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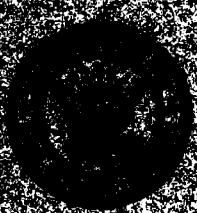
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The oxidative breakdown of lubricating oils and other organic compounds is often accompanied by the liberation of vapor phase oxidation products. A simple apparatus which uses a semiconducting tin oxide gas sensor has been employed to monitor the evolution of these products. The method permits complete automation of the oxidation stability testing procedure and an unambiguous indication of the relative oxidative stability of the compounds studied.

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## A SIMPLE ELECTRONIC APPARATUS FOR DETERMINING
## THE OXIDATION STABILITY OF LUBRICANTS
## AND OTHER ORGANIC COMPOUNDS

### INTRODUCTION

Resistance to oxidative breakdown is a very important requirement for many materials exposed to oxygen-containing environments. Lubricating oils in particular must remain oxidatively stable even at temperatures of several hundred degrees Celsius. Antioxidants are often added to inhibit the oxidation process but it is always necessary to test the lubricant under realistic conditions in order to determine the relative stability of a given lubricant-antioxidant system. Historically, numerous methods have been employed to determine the oxidative stabililty of lubricants including observation of increases in viscosity, acidity, and peroxide concentration, or decreases in the antioxidant concentration or oxygen pressure (using a bomb apparatus). All of these (except the bomb) require periodic sampling of the stressed lubricant and subsequent wet chemical analysis. These operations are tedious, labor intensive, and wasteful of the lubricant sample. The bomb requires relatively large sample volumes and is awkward to use. This work describes an alternative method for determining the relative oxidation stability of lubricants by monitoring volatile oxidation products with an electronic gas sensor.

The sensor used in this study employs a heated film of tin oxide whose electrical conductivity is modulated by the presence of combustible vapors (Figaro Engineering Inc., Osaka, Japan). A schematic view of the sensor is provided in Figure 1. The device
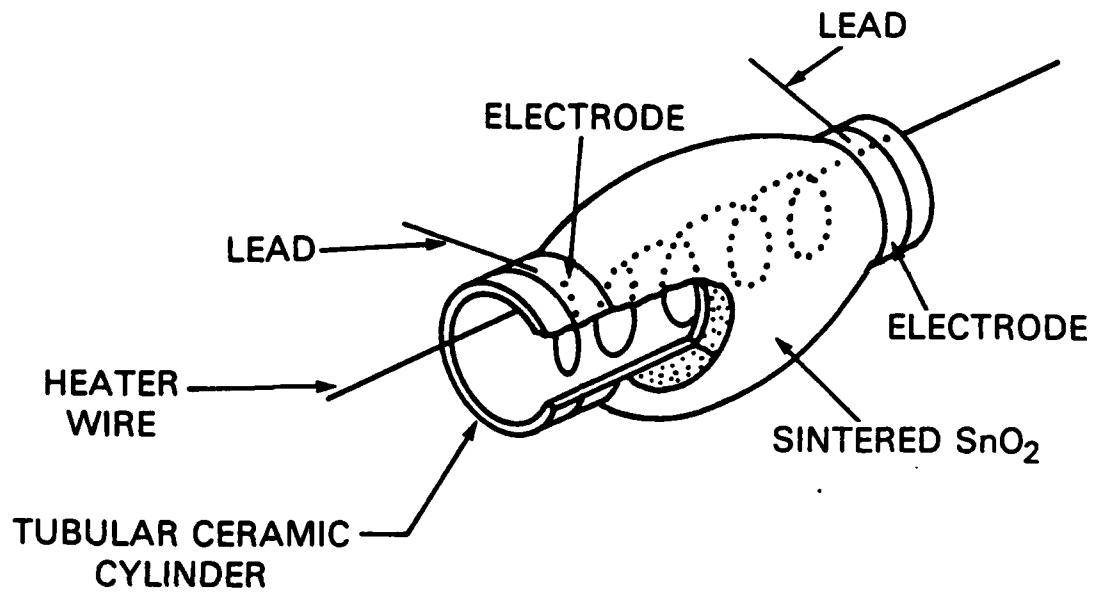
Fig. 1 - A schematic view of the Figaro tin oxide gas sensor. The electrical conductivity of the hot tin oxide film is highly sensitive to ambient vapors.

consists of a tubular ceramic form a few millimeters long which contains a heating filament and is coated on the outside with sintered tin oxide and a proprietary mixture of noble metal catalytic dopants. First reported in 1962 by Seiyama et al (1) metal oxide semiconductor vapor sensors have been widely used for detection of gas leaks, fires, explosive hazards and breath alcohol. The mechanism by which the sensor operates is not known in great detail. In general, it is known the atmospheric oxygen is strongly adsorbed onto the heated surface of the metal-oxide semiconductor. When a reducing gas interacts with this absorbed oxygen, charge transfer can occur between the semiconductor and absorbed species resulting in a change in the number of conduction band electrons of the semiconductor. Thus, the apparent conductivity of the hot semiconductor is increased dramatically by the presence of a small amount of vapor interacting with the semiconductor surface. In most cases the response is rapid and reversible. The selectivity of the sensor can be altered somewhat by the addition of noble metal catalysts to the metal oxide semiconductor. It is estimated that over 200 patents have been issued around the world for various metal oxide mixtures which enhance the selectively of this type of sensor to a variety of gases. Most tin oxide semiconductor gas sensors respond quite well to a broad range of combustible hydrocarbon vapors at concentrations above a few parts per million by volume. A sensitive, rapid and non-specific response to hydrocarbon is desirable for detecting lubricant oxidation products since it is

usually not known in advance exactly what the oxidation products will be. For more detailed information regarding metal oxide semiconductor vapor sensors the reader should consult references 2-4. Preliminary results using gas sensors for oxidation studies were presented in reference 5.

