



## An Improved Apparatus for Oxygen Bomb Testing<sup>1,2</sup>

A.R. COOPER, D.P. MATZINGER, and T.E. FURIA, Dynapol, 1454 Page Mill Road, Palo Alto, California 94304

### ABSTRACT

An improved oxygen bomb apparatus has been developed. The increased precision and readability of the continuous pressure recording allows a new method of end-point measurement. It was possible to use smaller test samples than any previously reported. Sample size and oxygen pressure were shown to be relatively unimportant variables. Temperature is the most useful variable for controlling test time. This is preferable over sample dispersion or addition of catalysts in terms of simplifying the procedure. Peroxide formation at the oxygen bomb test end point is three to four times the value at the end point of the Active Oxygen Method.

### INTRODUCTION

The need for an accelerated test to predict oxidative stability of fats, oil, and food products or to determine the effectiveness of antioxidants is well established. Typically, elevated temperatures and oxygen pressures are used to obtain experimental data in reasonable time. The most convenient tests are those based on a continuous measurement of oxygen pressure. The oxygen bomb test was developed (1,2) for fats, oils and food products from an ASTM test, which determined the oxidative stability of petroleum products (3,4). Typically, sample weights were 15-30 g, and the bomb was pressurized to 50-100 psig oxygen pressure (1). Later (2), it was found that the test period could be significantly decreased by dispersing a fat sample on a cellulosic material (Kimpac, Kimberly-Clark Corporation). Dispersion was not desirable when oils were tested because explosions occurred. A further modification to decrease test time was reported (5) in which a copper catalyst was introduced into the system. The test time has also been decreased by using higher temperatures (6) or by dispersing the test material on 4 mm glass balls (7).

In this report, an improved oxygen bomb test apparatus is described, and the effects of operational variables on the inhibition period were investigated.

### EXPERIMENTAL PROCEDURES

#### Design Considerations

The ASTM oxygen bomb (OB) test (4), as presently conducted with a commercially obtainable unit, generally uses a mechanical pressure measuring device (Foxboro 0-200 psig, 2 psig divisions), maintained at ambient temperature, connected to the heated pressure cell by a hollow metal tube. Volatile materials distill from the hot cell into this cold tube, and frequent cleaning is required. The pressure measurement is recorded on a circular chart, which is difficult to read to better than 0.25 psig. The oxygen bomb is usually heated in a boiling water bath. Thus, variation of test temperature is not possible.

After considering these deficiencies, it was decided to

design an improved test apparatus, which would have the following desirable features: (a.) The entire pressurized cell should be completely closed and maintained at a uniform temperature; (b.) the oxygen pressure should be readable to 0.1 psig or better; (c.) the test temperature should be easily varied and thermostatted to better than 0.25 C (at 100 psig and 100 C, a temperature change of  $\pm 0.25$  C will result in a pressure change of  $\pm 0.07$  psig); (d.) the oxygen pressure should be automatically recorded.

The four criteria listed were successfully achieved by using a 0-100 psig bonded strain gauge pressure transducer, which may be used up to 150 C (Transducers Inc., Whittier, CA 90606 Model No. GP-69F-100). It is small in size, and mounts conveniently onto the system. The details of how this transducer was installed onto a commercial, available oxygen bomb (Precision Scientific, Chicago, IL 60647) are shown in Figure 1. The original stem of the commercial oxygen bomb was cut off at a height of 2.25 in., measured from the upper surface of the oxygen bomb lid. With the exception of the threaded adapter, all other components were readily available and easily assembled. Oxygen is conveniently admitted through a quick disconnect fitting. The voltage source for the transducer and the zero and span calibration potentiometers are contained in a signal condi-

