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A PROPOSED REFERENCE MATERIAL FOR OXIDATIVE INDUCTION TIME BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT: A polyethylene film sample, inhibited with a hindered phenol antioxidant, is proposed as a Standard Reference Material for oxidative induction time (OIT) testing. The mean OIT values, derived from nine interlaboratory studies and for a number of experimental conditions, are presented. The material is found to be statistically homogeneous, a necessary condition for a reference material. Further, the effects of temperature, oxygen pressure, and storage time on the proposed reference material are explored. As a kinetic parameter, the OIT value appears to be decreasing with time but in a well behaved and predictable manner. The use of a table and graph permit the user of the material to estimate its OIT value in the future. Because the material has been thoroughly tested in a wide variety of OIT conditions, it appears to be the best currently available candidate and is offered for consideration as an OIT Reference Material.

KEYWORDS: calibration, differential scanning calorimetry, oxidation, oxidative induction time, oxidative stability, reference materials, thermal analysis

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Oxidative induction time (OIT) is a widely used parameter for the oxidative stability of polymers, edible oils, and lubricants. It is typically used as a quality control tool and to rank the effectiveness of various oxidation inhibitors added to hydrocarbon products. OIT is defined as the time to the onset of oxidation of a test specimen exposed to an oxidizing

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gas at an elevated isothermal test temperature. OIT is a kinetic parameter (that is, one dependent on both time and temperature) and is not a thermodynamic property.

The analytical precision and mean value for the OIT determination are known to depend on a large number of experimental parameters including isothermal test temperature, specimen mass and surface area, purge gas flow rate, and catalytic impurities [1]. Because of these effects, it is quite common for laboratories to get widely different OIT values when testing the same material. Interlaboratory correlation of results are likely to improve with the use of an OIT Reference Material of known characteristics to serve as a performance standard.

According to ISO Guide for Certification of Reference Materials - General and Statistical Principles, a good reference material has a number of desirable properties including a well-documented analytical value, homogeneity, stability, ready availability and traceability to a National Reference Laboratory (NRL). Unfortunately, an OIT Reference Material is not ideal since, by its nature, it does not meet all of these criteria. For example, OIT is not a thermodynamic property and is therefore not easily made traceable to a NRL. Further, OIT is a kinetic property so its value will likely change with time and therefore lacks stability.

Background

Over the last few years, a number of standard test methods for the OIT measurement have been developed, each with its own set of experimental conditions, aimed at optimizing the test for specific products (see Table 1). In each method, intra- or interlaboratory studies or both were conducted to test for ruggedness and provide a precision and bias statement for the standard test method.

One of the most thorough studies was that of ASTM Committee D9 on Electrical Insulation Materials which, in 1994, revised the OIT section to the ASTM Test Method for Physical and Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable Materials (D 4565). In the development of that revision, five interlaboratory studies were conducted in a series of ruggedness tests to explore one or more of the experimental parameters. As part of that work, a single test sample of polyolefin film was included at each stage of the work as an internal reference material. Over the four years of the test program, a very large amount of data was generated on this single material.

At the end of the ASTM Committee D9 test program, it was proposed that the polyethylene film internal reference material be considered as a Standard Reference Material for the OIT test. The National Institute of Standards and Technology (NIST) and ASTM were contacted to see if they would care to take on the responsibility for distribution of the material as an OIT Standard Reference Material. Both of these

TABLE 1 - ASTM standard methods for oxidative induction time.

Method	Title
D 3350	Specification for Polyethylene Plastics Pipe and Fittings Materials
D 3895	Test Method for Oxidative Induction Time of Polyolefins by Differential Scanning Calorimetry
D 4565	Test Methods for Physical and Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable
D 5483	Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry
D 5885	Test Method for Oxidative Induction Time of Polyolefin Geosynthetics by High Pressure Differential Scanning Calorimetry
E 1858	Test Method for Oxidative Induction Time of Hydrocarbons by Differential Scanning Calorimetry

organizations declined this offer because of the need for additional testing, the relatively small market opportunity, and instability of the reference material.