## EXPERIMENTAL

### Apparatus

The sensors used in this study were of the Figaro model 813 (obtained from Lumidor Safety Products Inc., Miami, Florida). A simple electronic circuit used to power the sensor heater and measure the conductivity of the tin oxide semiconductor is shown in Figure 2. The Figaro model 813 sensor heater is normally powered with 5 volts. The 6-ohm resistor reduces this to about 4 V to decrease the device temperature and sensitivity. This same potential provides a constant bias across the semiconductor. Variations in sensor conductivity thereby produce changes in current which can be processed in a simple operational amplifier circuit. In normal operation, the output of the circuit is set to zero (or any arbitrary baseline voltage) when the sensor is exposed to pure air. The sensitivity can be varied by selecting different feedback resistor values for the output op-amp.
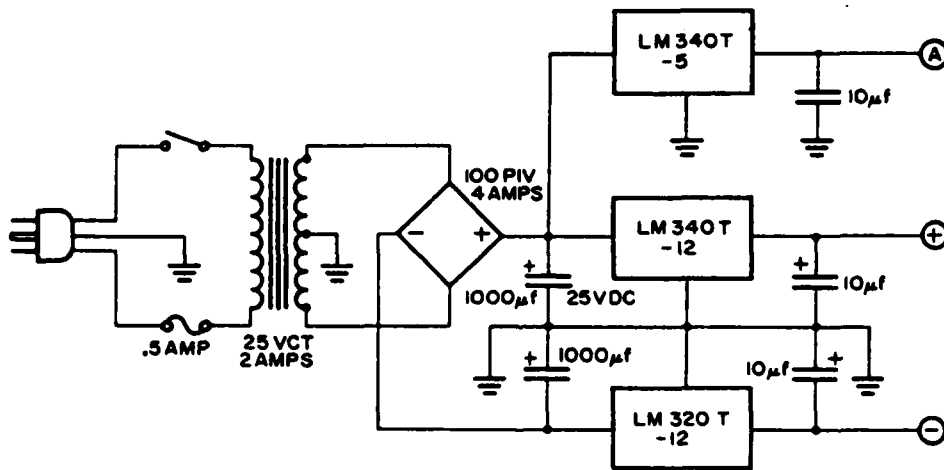
In this work the output was adjusted to -5 volts with the sensor disconnected. The signal was thus compatible with a +5 to -5 V analog to digital converter, and the amplifier parameters were independent of the sensor characteristics. Only the low

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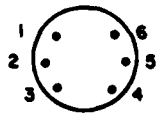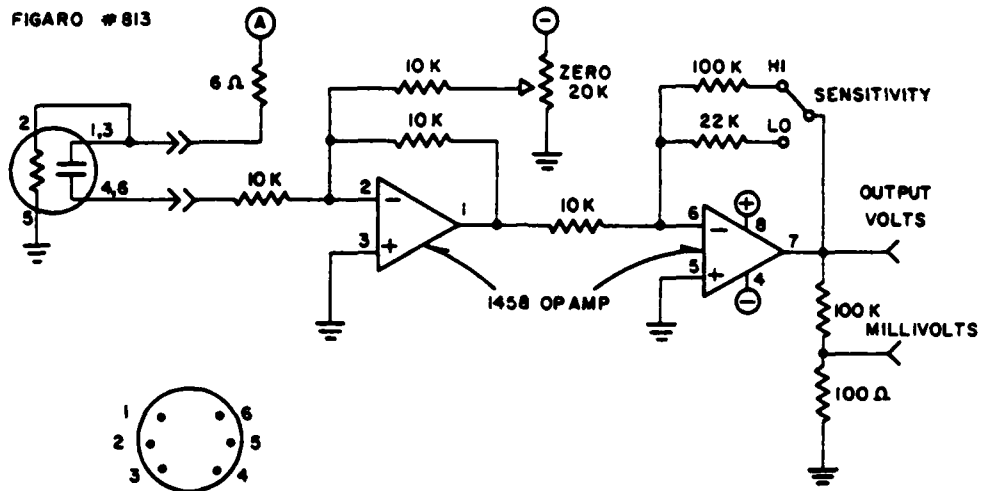
FIGARO #813

FIGARO #813
PIN CONNECTIONS
(BOTTOM VIEW)

(a)



(b)

Fig. 2 - Schematic diagram of the sensor signal conditioning
circuitry (a) and the associated power supply (b).

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sensitivity setting was implemented. Two- and four-channel units were made, with shared 12-V power supplies but separate 5-V regulators.

Oxidation of the lubricant samples was carried out in Pyrex glass cells (30 cm long. 1.0 to 1.5 cm inside diameter) through which dry air was bubbled at 25 ml per minute. The cells containing lubricant were heated in an oven at temperatures in the vicinity of 200°C, most commonly 220 ±0.5°C. The gas sensor was situated in a glass sleeve attached to the top of the oxidation cell by means of a ground glass taper joint adapter. Glass wool was placed between the cell and the sensor to minimize contamination by lubricant aerosols. This apparatus is shown schematically in Fig. 3.

Stripchart recorders were initially used to collect the sensor signals. Later, an "Apple II Plus" computer equipped with a clock and a sixteen-channel analog to digital converter was employed. A BASIC program initialized the system, started and stopped data collection, provided a summary of the status of all channels or a graphic display of the data from any channel, reduced the data to yield the induction period, and provided for diskette data storage and retrieval. An interrupt-driven machine language program collected data from the active channels, maintained status and time information, and tested the data to detect the rise in signal typical of the onset of oxidative breakdown of the lubricant. Data was taken every two minutes and retained in memory for 8 1/2 hours. Upon detection of
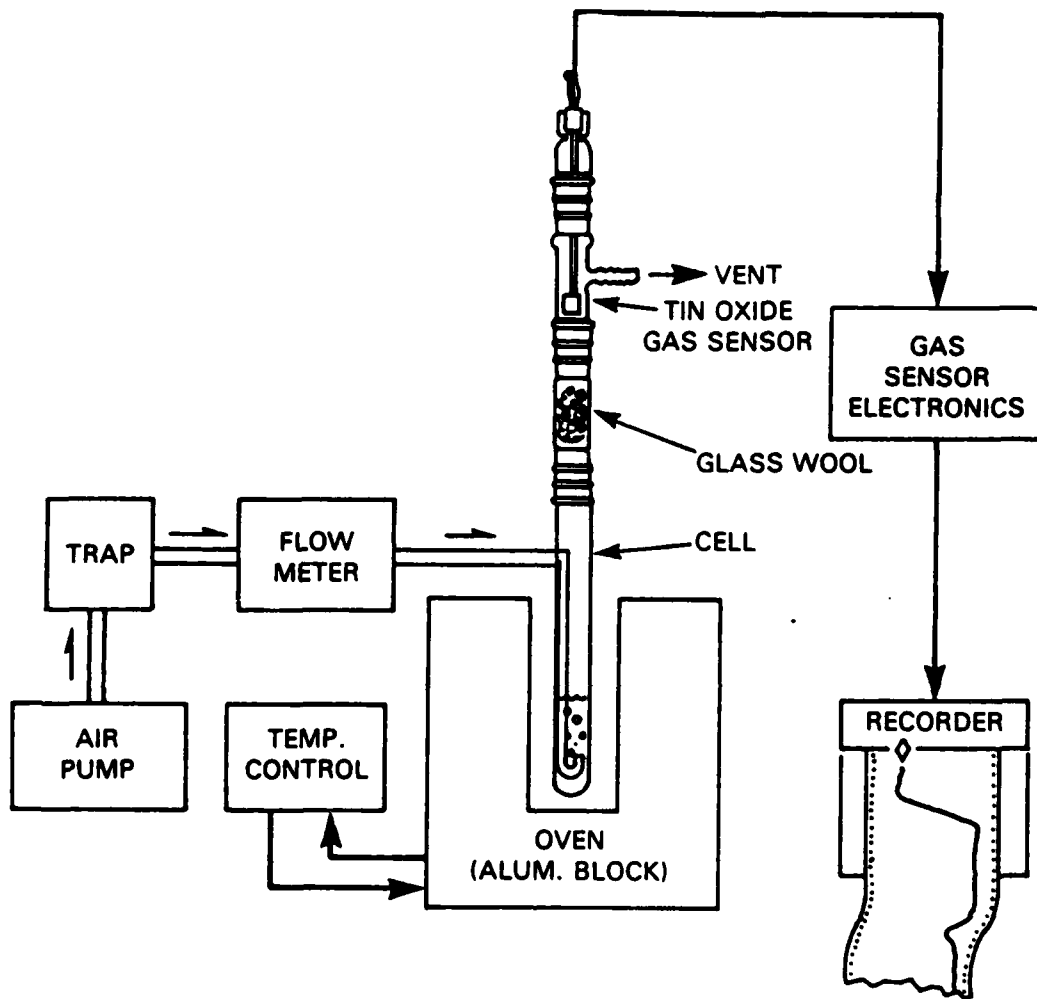
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Fig. 3 - Lubricant oxidation test apparatus.