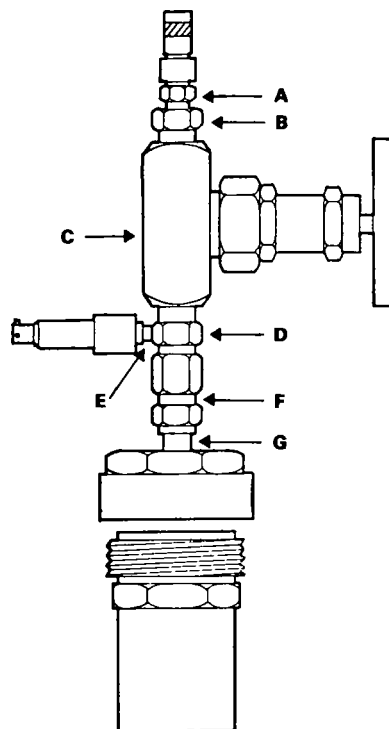


FIG. 1. Drawing of the improved oxygen bomb test apparatus showing details of construction: A. Swagelok quick-connect body SS-QC4-C-2PM; B. Cajon reducing bushing SS-12-RB-2; C. Shut-off valve, Whitey SS-12NBF 8; D. Cajon hex nipple SS-8-NH; E. Adapter, threaded to receive transducer and welded to Cajon hex nipple; F. Swagelok female connector SS-1010-7-6; G. Original stem 0.625 in. OD.

<sup>1</sup> Presented at the AOCS meeting, New Orleans, April 1976.

<sup>2</sup> Part I of a series on Evaluation of Antioxidant Performance.

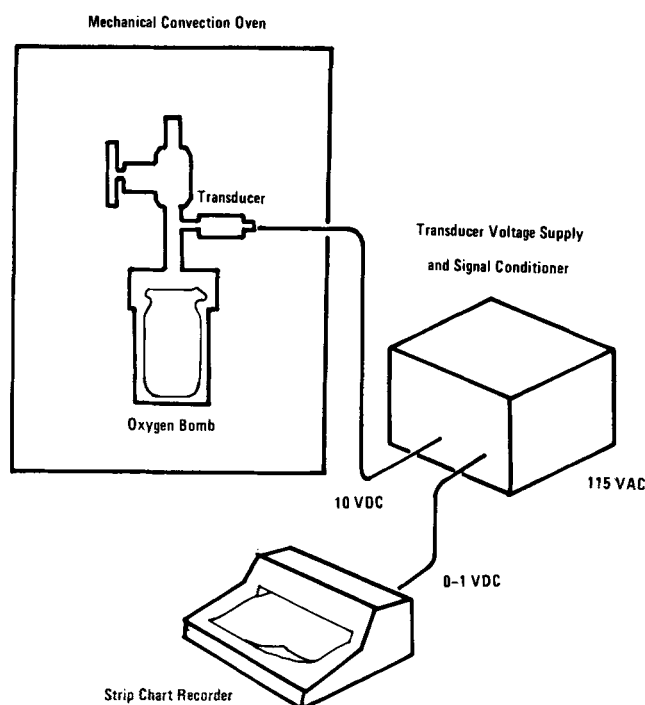


FIG. 2. Schematic diagram of the improved oxygen bomb test apparatus.

tioning module (Transducers Inc., TSC-71-1111-10R-000). The transducer range is 0-100 psig, which corresponds to 0-1 volt output from the signal conditioner. The signal is recorded, using a Heath Company strip chart recorder (Heath Company, Benton Harbor, MI 49022 Model No. SR-255-B). By applying known pressures to the transducer and measuring the output voltage, the hysteresis and deviation from linearity of the output signal was shown to be less than 0.07% of full scale. The oxygen bomb and the transducer are maintained at constant temperature in a Thelco Model 26 mechanical convection oven (Precision Scientific). The temperature control and setability were