The importance of this material was recognized by TA Instruments, and a large quantity of the polyolefin film was purchased from the original manufacturer. Since that original purchase, the material has been protected for future use, and additional testing has been performed. The material has been tested for key properties of homogeneity and stability and has been used in several additional interlaboratory studies.

It is the purpose of this paper, then, to collect the large amount of experimental information on this material and to propose the material as an OIT Standard Reference Material.

Material

The proposed OIT Reference Material is in the form of translucent film 0.22 mm (9 mils) in thickness. It is a high density polyethylene film, lightly stabilized with Irganox®1010, a hindered phenol antioxidant package. Its melting profile, as determined by ASTM

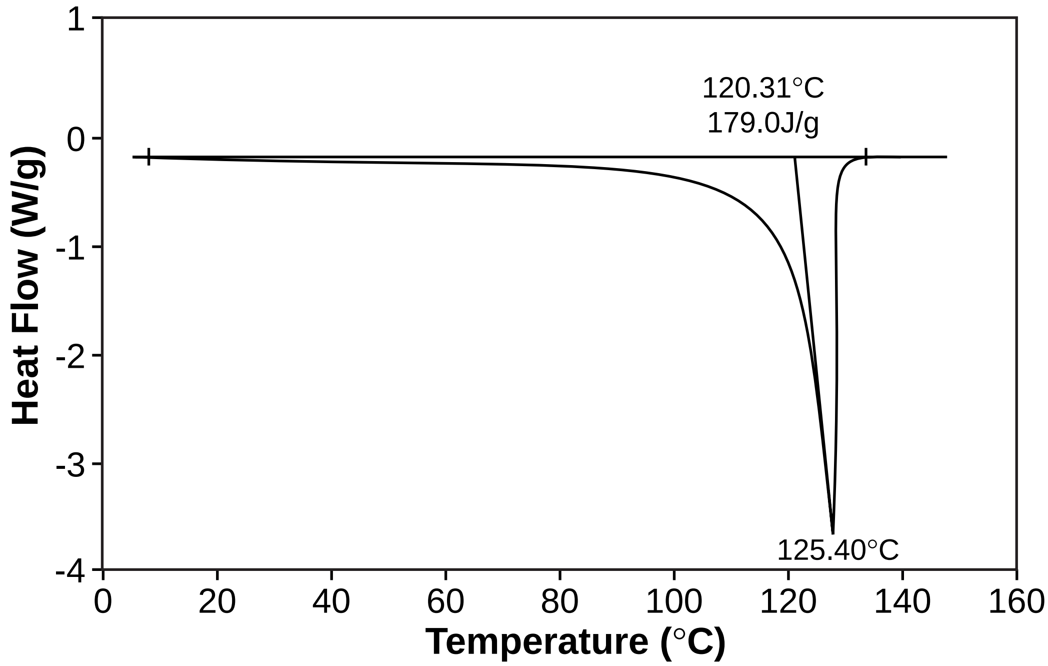

FIG. 1 — Polyethylene reference material melting profile.

Standard E 794 Test Method for Melting and Crystallization Temperatures by Thermal Analysis, is shown in Fig. 1 and has a peak melting temperature of 125°C. After manufacture, the film was warehouse stored in the dark as a roll. Before examination and preparation of the reference materials kits, the outer layer of this roll was withdrawn and discarded

The proposed reference material is packaged as two 8- by 13-cm sheets of the film, enough for more than 500 individual OIT measurements. Since antioxidant packages can be susceptible to migration between adjacent leaves of material, the two sheets are stored in an envelop of the same film which serves as a sacrificial barrier. These materials are then stored in an opaque polyolefin zip-lock bag to shield them further from environmental exposure.

<u>Homogeneity</u>

Before packaging, the roll of film was partitioned into a series of sections across the breadth and length for homogeneity testing of the antioxidant distribution. A single laboratory obtained OIT values using ASTM Test Method D 4565. The mean OIT resulting from this homogeneity testing, with 48 total determinations, was 30.0 min with a standard deviation of ±1.2 min.