VENT

TIN OXIDE
GAS SENSOR

GAS
SENSOR
ELECTRONICS

GLASS WOOL

CELL

RECORDER

TRAP

FLOW
METER

AIR
PUMP

TEMP.
CONTROL

OVEN
(ALUM. BLOCK)

breakdown, data collection in that channel was terminated so that the exact time of breakdown could be determined by the reduction routine. As 16 channels were more than were needed, another version of the software used the memory areas of eight of them to maintain the last 68 hours of data to provide a record of any changes occurring overnight or on weekends.

The machine language routine which tested the data for evidence of a sudden rise or "break" characteristic of oxidative breakdown examined 8 points in the 8 1/2 hours of data retained in memory. The earliest point was tested for zero to prevent detection of the start-up rise. A reference point on the baseline was determined, and two subsequent points were tested to ensure that the base line was reasonably constant. The last point, a point 2 hours old, and 2 intermediate ones were then tested for a sustained rise of 2 V in the signal. The criteria were made stringent to preclude termination of data collection by insignificant or temporary increases in the signal.

Reagents

This system was developed primarily for oxidation studies of ester base lubricants such as the pentaerythritol esters used in gas turbine engine and instrument bearing lubricants. Numerous tests have been made of formulated engine lubricants, commercial mixed-ester base stocks, pure esters such as pentaerythritol tetrahexanoate (PETH), and deuteratd analogs. The oils typically contained amine antioxidants, most commonly N-p-octylphenyl-alpha-naphthylamine (Octyl PAN), in concentrations of 0.5 to 2%.

## Procedure

After the oxidation cells were cleaned in a hot nitric and sulfuric acid bath, thoroughly rinsed, and oven dried, they were charged with 2 to 5 ml of lubricant containing an antioxidant and placed in the oven. Dry air was bubbled through the lubricant at a rate of 25ml per minute. The evolution of vapor phase oxidation products from the lubricant was monitored continuously with a gas sensor.

The determination of correlation of gas evolution with other indications of breakdown was made on a 20 ml sample of a commercial pentaerythritol ester with 0.5% of octyl PAN antioxidant at 200°C. Aliquots of approximately 1 ml were removed at regular intervals and analyzed for antioxidant concentration, acidity, and viscosity. Antioxidant concentration was determined by HPLC using a UV detector, acidity by titration, and viscosity at 38°C using a semi-micro capillary viscometer.

## Calibration

The rise in the sensor signal at breakdown was usually rapid compared to the length of the induction period, so that an arbitrary point on the rising curve could serve to mark the time of breakdown. However, calibration was considered worth while to quantify the signal in terms of organic vapor concentration, compare the sensitivities of individual sensors, and check their stabilities with age and use.

Known vapor concentrations were obtained by allowing organic liquids to reach equilibrium with their vapor in air in a closed

volume at a known temperature. The fraction of vapor, $F$, by weight, is found from

$$F = \frac{P_V M_V}{P_V M_V + 29 (P_O - P_V)} \tag{1}$$

where $P_V$ is the vapor pressure of the liquid at its temperature, $M_V$ is its molecular weight, and $P_O$ is the (atmospheric) pressure. The constant 29 is the average molecular weight of air. Barometric pressure changes in $P_O$ are usually negligible. The apparatus consisted of a 500-ml flask immersed in a thermostatted bath or ice bath and equipped with a stirring propeller in the vapor space. Two necks with ground-glass joints admitted sensors. A few drops of the organic liquid were placed in the bottom of the flask. The sensors were known to respond differently to various classes of organic compounds. Since the oxidation products of esters are oxygen-containing compounds such as organic acids and ketones, alcohols and ketones were selected as standards. They were of reagent grade or redistilled, with a maximum boiling range of 1°C.

The response of the signal conditioning circuits closely followed the relationship

$$R_S = 10^4 \frac{E_{max} - E}{E - E_{min}} \tag{2}$$

where $R_S$ was the sensor resistance and E was the output signal.
The signals were adjusted to -5 volts minimum with the sensor
circuits open. With the sensors shorted the maximum signal from
six conditioning circuits were found to range from 3.3 to 4.3
volts, with a mean of $4.0 \pm 0.2$ V. The relationship of Equation
(2) thus became

$$R_S = 10^4 \; \frac{4 - E}{5 + E} \tag{3}$$

The basic sensor response relationship found by Clifford and
Tuma (3) is

$$R_S = R_O (1 + KC)^{-\beta} \tag{4}$$

where $R_O$ is the sensor resistance in air free of organic
vapors, C is the vapor concentration, here expressed in parts
per thousand (ppt) by weight, and $\beta$ and K are constants dependent
on the sensor and nature of the vapor. Equations (3) and (4),
when combined, yield the expression

$$\ln (C + N) = \ln B + M \ln \left( \frac{9}{4 - E} - 1 \right) \tag{5}$$

where $N = 1/K$, $B = \dfrac{(10^{-4} R_O)^{1/\beta}}{K}$, and $M = 1/\beta$

Equation (5) is a power law expression of slope M and intercept
ln B. A curve fitting process was applied to the E vs C
calibration data to determine N, B, and M for each sensor. The
sensor constants could be determined from: $\beta = 1/M$, $K = 1/N$,

and $R_O = 10^4 (BK)^B$. Figure 4 is a plot of the power law curve from calibration data of a sensor. It can be seen that the data fit quite well, deviating from the curve only at very high concentrations. Figure 5 shows the same data plotted as E vs the logarithm of concentration. Figure 6 is a similar plot for another sensor.

