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OXIDATIVE INDUCTION TIME - A REVIEW OF DSC EXPERIMENTAL EFFECTS

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ABSTRACT: Over the past several years, a number of ASTM committees have explored a wide variety of experimental parameters affecting the oxidative induction time (OIT) test method in an attempt to improve its intra- and inter-laboratory precision. These studies have identified test temperature precision as a key parameter affecting OIT precision. Other parameters of importance are oxygen flow rate, specimen size, specimen pan type, oxygen pressure and catalyst effects. The work of Kuck, Bowmer, Riga, Tikuisis and Thomas are reviewed as well as the collective work of ASTM Committees E37, D2, D9 and D35.

KEYWORDS: differential scanning calorimetry, oxidation, oxidative induction time, oxidative stability, polyethylene, polyolefins, thermal analysis

Oxidative Induction Time (OIT) is an accelerated aging test. It provides an index useful in comparing the relative resistance to oxidation of a variety of hydrocarbon materials. The test consists of heating a specimen to an elevated temperature (often 200 °C) in a differential scanning calorimeter (DSC). Once temperature equilibrium is established, the specimen atmosphere is changed from inert nitrogen to oxidizing air or oxygen. The time from first oxygen exposure until the onset of oxidation is taken as the OIT value. This general procedure is applied, for example, to polyethylene wire insulation [1, 2], geosynthetic barriers [3], edible oils [4], lubricating oils and greases [5, 6]. Table 1 shows a few of the currently used application areas for OIT.

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Table 1 -- Applications

<u>Material</u>	<u>Applications</u>
Polyolefins	Wire and Cable Insulation
Polyethylenes	Pipe
Polyolefins	Geosynthetic Materials
Greases	Lubricants
Peanut Oil	Confections
Oils	Lubricants
Hydrocarbons	Fuels
Oils	Automatic Transmission Fluids

Most materials are tested to measure the effectiveness of the antioxidant package added to improve lifetime, although a few materials (e.g., edible oils) are tested in their natural, non-fortified state.

Background

The OIT procedure was first developed by Gilroy and coworkers at Bell Laboratory as a test procedure to screen polyethylene insulation used in telephone wire and cable for its oxidation resistance in pedestals [7]. The method first became available as a Western Electric specification [8] and later as ASTM Test Method for Copper Induced Oxidative Induction Time of Polyolefins [1]. Polyolefin manufacturers quickly embraced the procedure and began to apply it to other applications including raw resins, finished pipe [9], as well as to wire and cable insulation [2], and, most recently, geosynthetic waste pit liners [3].

It has long been known that the effectiveness of antioxidants, as measured by the OIT at high temperatures, may differ as a function of temperature [7, 10]. This may be due to a number of causes including changing mechanisms, loss of antioxidant due to volatilization at high test temperatures, etc. Many users would like to move the OIT test temperature closer to the actual use temperature to avoid some of these difficulties. Further, as additive packages have improved, OIT values have become progressively longer. In order to shorten the analysis time and to reduce test temperatures, increasing use is being made of Pressure DSC to accelerate the measurement at lower test temperatures.

The expanding applications for the OIT test method, the widespread use of Pressure DSC and improvements in apparatus electronics have combined to create increased interest in re-examination of the parameters of the OIT test method aimed at improving its precision. This interest has largely focus on improving inter- (between) laboratory reproducibility since intra- (within) laboratory repeatability is generally quite good. A general rule-of-

thumb is that interlaboratory reproducibility should be about twice the within laboratory repeatability. For much OIT work, the reproducibility is much poorer than this rule-of-thumb. This indicates that within a single laboratory, the same thing is done the same way every time but that there are differences in procedure in going from one laboratory to another.

Several authors, and groups of workers have (re)examined the effects of a number of experimental parameters on OIT values and their precision. It is the purpose of this paper, then to review and report on the efforts of ourselves and others in there efforts to improve the OIT test method.

Endpoint Selection

The onset of oxidation is taken as the endpoint for the OIT measurement. Two means of determining the oxidation onset are in use. The most common is the “extrapolated onset” in which tangents are drawn at the point of maximum rate of oxidation and the baseline prior to the oxidation. Their intersection is taken as the endpoint for the OIT measurement.