Figure 2 shows a histogram distribution of the OIT values determined in this homogeneity study. The number of OIT values within each 0.5-min range is displayed on the ordinate versus the OIT value on the abscissa. The shape of the curve is one indication of the

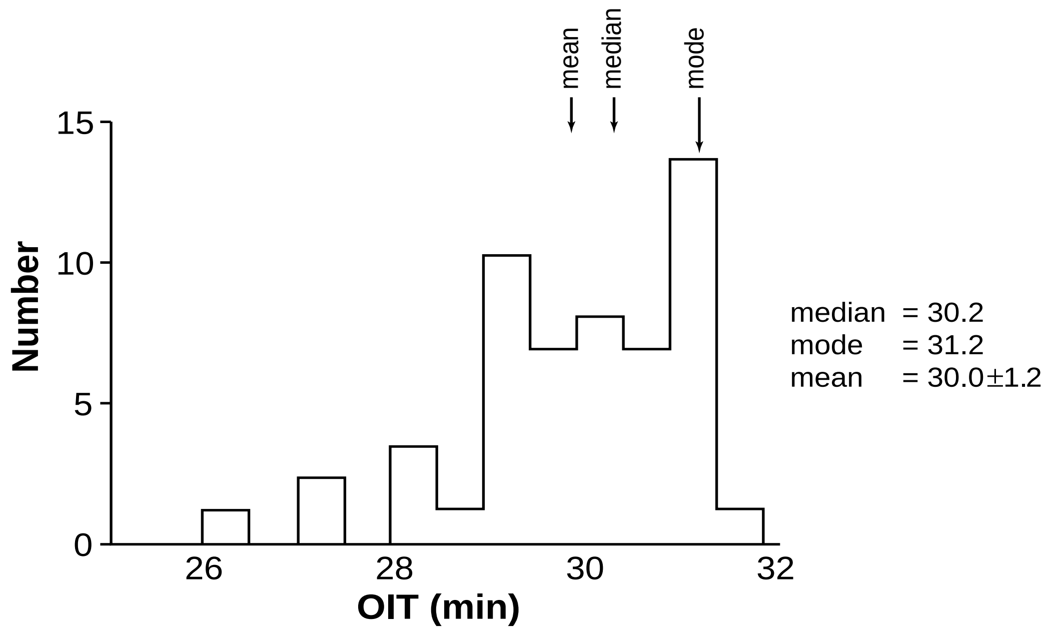

FIG. 2 — Distribution of OIT results.

randomness of the experimental data with a “bell shaped” distribution resulting if it is truly “normal.”

The distribution of results in Fig. 2 appears to be somewhat skewed toward lower values. The most probable mode value for the distribution is 31.2 min with the mean and median at 30.0 and 30.2 min, respectively. The mean is lower than the mode by 1.2 min (4%). Moreover, the mode is very close to the maximum value of 31.6 min.

This distribution of results was statistically tested for skewness using the Pearson’s index. The Pearson’s skewness index for this distribution is -0.39 indicating a slight skew toward to lower values. However, only indexes greater than ±1.0 are statistically significant in indicating skew [2]. Therefore, the data may be considered to have a normal distribution and to be amenable to gaussian statistics.

Figure 3 presents another graphical tool to test for homogeneity. Here the same OIT values are presented on the ordinate as a function of their juxtaposed position on the abscissa. The values are plotted around the mean value of 30.0 as an aid to the eye. The data may be visually inspected to detect whether there are any noticeable trends in the data or if there are clusters of measurements of the same OIT values. Such trends or clusters might exist, for example, if the antioxidant package is not well dispersed. Except for a cluster of four measurements near position 30 and another near position 45, the data appears to be quite random with regard to both magnitude and position, above or below the mean.