When the curve fitting constants for a sensor are known, the concentration corresponding to any observed signal can be determined from

$$C = B \left( \frac{9}{4 - E} - 1 \right)^M - N \qquad (6)$$

A separate computer program was written to display or print the stored data in either tabular or graphic form and either in terms of signal or concentration vs time. The calibration data were also used to standardize the induction period determination in the reduction of the breakdown curves. The end point signal for each sensor was that corresponding to a concentration of 13 ppt, which is the calibration point produced by i-amyl alcohol at 25°C. this permits a single-point calibraton to correct for sensor variations.
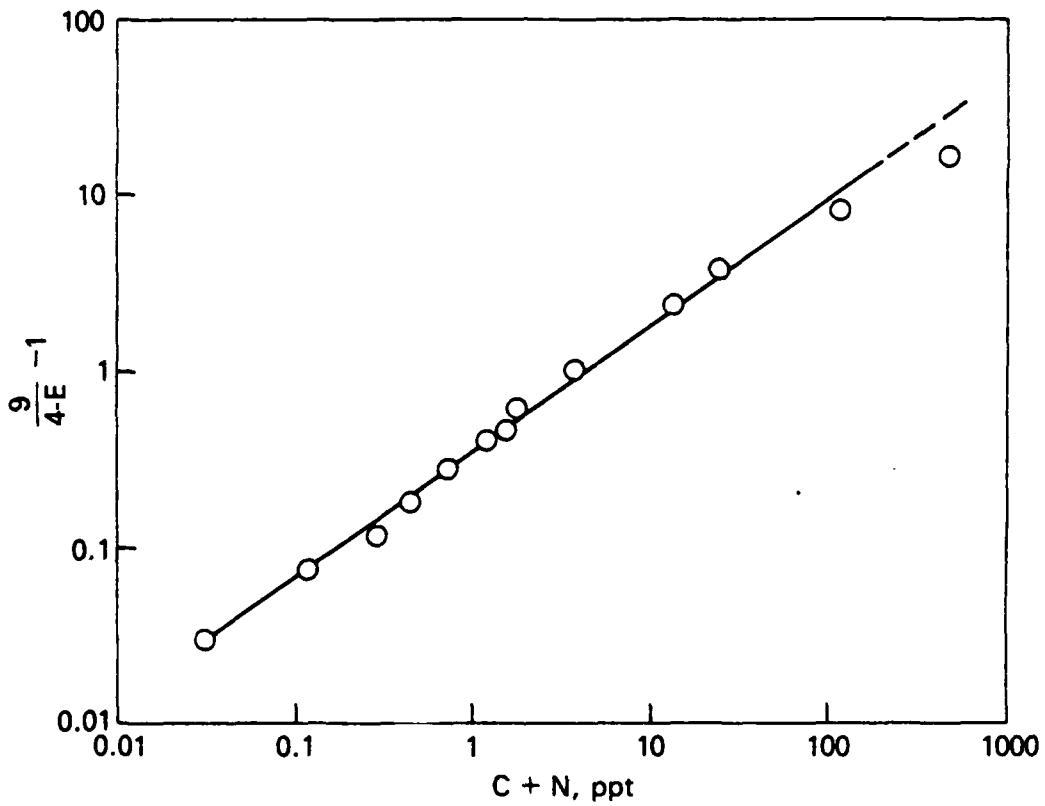
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Fig. 4 - Fitted log-log plot of a function of gas sensor signal
(E) vs a function of calibrating vapor concentration
(C). Data are from 1983 calibration of sensor "M,"
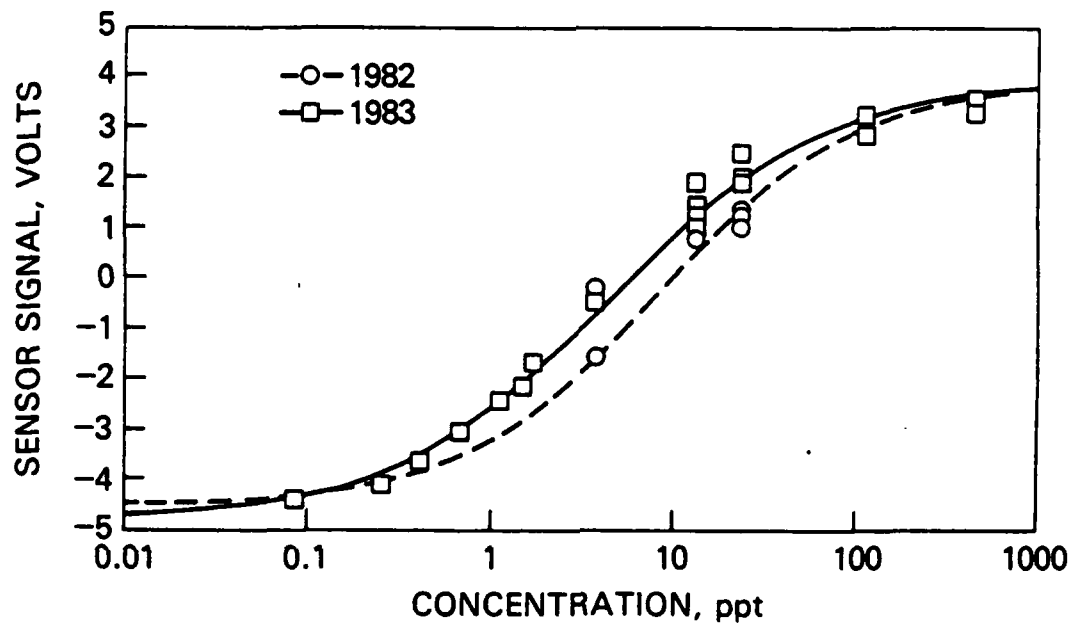using the means of signals from repeated measurements.

