Standard Test Method for
Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry[1]

1. Scope*

1.1 This test method outlines a procedure for the determination of oxidative-induction time (OIT) of polymeric materials by differential scanning calorimetry (DSC). It is applicable to polyolefin resins that are in a fully stabilized/compounded form.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards information is given in Section 8.

NOTE 1—This test method is similar to ISO 11357–6, but not equivalent. ISO procedure provides additional information not supplied by this test method.

2. Referenced Documents

2.1 *ASTM Standards:* [2]
D 4703 Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets
E 473 Terminology Relating to Thermal Analysis
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

3. Terminology

3.1 Definitions—Definitions of terms applying to thermal analysis appear in Terminology E 473.

3.2 *Description of Term Specific to This Standard:*

3.2.1 *oxidative induction time*—a relative measure of a material's resistance to oxidative decomposition; it is determined by the thermoanalytical measurement of the time interval to onset of exothermic oxidation of a material at a specified temperature in an oxygen atmosphere.

3.2.2 Abbreviations:

3.2.3 HDPE—high-density polyethylene.

3.2.4 LDPE—low-density polyethylene.

3.2.5 LLDPE—linear low-density polyethylene.

3.2.6 OIT—oxidative induction time.

4. Summary of Test Method

4.1 The sample to be tested and the reference material are heated at a constant rate in an inert gaseous environment (nitrogen). When the specified temperature has been reached, the atmosphere is changed to oxygen maintained at the same flow rate. The specimen is then held at constant temperature until the oxidative reaction is displayed on the thermal curve. The time interval from when the oxygen flow is first initiated to the oxidative reaction is referred to as the induction period.

4.1.1 The end of the induction period is signaled by an abrupt increase in the specimen's evolved heat or temperature and may be observed by a differential scanning calorimeter (DSC). The OIT is determined from the data recorded during the isothermal test.

4.2 The type of containment system used depends on the intended application use of the material being tested. Polyolefins used in the wire and cable industry typically require copper or aluminum pans, whereas polyolefins used in geomembrane and vapor-barrier film applications exclusively use aluminum pans.

4.3 Unless otherwise specified, the analysis temperature used in this test has been set arbitrarily at 200.0°C. For samples that have relatively low or high stabilization levels, a different temperature may be selected (typically between 180 and 220°C) to yield a thermal curve that can be interpreted and analyzed easily.

A Summary of Changes section appears at the end of this standard.

5. Significance and Use

5.1 The OIT is a qualitative assessment of the level (or degree) of stabilization of the material tested. This test can be used as a quality control measure to monitor the stabilization level in formulated resin as received from a supplier, prior to extrusion.

Note 2—The OIT measurement is an accelerated thermal-aging test and as such can be misleading. Caution should be exercised in data interpretation since oxidation reaction kinetics are a function of temperature and the inherent properties of the additives contained in the sample. For example, OIT results are often used to select optimum resin formulations. Volatile antioxidants may generate poor OIT results even though they may perform adequately at the intended use temperature of the finished product.

Note 3—There is no accepted sampling procedure, nor have any definitive relationships been established for comparing OIT values on field samples to those on unused products, hence the use of such values for determining life expectancy is uncertain and subjective.

6. Apparatus

6.1 *Differential Scanning Calorimeter*—As a minimum requirement, the thermal analysis equipment shall be capable of measuring heat flow of at least 10-mW full scale. The instrument recorder should be capable of displaying heat flow or temperature differential on the *Y*-axis and time on the *X*-axis. The time base must be accurate to ±1 % and be readable to 0.1 min.

Note 4—The OIT test is a function of a particular compound's stabilizer system and should not be used as a basis of comparison between formulations that might contain, different resins, stabilizers, or additive packages, or all of these.

6.2 *Gas-Selector Switch and Regulators,* for high-purity nitrogen and oxygen. The distance between the gas-switching point and the instrument cell should be kept small to minimize the switching volume.

6.3 *Analytical Balance,* 0.1-mg sensitivity.

6.4 *Bore-Hole Cutter,* 6.4-mm diameter.

6.5 *Specimen-Encapsulating Press.*

6.6 *Forceps, Scalpel, and Cutting Board.*

6.7 *Rotometer (Calibrated) or Soap-Film Flowmeter,* for gas-flow calibration.