The data was statistically examined for trends or clusters using the Shewhart rational subgroup technique [3]. In the Shewhart test, the data is partitioned into a series of

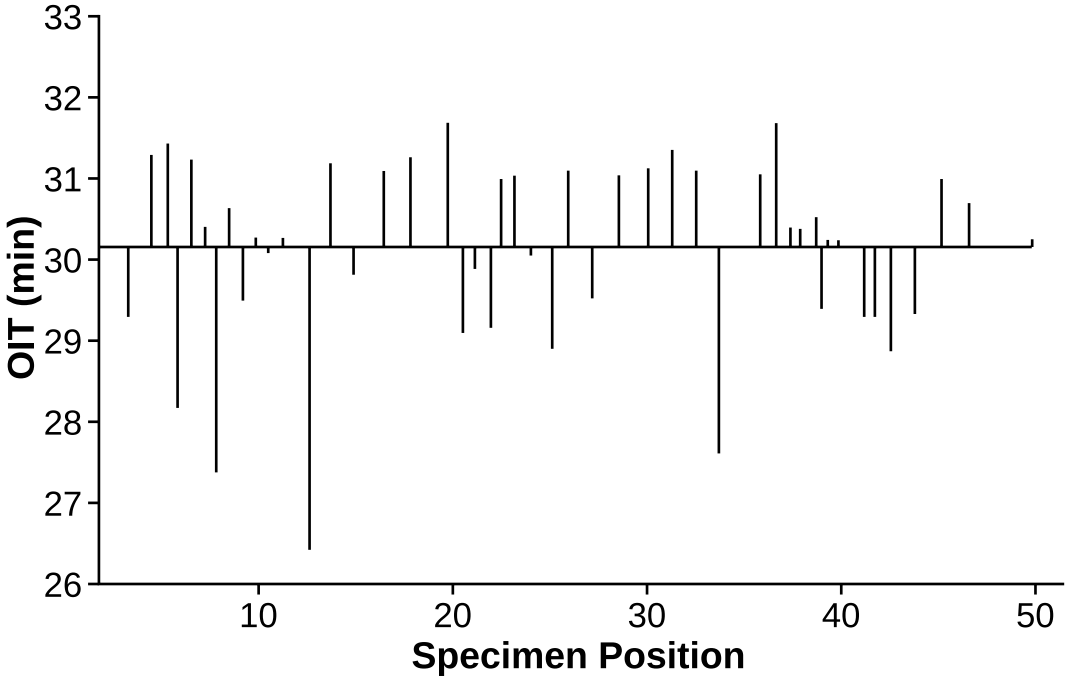

FIG. 3 — Distribution effect of position.

TABLE 2 — Interlaboratory test data.

ASTM Method	Temperature °C	Pressure MPa	Mean OIT, min	Repeatability %	Reproducibility %
E 1858[a]	195	0.10	29	4.3	15.
D 4565[b]	200	0.10	31	5.3	8.8
D 5885[c]	150	3.4	231	2.5	7.6
E 1858[a]	175	3.4	26	6.7	7.4
Mean				4.7	9.7

[a] Interlaboratory test performed in 1995 in support of E1858 as reported in Research Report E37-1018. Degrees of freedom df = (*n*-1) (*p*-1) = 7.

[b] Obtained from an independent interlaboratory test and are not taken from the research report for this method. df = 24.

[c] df = 15.

subgroups and the subgroup means and ranges are compared to the overall mean and range. This statistical treatment found no trends or clusters either for the subsets of $n = 3$ or 4. Therefore, the material is considered to be statistically homogeneous for the OIT determination.

Mean Values

The polyolefin film sample was used in a number of interlaboratory studies (ILT) aimed at generating precision and bias statements for several different OIT ASTM standards. The results of these ILT are presented in Table 2 showing the mean OIT, within laboratory relative repeatability (= r x 100% / mean) and between laboratory relative reproducibility (= R x 100% / mean). Overall pooled relative repeatability is approximately 4.7%, and pooled relative reproducibility is 9.7% This is consistent with the interlaboratory study rule of thumb that reproducibility is anticipated to be twice repeatability.