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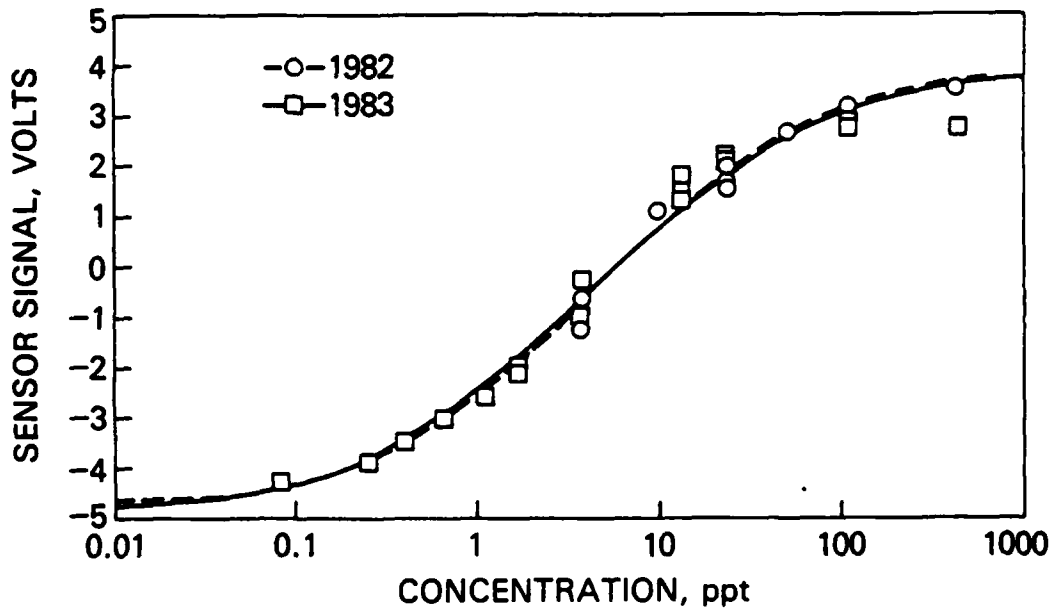Fig. 5 - Signals from sensor "M" produced by calibrating vapor
concentrations.

Fig. 6 - Signals from sensor "A" produced by calibrating vapor concentrations.

## RESULTS AND DISCUSSION

### Sensor Characteristics

Several sensors were calibrated in 1982 and checked again in 1983 after having been used in studies of oxidation stability (6,7). The derived parameters are given in Table 1. Some of the changes seen may have been due to refinements in the calibration procedure, and some to changes in the sensors with age and use. The $\beta$'s tended to decrease, and the K's and resistances to increase. Although the changes in the constants were sometimes quite large, the response curves did not necessarily change greatly. The two curves for sensor "A" in Fig. 6, for example, are nearly identical. The extent of change did not appear to be related to the amount of use, indicating that the changes did not result from progressive alteration or deterioration of the sensors.

Sensor response to increasing concentration was found to be rapid, as was the initial response to decreasing concentration. When turned on after a period of disuse, the minimum signal might not be reached for 1 to 2 hours. Full response to increased concentration was reached in a few to 20 minutes. In the calibration procedure a maximum stabilization period of 15 minutes was adopted, since little change occurred beyond that time. Recovery from exposure to high concentrations was initially rapid, and essentially completed in 10 to 30 minutes.

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Table 1 - Gas Sensor Constants

| Sensor | 1982 | | | 1983 | | |
|--------|------|------|--------------|------|------|--------------|
| | $\beta$ | K | $R_O$ Kohm | $\beta$ | K | $R_O$ Kohm |
| A | 0.71 | 23 | 270 | 0.66 | 150 | 690 |
| B | 0.82 | 8.5 | 260 | 0.71 | 78 | 370 |
| C | 0.91 | 7.0 | 210 | 0.68 | 25 | 230 |
| D | 0.88 | 13 | 300 | 0.51 | 310 | 300 |
| J | 0.88 | 2.8 | 260 | 0.96 | 2.0 | 160 |
| K | 0.77 | 8.2 | 150 | 0.56 | 180 | 330 |
| M | 0.78 | 4.5 | 160 | 0.72 | 34 | 350 |

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The sensor response speed was thus sufficient to follow the changes in gas evolution from the oxidation cells with little error.

The response of the sensors to moisture was small, being of consequence only at low organic vapor concentrations. At 100% relative humidity, responses equivalent to 0.1 to 0.6 ppt were measured. During the calibrations at low concentrations the flask was initially purged with dry air, and the "zero concentration" signals were measured with the sensors in dry air. Since the flow of air through the oxidation cells was also dried, moisture was present there only as a product of the oxidation.

## Oxidation Test Data

During the oxidation test runs, the computer (or chart recorder) displayed the vapor evolution rate as a plot of sensor signal vs time, and the resulting data could be reduced to plots of concentrations vs time. Plots for three tests are shown in Figs. 7, 8, and 9. Plots a, c, and e show the last 8 1/2 hours, with the markers on the ordinate 1 hour apart. Plots b, d, and f show the last 68 hours, with the markers 8 hours apart. Plots a and b are of the signal. Data collection continued 2 hours beyond the point at which the computer detected a "break" in this curve. Plots c and d are of organic vapor concentration, scaled as indicated. Plots e and f are also of concentration, with full scale being 13 ppt, the selected end-point level.

Figure 7 shows the results of a test which gave a fairly short induction period of 41 hours. On the 68-hour plots the

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Last 8 1/2 hours    Last 68 hours

**Signal
-5 to 5 V**

(a)        (b)

**Concen.
0 to 100
ppt**

(c)        (d)