The second method for establishment of the endpoint for the OIT determination is the point of “first-deviation-from-baseline”. In this approach, some "threshold" is set above the baseline prior to oxidation (say 0.05 W/g). The endpoint for the OIT determination is taken at the point where the exothermic event crosses that threshold.

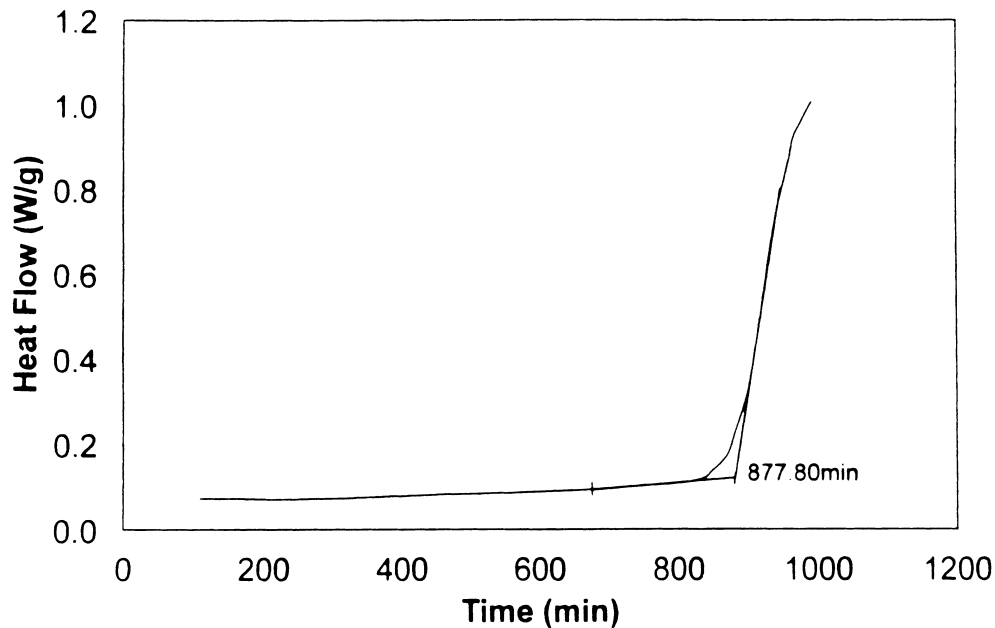


FIG. 1 -- Single stage oxidation endpoint determination.

If the oxidation exotherm is sharp, these two endpoint indicators produce similar results as seen in Figure 1 where the two values differ by only a few percent. Some materials, however, seem to have a multi-staged oxidation and the endpoint established by the two experimental procedures may be quite different as shown in Figure 2.

