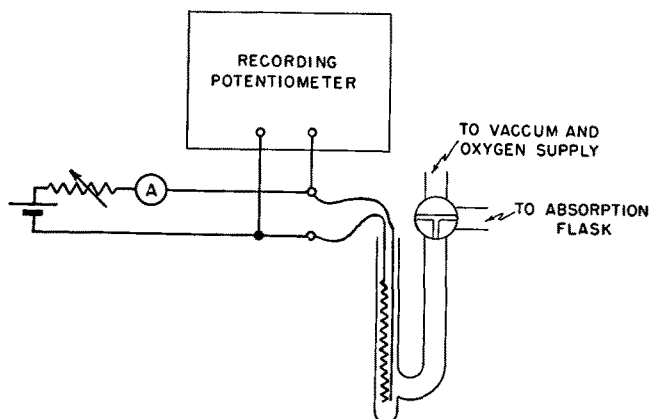


Fig. 1. Schematic diagram of resistor circuit.

<sup>1</sup> Presented at the meeting of the American Oil Chemists' Society, New Orleans, La., April 17-20, 1955.

<sup>2</sup> One of the Branches of the Agricultural Research Service, U. S. Department of Agriculture.

batteries in use at that time. The current requirement was decreased by constructing the elements of 26-gauge nichrome wire. Later an inexpensive, direct current power supply was substituted for the batteries (6). Because of the low voltage across the mercury-nichrome contact, considerable difficulty was encountered at first in maintaining a good contact. In fact, this trouble seems to be universal for a system of this sort, especially when the contact area is exposed to atmospheric conditions. The systems described elsewhere require meticulous preparation of the nichrome and mercury before satisfactory operation can be obtained. It was found that, if about 1 ml. of approximately 30% sodium hydroxide solution and a small piece of metallic aluminum were added to the element leg of the manometer, the mercury would wet the nichrome wire fairly well for a length of time varying from 3 days to 2 weeks. Cleaning consisted of removing the element temporarily, removing the caustic solution, rinsing with fresh caustic, refilling with caustic, and replacing the element.

A resistance element was tried which was constructed from several turns of fine copper wire wound on a small core. The copper-mercury surface has good contact properties, but as the mercury becomes oxidized and otherwise contaminated, there is a tendency for it to bridge across individual turns of the resistor, giving an erratic reading. If the turns are spaced far enough apart, the operation with copper resistors is at least as satisfactory as it is with nichrome wire. In any event the mercury must be removed from the manometer and cleaned at least once every 2 months.

**Inductance Circuit**

Recently another electrical system has been placed in operation. The design is somewhat more complicated, but experience with it to date indicates that it is superior to the resistance type. The schematic diagram of the electrical circuit is shown in Figure 2.

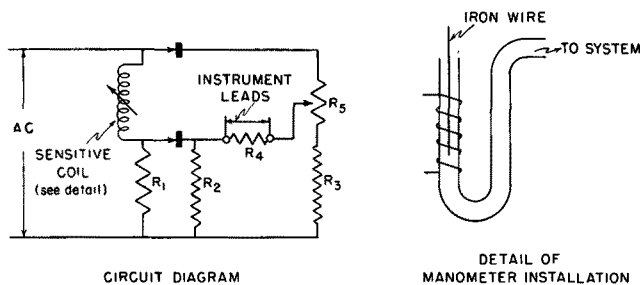


FIG. 2. Schematic diagram of inductance circuit.

Operation is based on the principle that the inductance of an air-core coil will increase if iron is inserted into the core. In this case an iron wire, floating on the mercury in the manometer, is lowered into the core as the mercury level drops. A low-voltage, 60-cycle current is applied to the coil in series with a resistor,  $R_1$ . The a.c. voltages on either side of the coil are rectified by the germanium diodes, and the resulting d.c. voltages are applied to the potentiometric circuit to the right. This d.c. circuit is designed so that the drop in voltage due to the reactance of the coil with no core may be balanced in such a way that a slight negative voltage may be applied to the meter.

Of course, the values of the components may be chosen to give the best performance with the particu-

lar meter and manometer used as accessories to the circuit. In our application the values and ratings are given in Table I.

TABLE I  
Parts List for Constructing Circuit Shown in Figure 2.