**Concen.
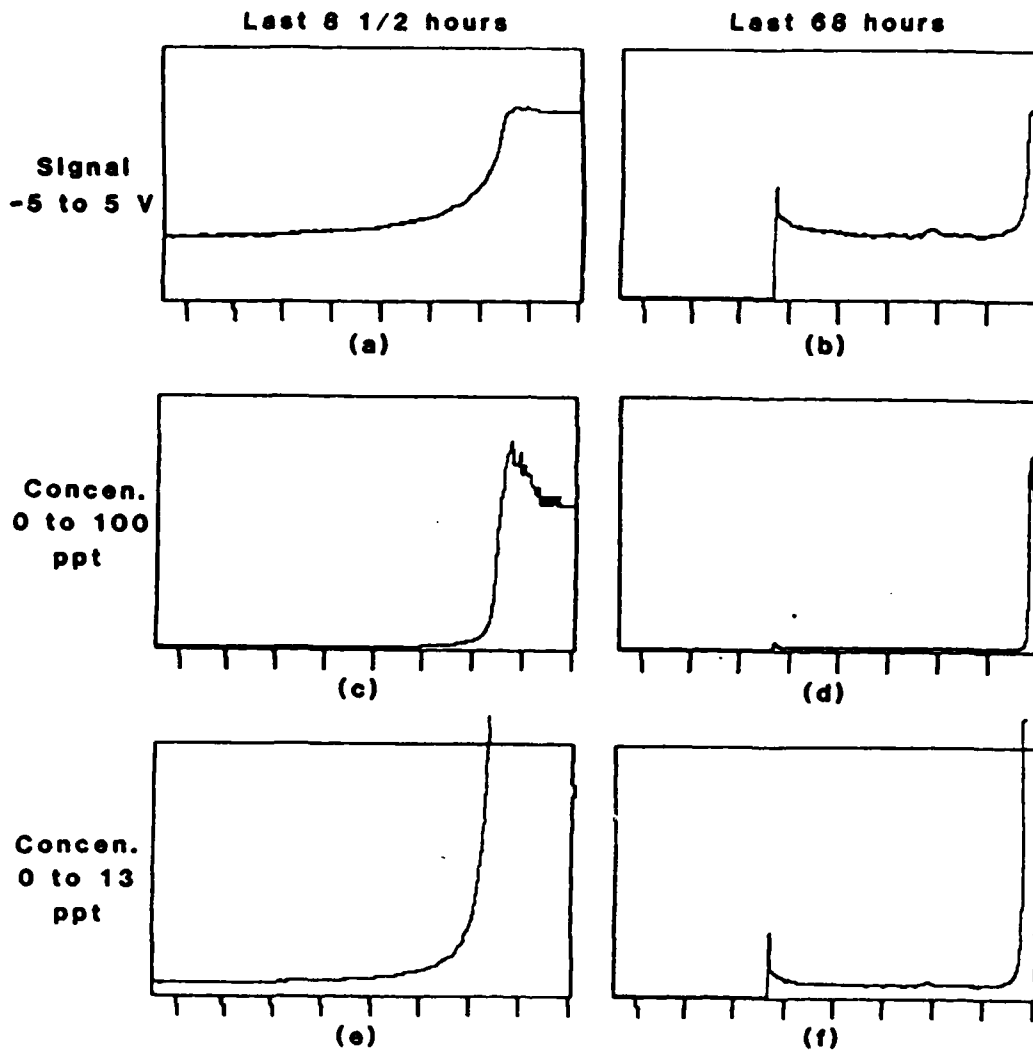0 to 13
ppt**

(e)        (f)

Fig. 7 - Plots of gas sensor data from test of 2 ml of PETH
containing 0.5% Octyl PAN and 200 ppm sodium at 220°C.
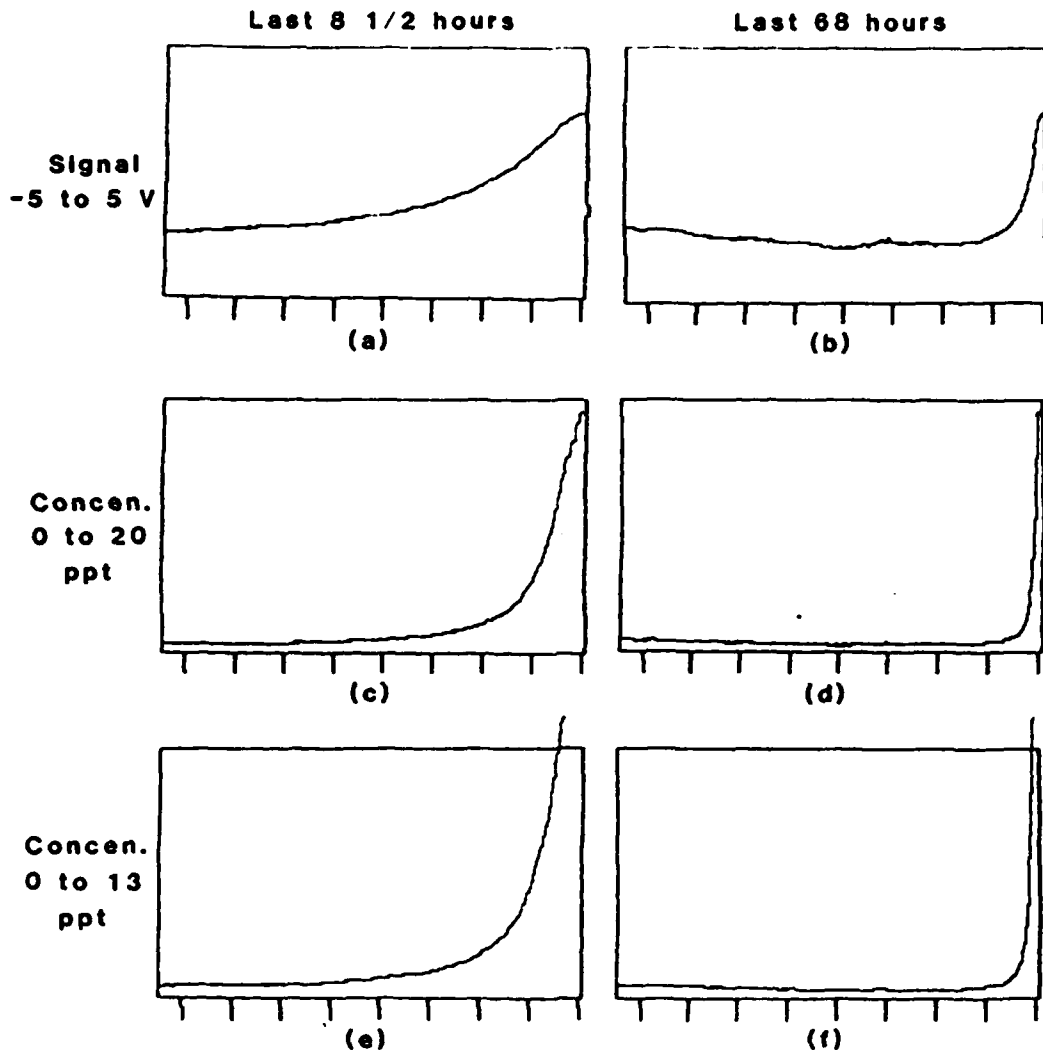Induction period = 41.0 hours, end of plot = 42.6 hours.