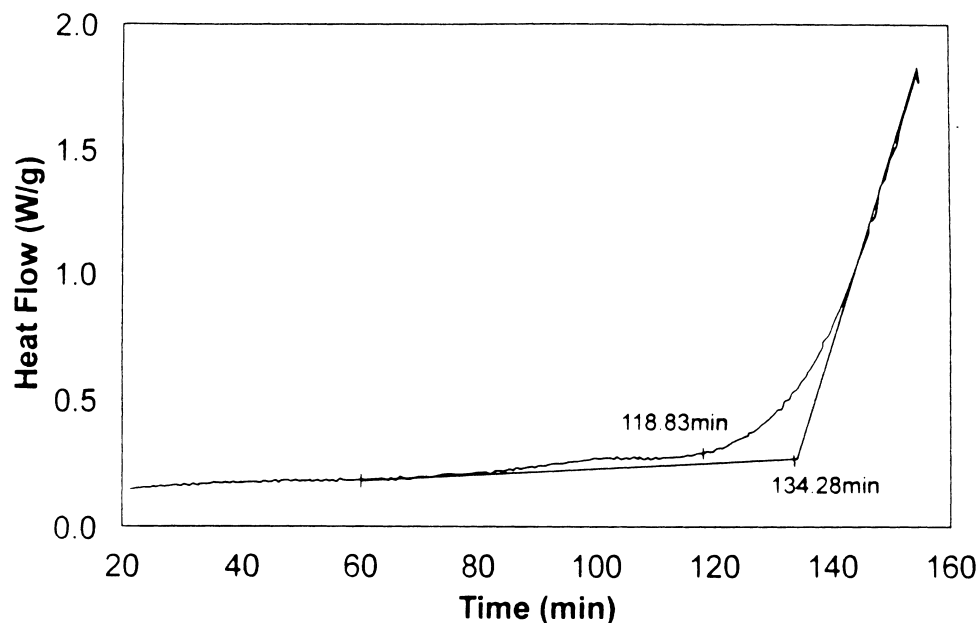


FIG. 2 -- Multistage oxidation endpoint determination

The selection of the method of determination of the OIT endpoint (i.e., extrapolated onset or first deviation) is the first parameter affecting the comparison of results from one laboratory to another. OIT values obtained by first deviation are usually lower than those obtained by extrapolated onset. Operators in a single laboratory commonly use the same

TABLE 2 -- Effect of endpoint selection on OIT precision.

<u>Endpoint Method</u>	<u>OIT Standard Deviation (min)</u>	
	<u>Within Lab</u>	<u>Lab-to-Lab</u>
First Deviation at 50 mW/g	4.5	7.3
Extrapolated Onset	2.8	7.2

approach, but workers in other laboratories may choose differing endpoint detectors. OIT results should identify the end point detector used to avoid this potential discrepancy.

Selection of the endpoint also affects the precision of the measurement. OIT precision, using extrapolated onset, usually has better precision than that using the first deviation from baseline. This is seen both in intralaboratory repeatability data and interlaboratory reproducibility values. ASTM's task group D9.18, working on an upgrade to ASTM D4565, obtained the OIT values for high density polyethylene insulation stripped from wire presented in Table 2. The OIT mean values for these tests were 122 and 126 min, respectively.

The within laboratory OIT precision values derived from the extrapolated onset is commonly two times better than that for the first deviation from baseline. For this reason, the extrapolated onset should be taken, wherever possible, as the endpoint indicator. The first deviation from baseline approach should be used only where this point on the oxidation profile provides specific information of interest to the researcher.

Effect of Temperature

The single most important influence in comparing OIT values from one laboratory to another is the test temperature of the method. Table 3 shows the effect slight changes in temperature can have on the OIT value for a high density polyethylene sample.

TABLE 3 -- Effect of temperature.

<u>Temperature</u> <u>(°C)</u>	<u>OIT</u> <u>(min)</u>
198.0	40.8
200.0	35.7
202.0	29.2

For this polyethylene sample, the effect of temperature on the OIT value is 2.9 min / °C or about 8.1 % / °C at the 200 °C test temperature. If the test temperature is not exactly the same in two laboratories or is not that called for in the test method, a serious discrepancy

is likely to result in comparing the results. This strong effect of test temperature is well known by those designing a test method [7] but may be ignored by the technologist who run the experiments because it requires instrument recalibration under conditions (i.e., isothermal operation) different than those used for most DSC experiments (e.g., 10 °C/min heating rate).

Precise temperature calibration along with the direct measurement and recording of sample temperature during the test are keys to overcoming lab-to-lab variability in OIT measurements. Some thermal analyzers have a strong temperature dependence on heating rate [11]. For this reason, temperature calibration must be carried out using a very low heating rate, usually 1 °C/min, to better simulate isothermal conditions.

Effect of Oxygen Flow Rate

A third experimental parameter which can effect the OIT value and its precision is the availability of the oxygen reactant. One of the factors affecting oxygen availability is flow rate.

OIT values are not strongly dependent upon reactant gas flow rates provided a necessary minimum flow rate is available. Unfortunately, this minimum level is quite close to the 50 mL/min commonly used [12]. Table 4 provides information on the effect of oxygen flow rate on the absolute value for OIT and on its precision, respectively, for a high density polyethylene sample.

TABLE 4 --Effect of oxygen flow rate on OIT.

<u>Flow Rate</u> <u>(mL/min)</u>	<u>OIT</u> <u>(min)</u>	<u>Precision</u> <u>(%)</u>
20	64	---
50	45	4.5
100	34	2.3

These results, and those of Ashby [12], indicate that around 50 mL/min flow rate, the OIT value may change 3.5 minutes (ca. 8%) for each 10 mL/min change in purge gas flow rate.