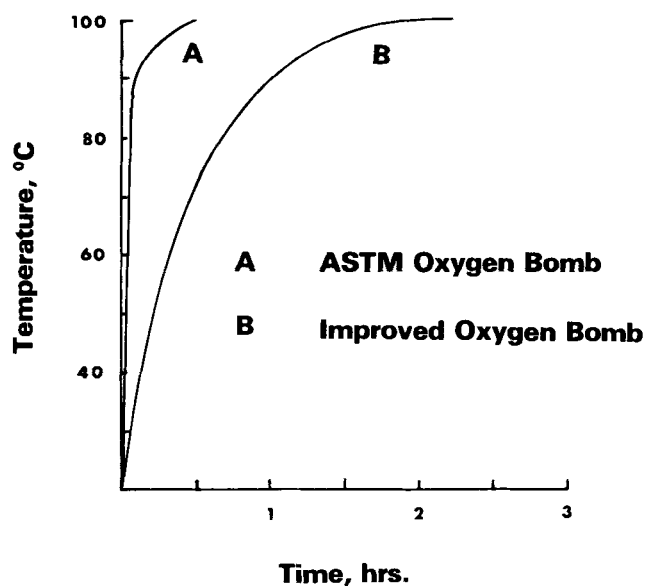


FIG. 3. A comparison of the time to reach test temperature for the ASTM and improved oxygen bomb tests. Ordinate: temperature C; abscissa: time, hours.

improved by installing a YSI Model 72 proportional controller (Yellow Springs Instrument Co., Yellow Springs, OH 45387). A schematic of the system is shown in Figure 2. The oxygen bomb is completely enclosed in a mechanical convection oven which maintains the entire pressurized system at uniform temperature. The only connections to the bomb are the electrical connections to the transducer.

## RESULTS AND DISCUSSION

The ASTM procedure (4) for oxidation stability of gasoline specifies 100 psig as the test pressure, 98-102 C test temperature and 50±1 ml of sample. The induction period is the time between placing the bomb in the controlled temperature bath and the break point. The break point is defined as the point in the pressure time curve

TABLE I  
Summary of Conditions Used in Oxygen Bomb Testing

Reference	System	Sample size g	Test temperature C	Initial oxygen pressure psig	Dispersion/catalyst	End point
1	Lard	15	100	100	--	Midpoint of first hour in which a 2 psig loss occurred
	Cottonseed oil	30	100	100	--	
	Potato chips	15	100	50	--	
2	Lard	6	100	50	Kimpac 1.5 g	ASTM
	Hydrogenated vegetable oils	6	100	50		
	Cottonseed oil	15	100	30	--	
	Foods (animal fats or hydrogenated vegetable oil)	30	100	100	--	
5	Fats and oils	6	100	50	Kimpac/ 25 ppm Cu <sup>2+</sup>	End of first hour in which a 2 psig drop occurred
6	Soy oil shortenings	10 (5-25)	135	110 (80-120)	--	Time to 2 psig drop
7	Lard	5 (43)	100	100	4 mm glass balls	Time to 2 psig drop
8	Peanut oil butter	50	135	110	--	Time to 2 psig drop
	Peanuts					

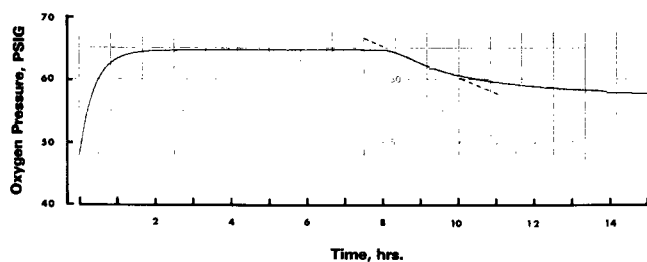


FIG. 4. Pressure transducer recording of the improved oxygen bomb test apparatus. Conditions: 1.0 g Wesson oil, 100 C; ordinate: oxygen pressure, psig; abscissa: time, hours.