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Fig. 8 - Plots of gas sensor data from test of 5 ml of MIL-L-23699 lubricant at 204°C. Induction period = 69.1 hours, end of plot = 70.4 hours.
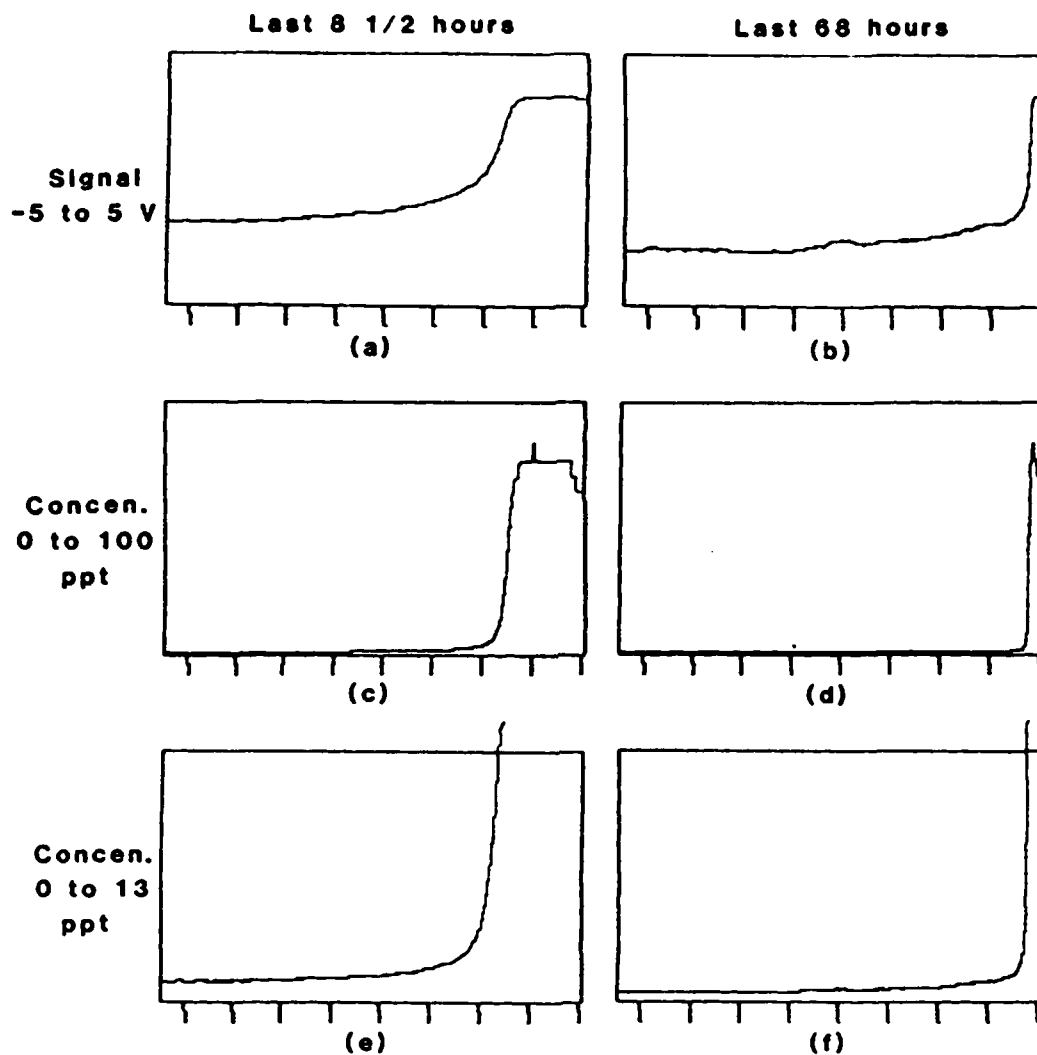
Fig. 9 - Plots of gas sensor data from test of 2 ml of PEdTH (PETH with acid deuterated), containing 0.5% Octyl PAN and 2000 ppm sodium at 220°C. Induction period = 344 hours, end of plot = 346 hours.

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beginning of the run can be seen, with the typical spike caused by the evolution of volatiles as the oil was brought up to 220°C. The data then fell to a baseline until the "break" in the curves indicating the evolution of vapor as the oxidative breakdown of the oil began. Due to the nonlinear relationship between signal and concentration, plots of the latter show this "break" more dramatically.

A commercial turbine engine oil with an induction period of 69 hours produced the unusually gradual and low "break" of Fig. 8. Long runs sometimes produced irregular or undetectably gradual "breaks." The results in Fig. 9, however, show a sharp "break" after an induction period of 344 hours. The steps and sharp spike in Fig. 9c and some others are artifacts resulting from digitization of the data.

Not all plots were of this expected profile. Occasional precursory bursts of vapor evolution occurred, and some "breaks" were double or stepwise. However, in most cases the true breakpoint was obvious or became obvious when the test was allowed to continue.

## Correlations

The changes in viscosity, acid number, gas evolution, and antioxidant concentration during the oxidation stressing of a pentaerythritol ester lubricant are presented in Fig. 10. A very close correlation can be seen between gas evolution rate and the classical indicators of oxidative breakdown. As the antioxidant become depleted after 20 hours of heating, the viscosity,
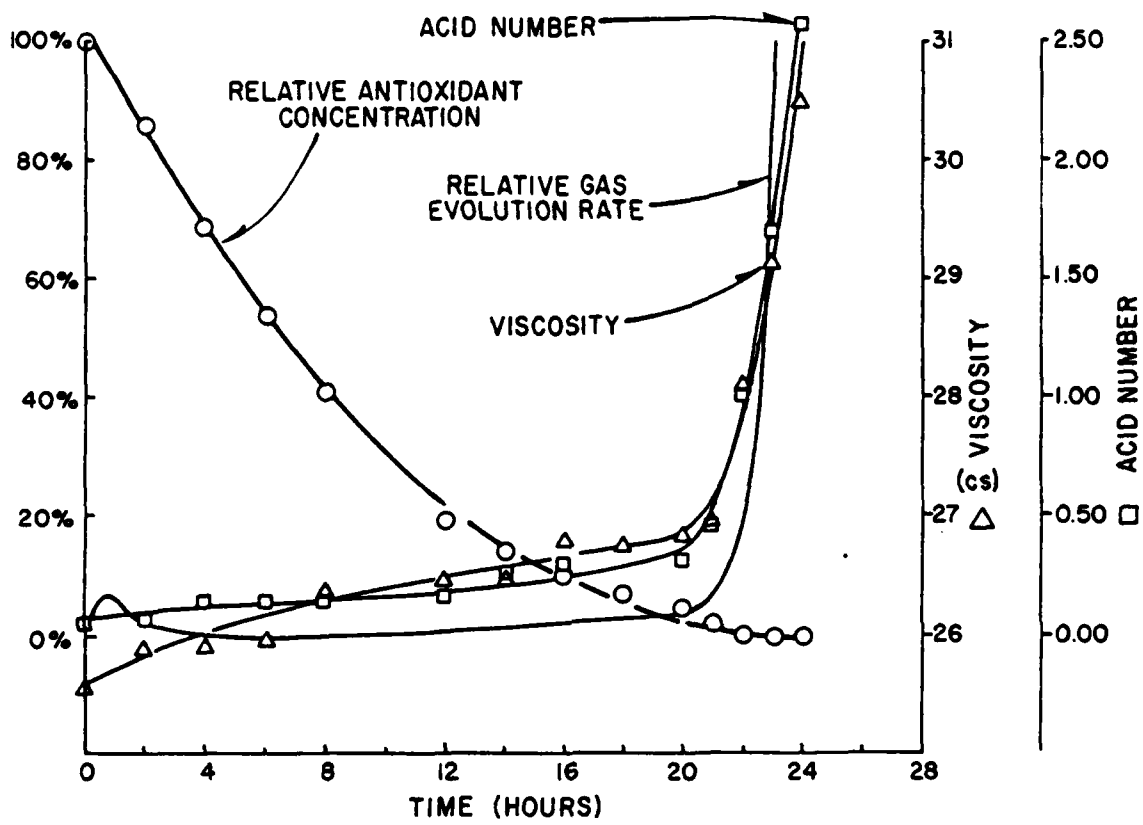
Fig 10 - Correlation of viscosity, acidity, and antioxidant
         concentration with gas evolution rate (sensor signal)
         during testing of a pentaerythritol ester containing
         0.5% Octyl PAN at 200°C.