Further information presented in Table 4 shows that precision improves with higher flow rates. Unfortunately, not all DSC instruments are capable of flow rates as high as 100 mL/min so most standard methods have settled on the 50 mL/min rate for instrument compatibility purposes. The flow rate must be limited, however, to a very narrow range of ± 5 mL/min, to improve both repeatability and reproducibility.

Floating ball type flowmeters are commonly used in the thermal analysis laboratory for the measurement and control of purge gas flow rates. Flowmeter readings, however, are dependent on the molecular weight of the gas measured and must be calibrated for each gas used. Calibration tables for common gases are supplied with most high quality flowmeters and the use of such calibration tables with oxygen is essential. Flowmeter inadvertently set on the commonly used nitrogen gas setting will produce a lower than expected flow rate with oxygen leading to longer than anticipated OIT values. For example, a setting which reads 50 mL/min for nitrogen produces a 43.1 mL/min flow of oxygen. This is outside of the permitted range and is sufficient to change the indicated OIT value by approximately 5%.

Interlaboratory imprecision due to reactive gas availability effects can come from a second source. This is the difference among instrument designs in directing the reactant gas onto the test specimen. In some instruments, the reactive purge gas blanketing of the test sample is ineffective in reaching the test specimen [13]. Users should contact their instrument suppliers for any purge gas modifications required to achieve high OIT precision. Specifically ASTM D4565 states, "in some power compensation DSC's, use of the two-hole platinum sample holder lids with a special "flow through" swing away block cover is recommended" in order to obtain accuracy's and precision equivalent to other unmodified instrumentation" [9]. Users should follow all such instructions in order to obtain the best reproducibility.

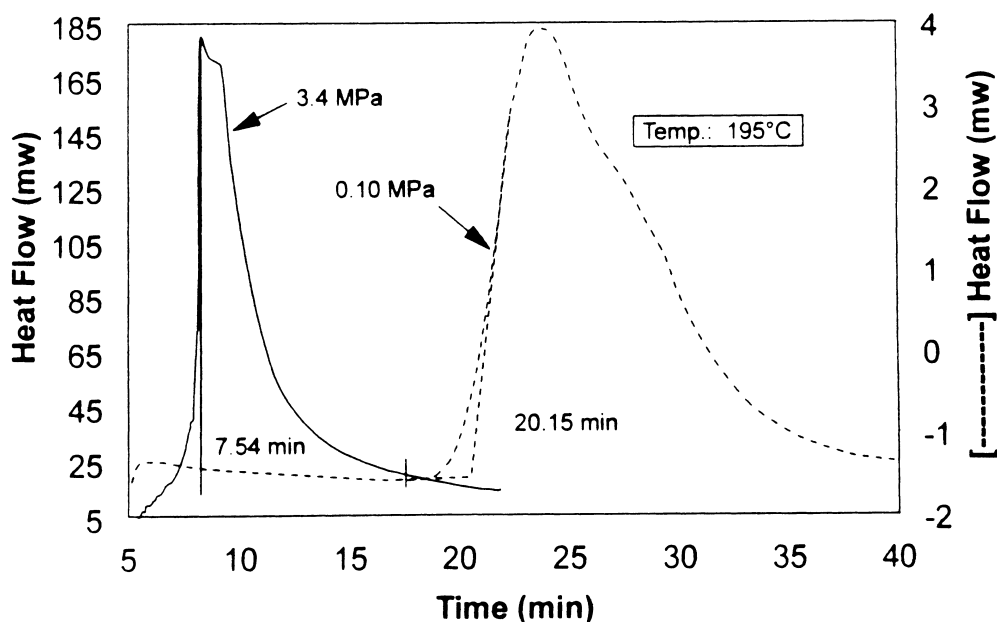


Fig. 3 -- Effect of oxygen pressure on OIT [14]

Effect of Oxygen Pressure

As in any oxidation reaction, the concentration of reactant oxygen has an effect on the OIT. Different OIT values will be obtained if air (with its 21% oxygen concentration) rather than pure oxygen is used as the reactive gas. Today, virtually all of the OIT test methods specify oxygen as the reactant gas.

The oxidation reaction rate can further be increased (and OIT values shortened) by using a Pressure DSC and elevated pressures of oxygen. Figure 3 illustrates, the reduction in OIT value resultant in operating at elevated oxygen pressure. In this case, the OIT of a lubricating grease is 20 minutes at atmospheric oxygen pressure, but is reduced to 7.5 minutes at 3.4 MPa (500 psi) pressure [14].