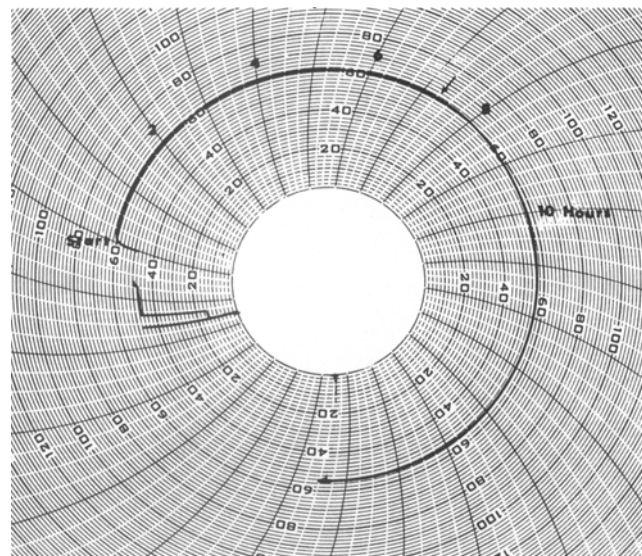


FIG. 5. Pressure recording of ASTM oxygen bomb test apparatus. Conditions: 1.0 g Wesson oil, 100 C.

which is preceded by a 2 psig pressure drop in 15 min, and succeeded by a drop of not less than 2 psig in 15 min.

The variables affecting the OB test results are temperature, oxygen pressure, sample size and surface area. Generally, when applying the OB test to food systems, no set of standard conditions has been employed. The test conditions described in the literature are summarized in Table I. A publication by Eastman Chemical Products Inc. (9) gives useful information on sample size and operating pressures for a wide variety of materials. It is apparent from the data of Table I that no uniform test procedure has evolved for the application of the oxygen bomb test to food systems. Generally large test samples have been required to produce end points which are easily measured. The end point has not been defined in a uniform manner. The effect of test pressure has not been thoroughly investigated. Increased temperatures and catalysts have been employed to reduce test times.

**Performance of the Improved Oxygen Bomb**

The oxygen bomb was assembled and pressure tested. A test was performed, with no sample in the bomb, at 100 C and 92.5 psig for 50 hr. The pressure during this time showed high and low values of 92.5 and 92.2 psig, respectively. The improved oxygen bomb, which is heated in an air bath, has a longer heat-up time compared with the use of the conventional water bath. The temperature-time curve calculated from the pressure-time trace is shown in Figure 3 for the improved and ASTM oxygen bombs.

The ASTM oxygen bomb, when placed in a boiling water bath, reaches 100 C in 0.5 hours. The improved oxygen

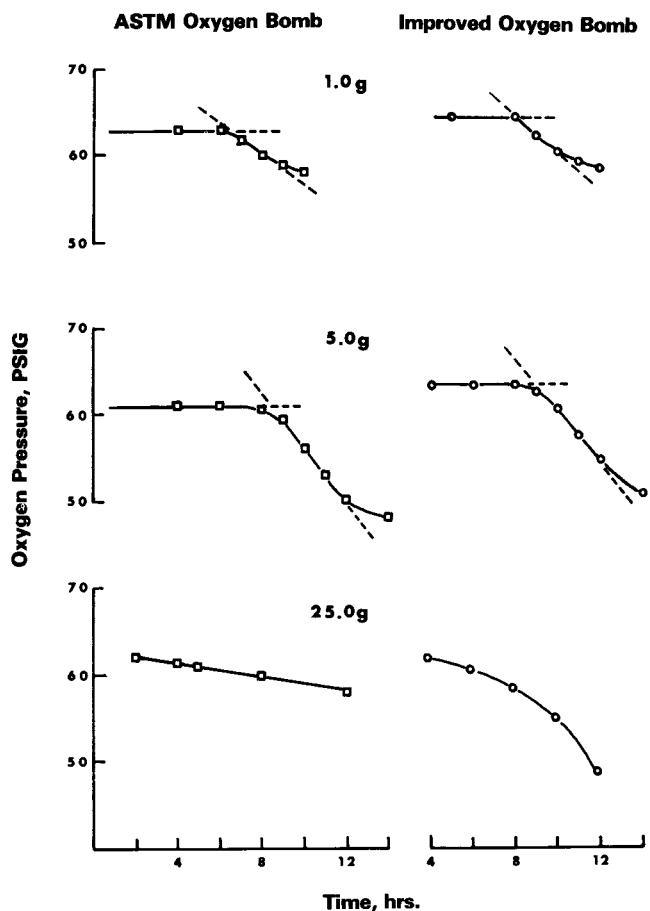


FIG. 6. Effect of sample weight on oxygen bomb test results at 100 C. Ordinate: oxygen pressure, psig; abscissa: time, hours.