TABLE 3 — Effect of temperature.

Temperature °C	Oxidative Induction Time, min at 0.10 MPa O_2	at 3.4 MPa O_2
200	30.0	9.8
190	—	14.4
180	96	25.2
175	132	—
170	—	47.1
165	385	—
160	676	95.4
155	882	—
150	—	208.
Pooled rel. std. dev.	4.1%	2.4%

Effect of Temperature

The OIT value is known to be strongly dependent on test temperature, with individual laboratories choosing slightly higher or lower test temperatures than the standard to meet local needs [1]. This reference material was tested in replicated ($n > 5$) determinations as a function of temperature to observe this effect both at 0.10 and 3.4 MPa oxygen

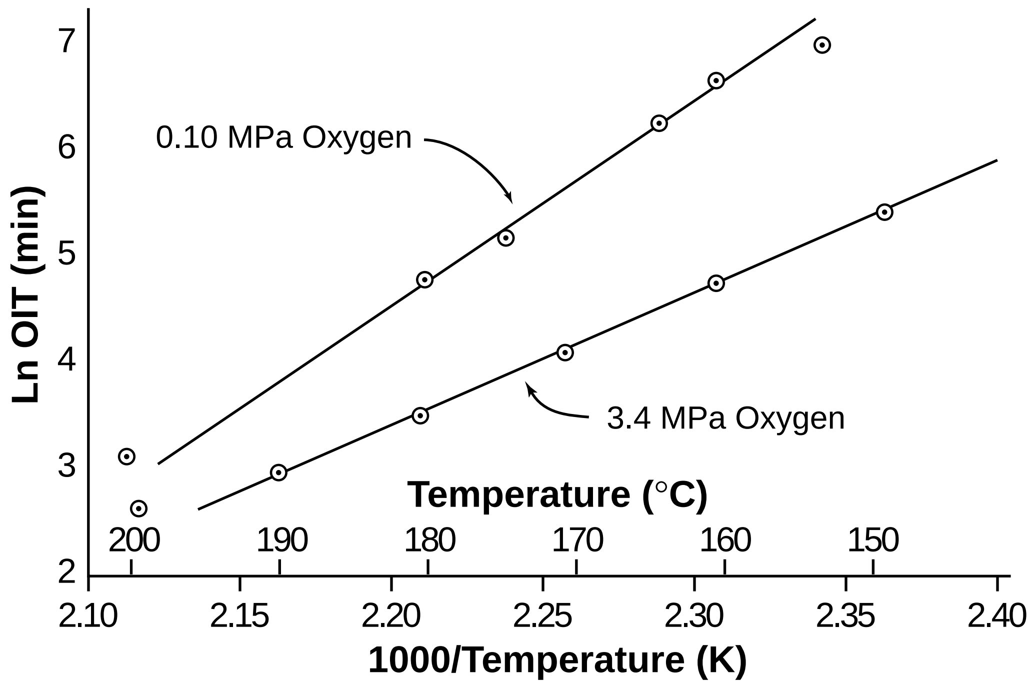

FIG. 4 — Effect of temperature.

pressure. The results of these tests are presented in Table 3. The same data are shown in graphical form in Fig. 4 where the logarithm of the OIT value is displayed versus the reciprocal absolute temperature. The straight line plots confirms the Arrhenius dependence of the OIT value as a function of temperature and the first order form of the general rate equation governing the process.

Effect of Pressure

Some OIT experiments are carried out under elevated oxygen pressure to shorten the analysis time or lower the test temperature to avoid volatilization of the antioxidant package. Table 4 shows the effect of oxygen pressure on the proposed reference material at two commonly used test temperatures.

The same data are presented in graphical form in Fig. 5 which displays the OIT values on the ordinate and oxygen pressure on the abscissa in a log-log form. The slope of the two lines appear nearly parallel.

TABLE 4 - Effect of pressure on OIT.