A number of workers, including Dugan [15], Tikuisis [16], and Thomas [17] have explored the effect of pressure on OIT values and have observed an Arrhenius type expression for partial pressures in excess of about 1.4 MPa (200 psi) with best results being obtained between 3.4 and 5.5 MPa (500 to 800 psi). The higher pressures are advantageous due to their insensitivity to small pressure changes and to the reduction in analysis time. In addition, higher pressures permit (lower) test temperatures to be used which are closer to actual end use conditions. For these reasons, virtually all of the pressure OIT work is done at pressure of 3.4 MPa or higher.

Effect of Catalysts (Sample Pan Materials)

The oxidation reaction is very sensitive to catalytic effects. It is well known that polyethylene insulation on copper wire has much lower OIT values than on aluminum wire or for the insulation alone. The original methods took advantage of the catalytic effects of copper oxide by running the test method in copper sample pans [1, 8]. This reduces the overall test time but induces interlaboratory imprecision due to different sources and conditioning of the copper pans used.

At least two workers, Riga [14, 18] and Kuck [13], have explored the effects of metal catalyst on the OIT value. Their work, based on DSC sample pans made from several different materials, is summarized in Table 5.

These results show that copper, stainless steel and platinum (all commercially available sample pans), catalyze the oxidation reaction of the test specimen. Standard commercial aluminum and non-commercial nickel pans show no catalytic effects. To obtain reproducibility, catalyst effects should be avoided through the use of standard aluminum sample pans. The price paid for this reproducibility is longer analysis times. Aluminum pans are required by several ASTM procedures [2,9].

Some operators make use of a stainless steel screen to keep the test specimen in place in the DSC pan by crimping it in place as a pseudo-lid. (Note that OIT measurements are to

be run in open pans with no lid in place.) Stainless steel, however, serves as a catalyst in the oxidation reaction. Workers who wish to make use of the screen principle should use an aluminum screen rather than the stainless steel. Use of stainless steel is likely to give shorter OIT values with poorer precision .

TABLE 5 -- Metal catalysis effect on polyethylene OIT.

<u>Metal</u>	<u>OIT (min)</u>	
	<u>Case 1[14,18]</u>	<u>Case 2 [13]</u>
Aluminum	47.9	36.5
Copper	21.4	----
Stainless Steel	38.9	26.9
Nickel	----	36.6
Platinum	----	30.5

Effect of Sample Mass and Form

Since OIT is a measure of a chemical reaction in which one of the reactants is a gas surrounding a condensed phase test specimen, the surface area of the specimen exposed to the oxygen is likely to be an important experimental parameter. The most precise OIT methods call for small (usually < 5 mg) and uniform (± 0.1 mg) test specimen sizes. If larger specimens are used, an appreciable portion of the specimen is shielded from the

reactive gas. Ashby showed that test specimens larger than about 5 mg had a relatively constant OIT value and argued for a selection of sample size in this region to minimize sample mass effects [12]. He further showed that specimens with exposed areas greater than 50 mm² appeared to have little change in OIT value with increased surface area. These results argue that there is, indeed, a surface area effect which must be considered.

Rhee illustrated for grease samples that specimen of the same weight but differing surface area produced markedly different OIT values as shown in Figure 4 [5]. He recommends that for liquid specimens, that Solid Fat Index (SFI) sample pans be used to produce a uniform sample area exposed to the oxygen when small specimen weights are used [6].

Specifying a large sample (to take advantage of mass and area insensitivities) is complicated by the fact that specimen size and shape often change upon heating through the melt. Polyolefin films, formed to obtain the maximum surface area for the minimum mass, tend to "bead up" into a ball upon melting. In this case, a uniform specimen size is more important than the test specimen weight.