bomb, which is heated by circulating hot air, reaches 90 C after one hour, and 100 C in 2.5 hours. This longer heat-up time using an air bath is also evident in the work of Blankenship et al. (8), where the pressure had equilibrated only slightly before the end point at the high temperature, 135 C, which they employed. This problem may be easily overcome by placing the modified bomb in a boiling water bath for 5-10 min after pressurization and prior to putting it inside the oven. A typical strip chart recording of the pressure transducer output is shown in Figure 4. This curve was obtained by maintaining 1.0 g of Wesson oil at 100 C at 64.8 psig. The constant oxygen pressure up to the end of the inhibition period showed a stability of better than 0.1 psig. The linear oxygen pressure decay during the initial oxidation reaction makes extrapolation to the time of the initial pressure drop very easy. This suggests the use of this extrapolation, which can be performed directly on the strip chart recording to obtain the inhibition time rather than some arbitrary number of psig loss which has been used previously. This new extrapolation method of determining end point will eliminate errors introduced by using an arbitrary pressure loss end point when different slopes of the oxygen pressure-time curve are experienced.

Because of the circular chart used with the ASTM oxygen bomb and the difficulty of reading the pressure accurately, the extrapolation in this case is not as accurate. A typical pressure recording from the commercially available ASTM oxygen bomb is shown in Figure 5. In this test, 1 g of Wesson oil was maintained at 100 C. Somewhere in the region of eight hr a pressure decrease is noticeable. A 2 psig pressure loss is difficult to measure accurately because this corresponds to a distance of 1 mm on the chart recording. If the pressure decrease is plotted and extrapolated

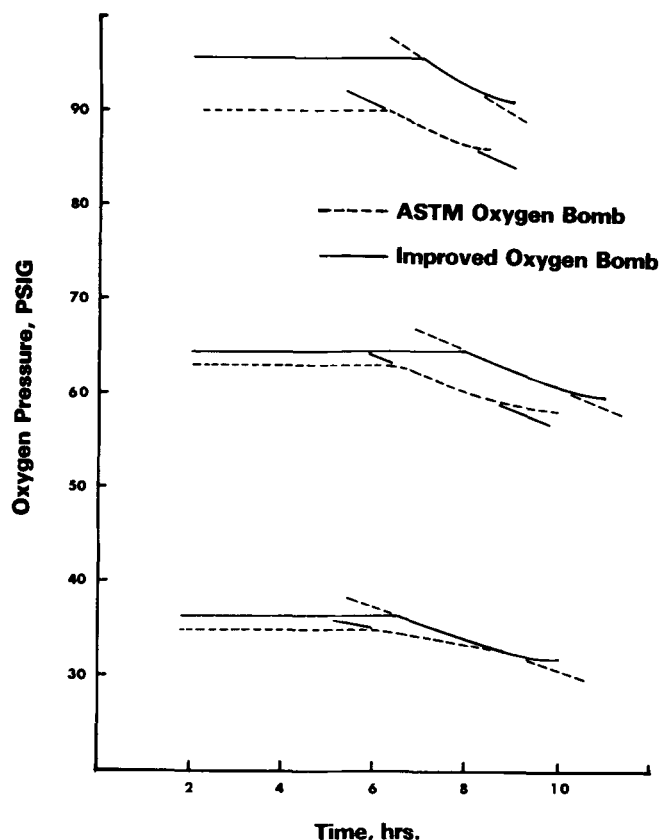


FIG. 7. Effect of pressure on oxygen bomb test results at 100 C and 1.0 g Wesson oil sample weight. Ordinate: oxygen pressure, psig; abscissa: time, hours; key: - - - - ASTM oxygen bomb ——— improved oxygen bomb.

to the original test procedure, the first noticeable pressure decrease is indicated by the arrow. However, this is subject to considerable error because the pressure decay curve cannot be read with sufficient accuracy.