Oxygen Pressure, MPa	Oxidative Induction Time, min	
	at 170°C	at 180°C
0.10	558.9	198.9
0.79	113.6	47.6
2.17	63.0	26.8
3.55	48.9	21.4
5.27	37.3	17.2
7.00	34.0	14.0
Pooled rel. std. dev.	7.6%	13%

Stability

The OIT value of the materials was tested using ASTM Test Method D 4565, in a single laboratory, by a large number (*n* > 10) of replicate measurements on several occasion, over a five-year period, providing an opportunity to study the long-term stability of the material. The mean values for the OIT determinations in a single laboratory over a series of nearly five years is presented in Table 5 with a pooled standard deviation for the series of measurements of ±1.3 min. These values are statistically different from each other based on the student t tests. Taking the earliest data obtained in October 1990 to represent 100%, subsequent tests in July of 1992 and August of 1995 show a 95 and 91% relative OIT value indicating that the OIT value of the polyethylene is decreasing with time.

OIT is generally considered to follow first-order kinetics. The straight line plots of Fig. 4, for example, suggest first-order kinetics. If the data from Table 5 are best fit to the first-order kinetic expression, then the decay of the material's OIT value with time may be estimated into the future. Table 6 shows the best fit OIT values calculated from this fitted kinetic expression. The first six values represent fitted historical data points and may be compared to actual experimental results in Fig. 6. The remaining points estimate future performance. Actual historical experimental data points taken from Table 3 and 5 are plotted on the curve at the corresponding date along with their experimental error bars.

The set of data is also presented in Fig. 5 in which OIT values are plotted as function of date. The use of that Table 6 and Fig. 6 permit the individual laboratory to estimate the OIT value at times into the future. In light of the scatter in the data, such an extrapolation

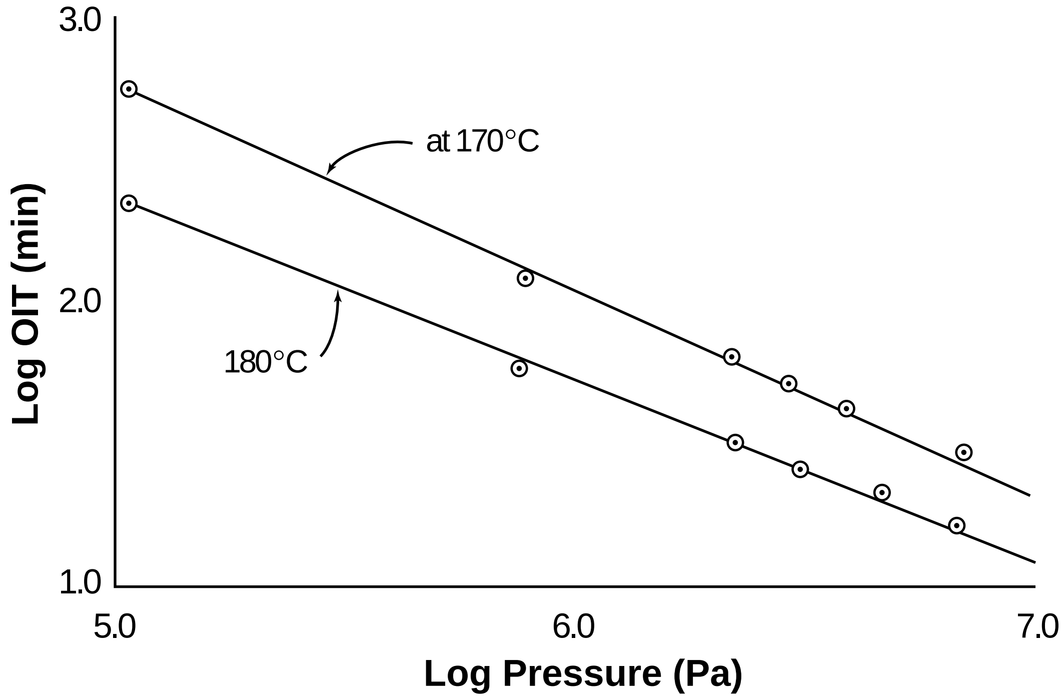

FIG. 5 — Effect of oxygen pressure.