6.8 *Specimen Holders*—Degreased aluminum or oxidized-copper pans (6.0 to 7.0-mm diameter, 1.5-mm height). Use the appropriate pan type for the material being tested.

Note 5—Aluminum lids are required for temperature calibration.

Note 6—Both types of pans are commercially available. Alternatively, the copper pans can be fabricated manually. Details on copper pan preparation and oxidation as well as instructions for aluminum pan conditioning (degreasing) are given in Annex A2-Annex A4.

Note 7—The material composition of the specimen holder can influence the OIT test result significantly (that is, including any associated catalytic effects).

6.9 *Compression-Molding Device with Heated Platens.*

6.10 *Spacer Plates, Shim Stock, Caul Plates, etc.*

6.11 *Mylar[3] (Polyester Film) or Teflon[3] (Polytetrafluoroethylene) Coated Cloth,* for sample-plaque preparation.

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[3] Mylar and Teflon are registered trademarks of DuPont.

6.12 *Thickness Gage.*

6.13 *Laboratory Gas Burner,* for copper-pan oxidation.

6.14 *Boiling Flask,* with condenser and heating mantle.

6.15 *Forced-Air Oven.*

7. Reagents and Materials

7.1 All chemical reagents used in this procedure shall be analytical grade unless otherwise specified.

7.2 *Oxygen*—Ultra-high-purity grade (extra dry).

7.3 *Nitrogen*—Ultra-high-purity grade (extra dry).

7.4 *Aluminum Pan Degreasing Solvent.*

7.5 *Indium* (99.999 % purity).

7.6 *Tin* (99.999 % purity).

8. Hazards

8.1 Oxygen is a strong oxidizer that accelerates combustion vigorously. Keep oil and grease away from equipment using or containing oxygen.

8.2 The use of pressurized gas requires safe and proper handling.

9. Sampling

9.1 The following sample preparation procedures are recommended: the test sample is compression molded into sheet format (thickness of 250 ± 15 μm) prior to analysis to yield consistent sample morphology and weight. Specimen disks (6.4-mm diameter) cut from the sheet will have a weight of approximately 5 to 10 mg, depending on sample density.

Note 8—If the sample requires homogenization prior to analysis, the melt compounding procedure given in Appendix X1 is recommended. Poor sample uniformity will affect test precision adversely.

9.1.1 Meter out the required mass of the sample and place the material in the center of the appropriately sized spacer between two sheets of Mylar[3] or Teflon[3] coated cloth and two caul plates.

9.1.2 Place the assembly into the compression-molding device. The preheat and pressing temperature should be 160°C for polyethylene and 190°C for polypropylene.

9.1.3 Heat the sample with appropriate pressure and time settings to obtain a plaque with uniform thickness.

9.1.4 Remove the plaque assembly and place it between two thick steel plates (heat sink) and cool the plaque to ambient temperature. Alternatively, the plaque can be quenched in ice water.

9.1.5 Determine the average thickness of the sheet to ensure that it is within the allowable tolerances.

9.1.6 Use the bore-hole cutter to punch out a disk from the plaque and record the specimen weight.

9.1.7 Place the specimen disk into the appropriate pan type. Use an identical empty pan as the reference. (Do not crimp or seal the pans.)

Note 9—The test sample may also be prepared using Practice D 4703, Annex 1 (Procedure C), with the exception that controlled cooling is not necessary.

10. Procedure

10.1 *Instrumental Calibration*—This procedure uses a two-point calibration step. Indium and tin are used as the calibrants

since their respective melting points encompass the specified analysis temperature range (180 to 220°C). Calibrate the instrument in accordance with the manufacturer's instructions using the following procedure. The calibration step should be performed at least once per month.

10.1.1 Place 5 ± 0.5 mg of indium/tin into an aluminum sample pan. Place an aluminum cover over the pan, and seal using the encapsulating press. Prepare an empty sealed pan to be used as the reference. Place the specimen and reference pans into their respective locations in the instrument cell.