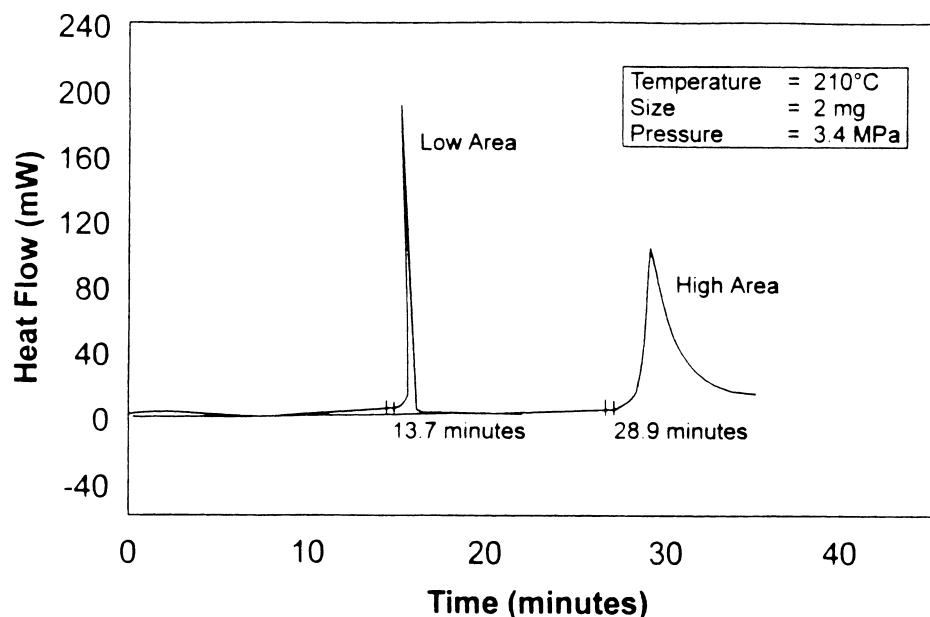


FIG. 4 -- Effect of area on OIT [4]

Effect of Time

The repeatability standard deviation for the OIT measurement is nearly constant in the 2 to 3 minute range and is not strongly dependent upon the OIT value itself. This means that precision should be stated in the form of standard deviation and not as percent relative standard deviation. This has the effect of dramatically increasing the relative standard deviation as the OIT values decrease. For example, at 3 min standard deviation becomes a 20% relative standard deviation for a 15 minute OIT value but is only 4% for a 75 minute OIT value

Because of this effect, experimental conditions should be selected so that the OIT values are longer than 15 minutes. Values larger than 15 minutes will permit reasonable relative standard deviation values to be obtained. At the upper end, experimental conditions are often selected so that the maximum OIT values are less than 100 minutes to improve productivity.

While the repeatability and reproducibility of the OIT test method will have some dependence on the sample itself, the best available within laboratory repeatability standard deviations (68% confidence limit) is about 1.6 min. and lab-to-lab reproducibility is about 3.1 min. Most ASTM test methods use the 95% confidence limit, 2.8 times the standard deviation. OIT results, each the mean of duplicate determinations, should be considered suspect if the within laboratory repeatability is greater than 4.5 min and interlaboratory reproducibility is greater than 8.7 min (in the best case).

Summary

The OIT method is very sensitive to a number of experimental conditions including temperature, oxygen flow rate, method of onset determination, specimen mass and surface area. To obtain the best precision, experimental conditions must be maintained within a very narrow set of conditions. Under such carefully controlled conditions, repeatability as good as 4.5 min and reproducibilities as good as 8.7 minutes may be obtained.

The most important effect on reproducibility is calibration of the apparatus for the identified test temperature. This parameter has a bias of 8 % / °C in OIT value. The second most influential parameter on both interlaboratory reproducibility and intralaboratory repeatability is the flow rate of the reactive oxygen used in the test method. A bias on the order of 8 % / 10 mL/min change in flow rate may result. Calibration of the flow measuring apparatus for oxygen use is essential.

Acknowledgments

Thanks are given to the many workers, cited and non-cited, who contributed to this effort. In some cases, the contributions of individual scientists and organizations were cited here, but much of the reported work took place in task groups. Many individuals from a large number of organization contributed in the this way. A few of the organization which contributed to this work are listed Table 6.

TABLE 6 -- Organizations studying oxidative induction time.

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- o ASTM Committee D2 on Petroleum Products
 - o ASTM Committee D9 on Wire and Cable Insulation
 - o ASTM Committee D20 on Plastics
 - o ASTM Committee E37 on Thermal methods
 - o ASTM Committee D35 on Geosynthetics
 - o Institute of (British) Petroleum
 - o National Institute for Standards and Technology
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