Part	Specifications
Coil	700 turns of 23-ga. cotton-covered copper wire on 8 mm. i. d. non-magnetic core 3" long.
Float	14-ga. iron wire 5.5" long in 4 mm. o. d. glass tubing, sealed at bottom and with 3 spacers on periphery.
$R_1$	100 ohms, 5-watt resistor.
$R_2, R_3$	1,000 ohms, 1-watt resistors
$R_4$	100 ohms, 1/2-watt resistor
$R_5$	100 ohms, wire wound potentiometer
Diodes	2 each general purpose (1N34 or equal) at each location.
Power source	Secondary of 3.2-volt filament transformer, rated 2 amps. max. secondary output. Loaded with 25 ohms, 10-watt resistor across secondary windings.

The typical response in instrument reading as the core moves into the coil is shown in Figure 3. It will be noted that the response is not linear over the first and last portions of the curve. In operation, the float containing the iron wire is removed from the manometer, and the control ( $R_5$  in Figure 2) is adjusted so that the instrument records at the lower end of the

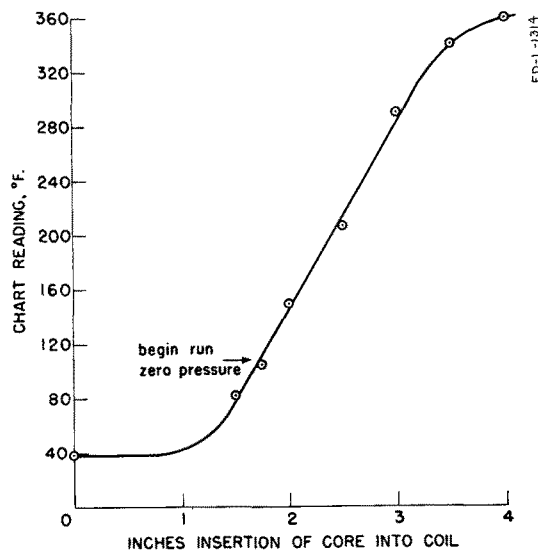


Fig. 3. Response curve for inductance circuit.

scale. The float is then replaced in the manometer, and the coil is moved to a position such that an instrument reading on the linear portion of the response curve is obtained. The manometer is then connected to the flask, and any subsequent movement of the float is recorded by the instrument as a deviation from the zero setting.

The low cost and ruggedness of this circuit should make it an attractive one for application to pressure measurement in general. Due to the lack of electrical contact with the manometric fluid, it should also be applicable to oil or water manometers, thus increasing the sensitivity of a variety of operations involving the measurement of pressure. The proper design of a float for oil or water is one of the problems encountered.

Figure 4 is a tracing of an actual curve obtained with the inductance apparatus. The sample was a deodorized soybean oil. The straight line in the center is the bath temperature during the run, and the line on the left side is the cold-junction temperature

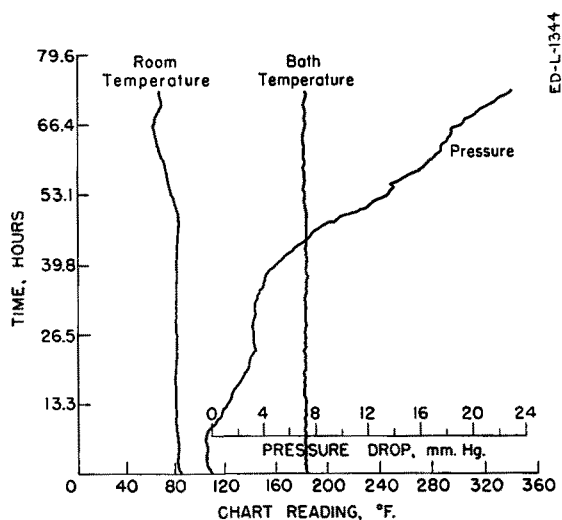


FIG. 4. An oxidation curve obtained with the inductive apparatus.

at the instrument. The recorder was attached to a timing clock so that a complete cycle was printed only once every half hour. The graph represents a 73-hr. run. It will be noted that the upper portion of the curve appears to deviate from linearity. This is due to the fact that the printed points for e.m.f. reflect changes in temperature at the cold junction. If the cold-junction compensator had been removed from the instrument, a straighter curve would have been obtained; but the bath temperature curve then would have shown a deflection due to changes in the ambient temperature. From this curve the major break-point can be easily seen. Approximate calculations to convert scale readings to standard cc. of oxygen absorbed indicate that, on this curve, a 100-degree change represents 2.1 cc. absorption. Since a 1-g. sample was used, the break-point occurred after about 0.8 cc. per gram was absorbed, and at a time of about 38 hrs.