10.1.2 Turn on the nitrogen-gas flow at a rate of 50 mL/min (with an absolute pressure of 140 kPa).

10.1.3 Use the following melting profiles:

Indium: = ambient to 145°C at 10°C/min, 145 to 165°C at 1°C/min

Tin: = ambient to 220°C at 10°C/min, 220 to 240°C at 1°C/min

NOTE 10—The specified heating rates are for calibration use only.

10.1.4 Adjust the temperature-calibration software (or potentiometer) to set the melting point at 156.63 and 231.97°C[4] for indium and tin, respectively. The melting point of the calibrant is defined as the intercept of the extended baseline and the extended tangent to the first slope of the endotherm (that is, the onset). See Fig. 1.

NOTE 11—An inadequate melting thermal curve is occasionally obtained due to poor surface contact of the calibrant material to the pan surface. If this occurs, repeat the calibration step. (After one melting/crystallization cycle the calibrant material should coat the bottom of the pan evenly.)

10.2 *Instrument Operation:*

10.2.1 Load the specimen and reference pans into the cell.

10.2.2 Allow 5 min for a nitrogen prepurge prior to beginning the heating cycle to eliminate any residual oxygen. Commence programmed heating of the specimen (under nitrogen flow of 50 ± 5 mL/min) from ambient temperature to 200°C (set point) at a rate of 20°C/min.

10.2.3 When the set temperature has been reached, discontinue programmed heating and equilibrate the sample for 5 min at the set temperature. Turn on the recorder. If the instrument being used does not have an isothermal temperature-control-mode feature, follow the alternate procedure outlined in Annex A1 or alternatively ensure accurate temperature control by monitoring and adjusting continually, as required.

10.2.4 Once the equilibrium time has expired, change the gas to oxygen at a flow rate of 50 ± mL/min. (Record this event.) This changeover point to oxygen flow is considered the zero time of the experiment.

10.2.5 Continue isothermal operation until at least 2 min have elapsed after the steepest point of the exotherm has been displayed (see Fig. 2). At the tester's discretion, the test may be terminated if time requirements stated in the product's specification have been met.

10.2.6 Upon completion of the test, switch the gas selector back to nitrogen and cool the instrument to ambient temperature. If additional testing is being conducted, cooling the instrument cell below 60 to 70°C should be sufficient to avoid any premature thermal oxidation of the sample.

10.2.7 Test frequency is established by the user. As a minimum requirement, samples should be tested in duplicate with the mean value reported.

10.2.8 Clean the DSC cell of contamination by heating to 500°C for 5 min in air (or oxygen) prior to conducting measurements and between the testing of different formulations.