Investigation of operational parameters were performed, using Wesson oil as a test material. This is a blend of cottonseed oil and soybean oil. It is a convenient material to use, as it is readily available and has no antioxidant materials added.

#### Effect of Sample Weight

In order to maximize the surface area to volume ratio, small samples are desirable. Small sample size is also important if the test solute or an experimental antioxidant is available in limited quantities. Typical results are shown in Figure 6 for 1.0 g, 5.0 g, and 25.0 g sample sizes of Wesson oil. The tests were performed at 100 C at ca. 60 psig oxygen pressure. The results show little difference in the inhibition times obtained by the extrapolation technique in the improved oxygen bomb, using 1 or 5 g samples. In comparison, a larger difference is noted between the 1.0 g and 5.0 g samples for the ASTM oxygen bomb, which may be due in part to the error involved in replotting the data from the circular chart. At 25.0 g sample loads, distinctly different results are obtained between the ASTM and improved oxygen bombs, and no convenient extrapolation could be performed. On the basis of these results, a 1.0 g sample load was chosen for further testing.

#### Effect of Oxygen Pressure

Using a 1.0 g sample of Wesson oil and 100 C, tests were conducted at 35, 65, and 95 psig and showed no significant effect of pressure on that inhibition time, using either oxygen bomb. The results shown in Figure 7 demonstrate

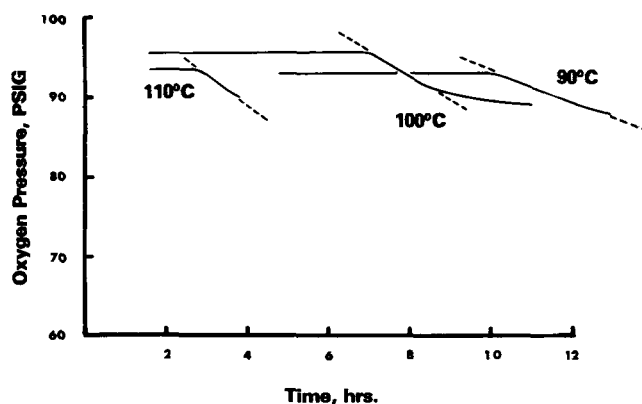


FIG. 8. Effect of temperature on improved oxygen bomb test results using 1.0 g Wesson oil sample. Ordinate: oxygen pressure, psig; abscissa: time, hours.

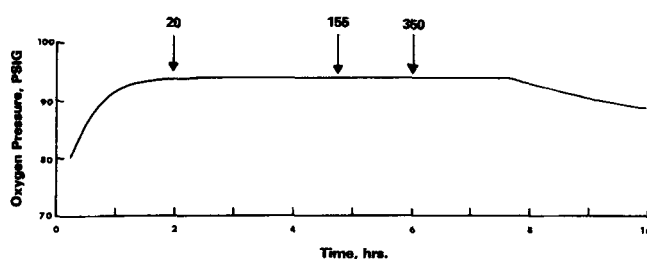


FIG. 9. Peroxide formation in the improved oxygen bomb test using 1.0 g Wesson oil at 100 C, peroxide values in meq/Kg. Ordinate: oxygen pressure, psig; abscissa: time, hours.

that the test pressure is relatively unimportant when testing the oxidative stability of unstabilized oils.