The entire apparatus is extremely simple and thus requires only a moderate amount of care in the operation. The simplifications employed do introduce questions as to the theoretical accuracy of the system. For example, the use of atmospheric pressure as a

reference for the pressure changes which occur in the closed flask will cause some fluctuation due to barometric pressure changes. The magnitude of change is a characteristic of the system design, and its effects can be computed. For the curve shown in Figure 4, a 1-in. change in barometric pressure will cause a 4-mm. change in mercury level, or about 6% of the total change observed. For extremely precise measurement therefore the system should be modified or the readings corrected for the fluctuations in barometer, line voltage and frequency, instrument calibration, and so forth. Where determination of the absolute magnitude of oxygen absorption is of minor importance in relation to determination of the time at which the change of rate or break-point occurs, the additional expense of including these refinements becomes unwarranted.

### Summary

Two sensitive but inexpensive electrical circuits have been described which translate change in mercury level in a manometer to an electromotive force of sufficient magnitude so that it may be applied to a standard d.c. potentiometric recorder. The recording manometer, when coupled with a simple closed system containing a small amount of lipid material and oxygen or air, can be adapted to determine continuously the cumulative absorption of oxygen by the oil or fat. The break-point, a measure of the stability of the sample, may be obtained from the resulting curve. The apparatus has been successfully employed to determine the oxidative stability of hydrogenated soybean oil, and because of the small amount of attention required, it should be readily adaptable to quality control of edible oil and fat products. The recording manometer should be useful also for measuring and recording pressure changes in other systems.

### REFERENCES

1. Beal, R. E., and Lancaster, E. B., *J. Am. Oil Chemists' Soc.*, **31**, 619-625 (1954).
2. Gilmont, R., Levenson, H. S., and Elder, L. W., *Oil and Soap*, **23**, 248-252 (1946).
3. Lancaster, E. B., Beal, R. E., Jones, E. P., Dutton, H. J., Evans, C. D., and Cowan, J. C., *J. Am. Oil Chemists' Soc.*, **32**, 9-13 (1955).
4. Price, R. P., and Zemany, P. D., *Rev. Sci. Inst.*, **21**, 261 (1950).
5. Svec, H. J., and Gibbs, D. S., *Rev. Sci. Inst.*, **24**, 202-204 (1953).
6. Sylvania Electric Products Inc., New York, N. Y., "Electronic Shortcuts for Hobbyists," 26-27 (1951).

[Received August 15, 1955]

## Fractionation of Heat-Bodied Linseed Oil with Urea and Acetone

T. N. MEHTA and S. A. SHARMA, Laxminarayan Institute of Technology, Nagpur University, Nagpur, M.P., India

THE POSSIBLE MODES of heat polymerization are numerous, and the mechanism of polymerization proposed by Kapplmeier (1) and Scheiber (2) is generally accepted. However there is not much unanimity of opinion about the constitution of products formed during the reaction. Such studies are complicated by the fact that mixed glycerides undergo inter- and intramolecular reactions besides cyclization to form complex linear and three-dimensional polymers.

Many workers have investigated the principal reactions that take place during the heat-bodding of oils containing triglycerides that have two or more

polyene fatty acid groups. The reaction may be intermolecular between the fatty acid components of two different glycerides or may be intramolecular between two fatty acid components of the same glyceride molecule, resulting in the formation of an intrapolymer (intradimer) and some loss in unsaturation. The intramolecular reaction may also take place in a single fatty acid component of a triglyceride molecule. Hydrolysis of this product yields a cyclic monomer fatty acid. The rate of the polymerization reaction is measured by the drop in iodine value and increase in the molecular weight. Generally the molecular weights are found to be lower than that which would be ex-