10.3 *Thermal Curve Analysis*—The data is plotted with the heat-flow signal normalized to sample mass (that is, W/g) on the *y*-axis, versus time on the *x*-axis. The *x*-axis should be expanded as much as possible to facilitate analysis.
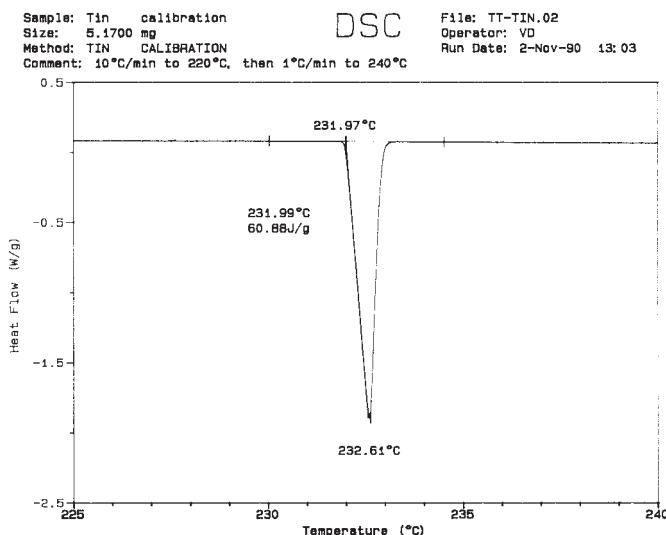
[4] See Practice E 967.
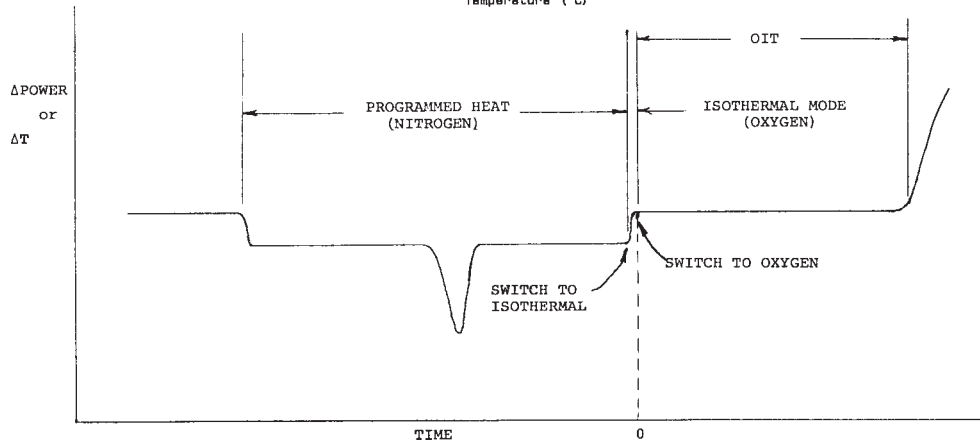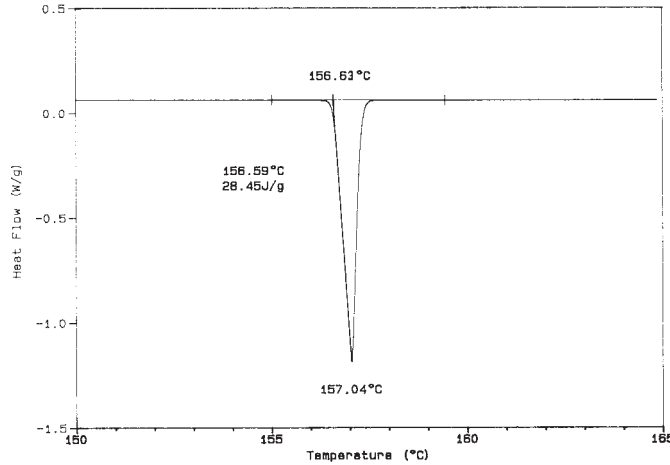

FIG. 1 Indium and Tin Melting Thermal Curves

FIG. 2 Evaluation of OIT from Recorded-Time-Based Thermal Curve

10.3.1 Extend the recorded baseline beyond the oxidative reactive exotherm. Extrapolate the steepest linear slope of this exotherm to intercept the extended baseline (see Fig. 3).

10.3.2 The OIT is measured to within ±0.1 min from zero time to the intercept point.

10.3.3 The tangent method used to measure the oxidation time is the preferred method, but the selection of the appropriate tangent to the exotherm sloped line may be difficult if the exothermic peak has a leading edge. Exothermic peaks with leading edges may occur if the oxidation reaction is slow.

NOTE 12—If the selection of the appropriate baseline is not obvious using the tangent method, try the offset method. Draw a second baseline parallel to the first baseline at a distance of 0.05 W/g above the first baseline. The intersection of this second line with the exotherm signal is defined as the onset of oxidation. The time from this intersection to zero time is the OIT.

NOTE 13—Other gas-flow rates or specimen weights, or both, may be used if shown to be equivalent.
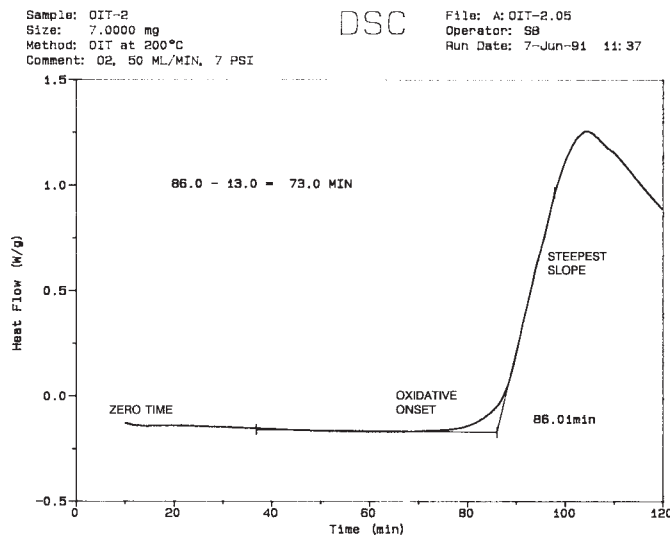
11. Report