TABLE 5 — Effect of time.
(temperature = 200°C; oxygen pressure = 0.10 MPa)

Date Tested, mo/yr	Mean OIT, min	Relative OIT, %
10/90	33.0	100.0
07/92	31.5	95.4
08/95	30.0	90.9

TABLE 6 — Calculated OIT values and the effect of time.

Date, mo/yr	OIT, min
01/90	34.28
01/91	33.33
01/92	32.40
01/93	31.51
01/94	30.64
01/95	29.81
01/96	28.97
01/97	28.16
01/98	27.38
01/99	26.63
01/00	25.89
01/01	25.17
01/02	24.47
01/03	23.80
01/04	23.14

must be used with caution as ongoing efforts will be needed to verify this change of the OIT value with time.

Conclusion

In summary, a polyethylene film sample is proposed as a reference material for OIT testing. The OIT values of the material have been thoroughly tested by at least nine interlaboratory test programs over a period of more than five years, making this one of the most well-characterized OIT materials. Further, the material has been found to be statistically homogeneous, a necessary condition for service as a reference material. As a parameter dependent on test time and temperature, the OIT value appears to be decreasing with time but in a well behaved and predictable manner. The use of a table and graph permit the user of the material to estimate its OIT value in the future. The effect of temperature and oxygen pressure have also been explored permitting the user of the reference material to estimate OIT values under experimental conditions different than those of the standards. At present, this material is considered the best available reference material for oxidative induction time testing.

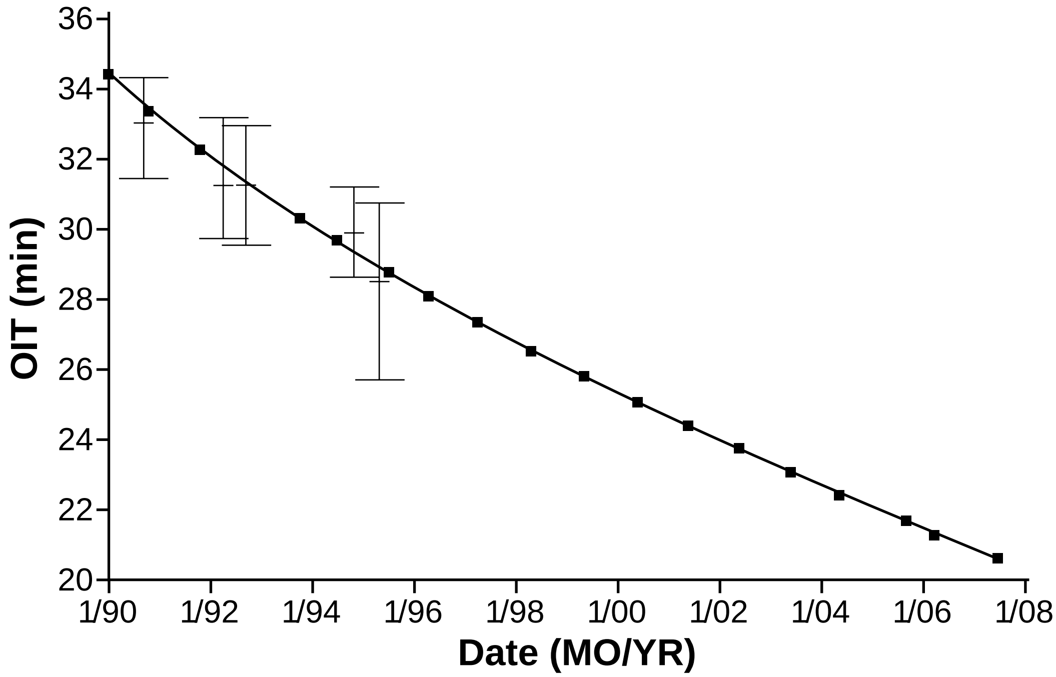

FIG. 6 — OIT decay with time.

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