#### Effect of Test Temperature

With the improved oxygen bomb, the test temperature is easily varied. The results of testing at 90, 100 and 110 C are shown in Figure 8. These tests were made with 1 g samples of Wesson oil at ~95 psig. The results show a considerable dependence on test temperature. On average, for each degree above 100 C, the inhibition time is decreased by 0.5 hr. For each degree below 100 C, the test time is increased by an average of 20 min. This shows that test times may be conveniently altered by varying test temperature. It also demonstrates that, for accurate results, the test temperature must be accurately regulated. At these pressures a 1 C change in temperature results in a 0.3 psig pressure change. This would be easily detected using the pressure transducer, but not with the ASTM apparatus. Thus, the increased sensitivity of the pressure measurements also provides a useful check on temperature control.

#### COMPARISON OF OXYGEN BOMB TEST RESULTS WITH OTHER METHODS

The only accelerated oxidative stability test which is recognized as an official procedure is the Active Oxygen Method (AOM) (10). The Schaal oven test is often used for stability testing, and it is based on organoleptic evaluation of products after accelerated storage. Several attempts have been made (1,2,8,11,12) to correlate results from the oxygen bomb, AOM, and Schaal oven tests, often with conflicting results. The AOM end point is determined as the time to reach 100 milliequivalents per Kg (13) when the sample is maintained at 97.8 C, with a constant air flow through the sample 2.33 ml/sec. We have performed the oxygen bomb test with 1 g of Wesson oil at 100 C and 93 psig, and determined the peroxide value at various times.

Each sample for peroxide determination was taken from a separate experiment. The results of the peroxide titrations in meq/Kg of oil are shown in Figure 9, with arrows indicating the time at which they were determined. It is clear that the AOM end point of 100 meg peroxide per Kg of oil occurs long before the rapid oxidation process begins, which is the end point measured in the oxygen bomb test. Further careful studies are required to fully evaluate the correlation between these three methods.

The oxygen bomb test should correlate with the weight gain test (14-18), where weight increases of 2-10% are measured. Both methods are measuring the same phenomenon, the rapid autooxidation step. However, the oxygen bomb has the advantage of continuous automatic recording.

## REFERENCES

1. Gearhart, W.M., B.N. Stuckey, and J.J. Austin, JAOCS 34:427 (1957).
2. Stuckey, B.N., E.R. Sherwin, and F.D. Hannah, Jr., Ibid. 35:581 (1958).
3. ASTM Committee D-2, "ASTM Standards on Petroleum Products and Lubricants," 1955, p. 254.
4. ASTM Designation D525-74, "Oxidation Stability of Gasoline (Induction Period Method)," 1974, p. 269.
5. Pohle, W.D., R.L. Gregory, and B. Van Giessen, JAOCS 40:603 (1963).
6. Bennett, J.E., and M.J. Beyer, Ibid. 41:505 (1964).
7. Inglis, D.B., and D.J. Willington, Chem. and Ind., 20:905 (1976).
8. Blankenship, B.R., C.E. Holaday, P.C. Barnes, Jr., and J.L. Pearson, JAOCS 50:377 (1973).
9. Publication No. ZG-195, Eastman Chemical Products Inc., Kingsport, Tennessee, June, 1973.
10. Official and Tentative Methods of the American Oil Chemists' Society Tentative Method Cd. 12-57, 1959 Revision.
11. Pohle, W.D., R.L. Gregory, and J.R. Taylor, JAOCS 3:226 (1962).
12. Pohle, W.D., R.L. Gregory, T.J. Weiss, B. van Giessen, J.R. Taylor, and J.J. Ahern, Ibid. 41:795 (1964).
13. Official and Tentative Methods of the American Oil Chemists' Society, Official Method Cd. 8-53, 1966.
14. Ikeda, N., and K. Fukuzumi, JAOCS 53:618 (1976).
15. K. Fukuzumi, N. Ikeda, and M. Egawa, Ibid. 53:623 (1976).
16. N. Ikeda, and K. Fukuzumi, Ibid. 54:355 (1977).
17. N. Ikeda, and K. Fukuzumi, Ibid. 54:360 (1977).
18. Ke, P.J., D.M. Nash, and R.G. Ackman, Ibid. 54:417 (1977).

[Received April 17, 1978]