11.1 Report the following information:

11.1.1 Identification of the sample,

FIG. 3 Determination of OIT

TABLE 1 Precision and Repeatability—Oxidative Induction Time (min) of Polyethylenes

Material	Average	S_r	S_R	r	R
LDPE	24.0	2.8	4.3	8.0	12.2
LDPE	83.4	9.2	17.4	25.7	48.8
LLDPE	120	7.8	14.6	21.9	40.8
HDPE	163	8.3	21.7	23.2	60.9

11.1.2 Type of sample pan,

11.1.3 Test temperature used,

11.1.4 Measurement technique used (that is, tangent method or offset method), and,

11.1.5 Average OIT in minutes (three significant digits).

12. Precision and Bias[5]

12.1 The data in Table 1 is based on a round robin conducted in 1991 in accordance with Practice E 691, involving four polyethylene materials tested by eleven laboratories. The test materials were obtained from three laboratories. The OIT of each sample was determined in duplicate on two separate days (that is, a total of four OIT determinations). Of the fourteen laboratories that participated in the round-robin exercise, eleven laboratories used heat flux-type instruments and three laboratories used power compensation-type instruments.

NOTE 14—The precision and bias data for other polyolefins may differ from the polyethylene material data shown in Table 1.

NOTE 15—The sample preparation steps for each test material (that is, sheet compression molding) were performed by one laboratory. Each participating laboratory received a set of specimen disks die cut from each of the molded sheets and samples of indium and tin required for instrument calibration. Each participating laboratory furnished its own specimen holders.

12.2 The following explanations of r and R (12.3-12.3.3) are intended to present only a meaningful way of considering the approximate precision of this test method. The data in Table

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[5] Supporting data are available from ASTM Headquarters. Request RR:D 20 – 1178.

1 should not be applied rigorously to acceptance or rejection of material, as those data are specific to the round robin, and may not be representative of other lots, conditions, materials, or laboratories. Users of this test method should apply the principles outlined in Practice E 691 to generate data specific to their laboratory and materials, or between specific laboratories. The principles of 12.3-12.3.3 would then be valid for such data.

12.3 *Concept of r and R*—If S_r and $—S_R$ have been calculated from a large enough body of data, and for test results that were averages from testing four specimens, the following applies:

12.3.1 *Repeatability Limit, r* (comparing two test results for the same material, obtained by the same operator using the same equipment on the same day)—The two test results should be judged not equivalent if they differ by more than the *r* value for that material.

12.3.2 *Reproducibility Limit, R* (comparing two test results for the same material, obtained by different operators using different equipment in different laboratories)—The two test results should be judged not equivalent if they differ by more than the *R* value for that material.

12.3.3 Any judgment in accordance with 12.3.1 or 12.3.2 would have an approximate 95 % (0.95) probability of being correct.

12.4 *Bias*—There are no recognized standards by which to estimate the bias of this test method.

13. Keywords

13.1 differential scanning calorimetry; oxidative induction time; polyolefins

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ANNEXES

(Mandatory Information)

A1. ALTERNATE OIT DETERMINATION

A1.1 If the DSC instrument being used does not have an isothermal temperature-control-mode feature, the following procedure can be used for OIT determination. Commence programmed heating (under a nitrogen flow of 50 ± 5 mL/min) from ambient temperature and record the thermal curve. Continue heating until 200.0 ± 2°C is reached. Discontinue programmed heating and equilibrate the specimen for 5 min to a constant temperature. Measure and record this temperature to ±0.1°C. Once the equilibrium time has expired, change the gas to oxygen at a flow rate of 50 ± 5 mL/min. This changeover point to oxygen flow is considered the zero time of the experiment. Continue isothermal operation until at least 2 min have elapsed after the steepest point of the exotherm has been displayed (see Fig. 2). Upon completion of the test, switch the gas selector back to nitrogen and cool the instrument to

ambient temperature. Repeat the entire test on a new sample, thereby generating a second exotherm. The isothermal portion of these two tests must be different from each other by at least 1°C, but within ±2°C of the set temperature (for example, 200.0 ± 2°C).