acidity, and gas evolution increased rapidly and simultaneously, indicating the end of the induction period.

## Reliability

During the recent oxidation stability studies, 124 tests were run during a period of 16 months with the computer monitoring the sensors. In 95 cases the "break" in the signal occurred and was detected by the computer. In 24 cases "breaks" were observed on the plot display but did not meet the criteria of the detection scheme. Reduction of the data at the time or of stored data yielded induction periods for all of these.

Seven of the 24 were the result of very short induction periods of less than 4 hours. Six were gradual or irregular "breaks," usually in long runs of 300 or more hours. The precision of some of these determinations was limited by the lack of a sharp "break" point. Another 6 had unusually high baselines or small "breaks" not meeting the 2-volt rise criterion. Three runs above 240°C and one in a large (100-ml) cell were also not detected because of the high baseline. In one case a "break" occurred, but the signal dropped too low during the 2-hour confirmation period.

In only the 5 remaining cases were no "breaks" seen. Four of these were tests of formulations with a particularly stable deuterated ester having a high sodium content. Although it degraded in these runs, which were from 850 to 2000 hours long, it usually did so gradually, so that no rapid change in vapor evolution was detected. On another occasion it behaved "properly" and yielded the "break" shown in Fig. 9. The last

case was that of a petroleum oil. The vapor evolution rapidly rose to a moderate level of 9 ppt and remained there, showing no "break." It is possible that the wide boiling range of most petroleum oils makes them unsuitable for testing with the gas sensor system, but some lower temperature might be found to give better results. Synthetic hydrocarbon lubricants have been tested by this technique and found to respond as the esters do.

The repeatability of the results was not limited by the sensor system. Although repeat tests in different cells or made at different times might vary by 5 or 10%, multiple sensors fitted to the same cell yielded induction periods varying by only a few minutes.

During the many months of continuous operation, no sensors failed or changed radically in sensitivity. The only problem encountered was occasional noisy or erratic data resulting from corrosion of the sensor sockets by the acidic oxidation products, which was corrected by cleaning the socket contacts.

Sensitivity Limits

As can be seen from Figs. 5 and 6, the most useful concentration range for the sensors is from 0.1 to 100 ppt. This appears to be about optimum for the size cells, temperature, and air flow used in this work. With larger cells, higher temperatures, or lubricants with higher vapor pressures the increased vapor evolution exceeds this limit, and the sensor response is diminished. Although further changing the amplifier gain or sensor temperature may be helpful, the departure of the sensor response from the relationship of Equation (4) as

saturation approaches might remain a problem. Controlled
dilution of the cell effluent before passing it over the sensor
should be a workable solution, though it complicates an
inherently simple system. Increasing the rate of air flow
through the cell would also help, but might affect the results of
the test by cooling the oil, causing foaming, or depleting the
sample by aerosol formation.

Specification Testing

In 1981, 8 samples of MIL-L-23699 turbine engine lubricants
were provided by the Naval Air Propulsion Center (NAPC) for
oxidation testing with the NRL gas sensor apparatus. The results
showed good repeatability (5% relative error) and correlated
with the initial antioxidant concentrations (8). Most of these
tests were made using a different model gas sensor, and before
implementation of computerized data collection and reduction.

Three more samples which had been subjected to the corrosion
and oxidation stability test of MIL-L-23699 were provided by NAPC
in 1983. In this test, based on Method 5308.6 of Federal Test
Method Standard No. 791, 100 ml of lubricant was held at 400°F
(204°C) for 72 hours in the presence of air and metals. Two
tests of each sample were made with the NRL apparatus, using 5 ml
of lubricant at 400°F (204°C) without metals. Comparative results
are given in Table 2. The maximum vapor concentrations include
the 2-hour period after breakdown detection.

Table 2 - Oxidation Test Results with MIL-L-23699 Lubricants

| Sample Number Corr.-oxidation, 72 hr. | 1136 Failed | | 1137 Passed | | 21778 Passed | |
|---|---|---|---|---|---|---|
| Gas sensor test run | 1 | 2 | 1 | 2 | 1 | 2 |
| Induction period, hr. | 46.1 | 42.1 | 135* | 160 | 69.1 | 73.2 |
| Max. vapor conc.,ppt | 55 | 53 | 7* | 47 | 19 | 39 |

*.Test run stopped manually

Sample 1136, which failed both total acid number and viscosity requirements, also had induction periods well under 72 hours when tested with the gas sensors.  Sample 1137 passed the corrosion and oxidation test, and was found to have induction periods well in excess of 72 hours.  The first run was manually terminated prematurely after a rise in the signal was seen.  The low  maximum concentration indicates that this was not a true breakdown.  This sample failed the sediment requirement of the specification, and sediment and deposits were seen in the cells after the runs.  Sample 21778 passed the corrosion and oxidation test, but the gas sensor tests showed that it may have been close to failure.  The data shown in Fig. 8 were from the first run with this sample.

Conclusions

This relatively simple method has been employed successfully in the determination of lubricant oxidative stability, and may be applicable to a broader range of materials whose oxidative stability must be determined.  The technique worked well with small sample volumes, which is important when costly research grade material such as deuterated fluids are being evaluated.

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The computerized system is particularly attractive in situation where simultaneous automated testing of multiple samples is desired.

A major advantage over previous techniques for research purposes is the provision of exact induction period data and real-time indication of breakdown. Frequent tedious sampling and acid number or viscosity measurements were formerly required. In specification testing only one sample need be examined, but the elimination of these manual tasks still might provide a substantial saving of labor.

## ACKNOWLEDGMENTS

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