A1.2 Extend the recorded baseline beyond the oxidative reactive exotherm. Extrapolate the slope of this exotherm to intercept the extended baseline (see Fig. 3). The OIT is measured to within ±0.1 min from zero time to the intercept point. Make a plot of OIT versus temperature. Interpolate between the two actual temperature values until an OIT is obtained that corresponds exactly to the set temperature (for example, 200.0°C). A sample calculation is given in Fig. A1.1.
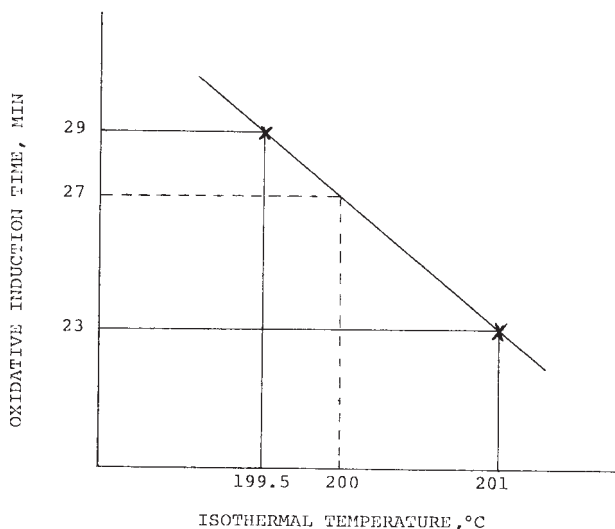
**FIG. A1.1 Example of the Linear-Interpolation Technique Used to
Estimate the OIT at 200.0°C**

A2. PREPARATION OF COPPER PANS

A2.1 Punch out a 10-mm diameter disk from a 0.10-mm
thick soft-copper strip. Using a punch and die tool, draw the
copper disks to form shallow holders. The lower 1.5 to 1.8 mm
of the side of the holder must be straight and even, but the edge
sections above may be irregular or ragged. The diameter of the
holder at the base must be from 6.6 to 6.9 mm. Trim off the
ragged edges.

A3. OXIDATION OF COPPER PANS

A3.1 Prepare fresh copper oxide coatings on the copper
pans by placing each pan in the flame of a gas burner until it
begins to glow (approximately 5 to 10 s). Rotate the pan in the
flame slowly to ensure a uniform oxide coating. Remove the
pan from the flame and allow it to cool to room temperature
(approximately 30 s).

A4. ALUMINUM PAN DEGREASING

A4.1 Condition aluminum pans and lids (lids used for
calibration only) prior to use. Reflux the pans and lids in a
low-boiling solvent such as cyclohexane for 30 min, and then
dry them in a forced-air oven at 40 to 50°C.

APPENDIX

(Nonmandatory Information)

X1. SAMPLE HOMOGENIZATION

X1.1 If desired, the test sample may be homogenized prior
to OIT analysis to minimize local variations of stabilizer
concentration. A torque rheometer equipped with a mixing
head is suitable for such purposes.

X1.2 Each sample should be blended at 60 r/min for 10
min, using a chamber temperature of 150 to 160°C for
polyethylene resins and 180 to 190°C for polypropylene resins.

The mixing chamber should be purged with nitrogen to
suppress polymer and additive degradation.

X1.3 After a mixing time of 10 min, quench-cool the
samples in liquid nitrogen or ice water. After sufficient cooling,
compression mold the required amount of material into sheet
format.

SUMMARY OF CHANGES

This section identifies the location of selected changes to this test method. For the convenience of the user, Committee D20 has highlighted those changes that may impact the use of this test method. This section may also include descriptions of the changes or reasons for the changes, or both.

D 3895 - 03:
(*1*) Revised ISO statement in Note 1.
D 3895 - 02:

(*1*) Revised Notes 1 and 9.
(*2*) Changed Practice D 1928 to D 4703 in Referenced Documents section.