Designation: D7444 – 11

Standard Practice for
Heat and Humidity Aging of Oxidatively Degradable Plastics[1]

This standard is issued under the fixed designation D7444; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice indicates how to test the oxidative degradation characteristics of plastics that degrade in the environment under atmospheric pressure and thermal and humidity simulations, only, in the absence of any selected disposal environment such as soil, landfill, or compost. This practice does not by any extension or extrapolation of data or results generated indicate that such plastics are suitable for or will degrade on disposal in these said environments. It is particularly noted that in real world environments such as soil, compost and landfill oxidations, if they occur, will predominantly be under conditions where other interfering ingredients are present and, in the case of landfill, at sub-atmospheric oxygen concentrations. This practice, therefore, can only result in a relative ordering of the potential for oxidation of plastic materials under the conditions tested, which are not always reflective of their behavior in a particular real world disposal systems. Prediction of the oxidation of a plastic under real world disposal conditions is an essential further testing in appropriate methodologies, such as Test Method D5338 for composting. No claims can be made for real world behavior based on this practice.

1.2 This practice is only intended to define the exposure conditions of plastics at various temperatures in air at atmospheric pressure under controlled humidity levels for extended periods of time. The humidity levels and temperature ranges are selected to be within the variable recorded seasonal ranges (upper and lower levels) generally observed in disposal sites where such plastics are discarded. For example: soil (15 to 40 percent moisture); landfill (35 to 60 percent moisture), and compost (45 to 70 percent moisture). It is optional to expose the plastic at zero humidity, if comparison with specified humidity ranges is of interest. Only the procedures for heat and humidity exposures are specified, not the test method or specimen, necessary for the evaluation of the heat and humidity exposure effects. The effect of heat and humidity on any particular property is determined by selection of the appropriate test method and specimen; however, it is recommended that Practice D3826 be used to determine the embrittlement endpoint, which is defined as that point in the history of a material when 75 % of the specimens tested have a tensile elongation at break of 5 % or less at an initial strain rate of 0.1 mm/mm min.

1.3 This practice is used to compare the effects of heat and humidity at any selected temperature, such as those found in the mentioned disposal environments, on the degradation of a particular plastic by selection of an appropriate test method and specimen.

1.4 This practice is to be used in order to apply selected exposure conditions when comparing the thermal-aging characteristics at controlled humidity levels of plastic materials as measured by the change in some property of interest (that is, embrittlement by means of loss of elongation, molecular weight, disintegration, etc.). It is very similar to Practice D3045 but is intended for use in evaluating plastics designed to be oxidized easily after use. The exposure times used for this practice will be significantly shorter than those used for Practice D3045

1.5 The type of oven used can affect the results obtained from this practice. The user can use one of two methods for oven exposure. Do not mix the results based on one method with those based on the other one.

1.6 *Procedure A: Gravity-Convection Oven*—Recommended for film specimens having a nominal thickness not greater than 0.25 mm (0.010 in.).

1.7 *Procedure B: Forced-Ventilation Oven*—Recommended for specimens having a nominal thickness greater than 0.25 mm (0.010 in.).

1.8 This practice recommends procedures for comparing the thermal and humidity aging characteristics of materials at a single temperature under dry or selected humidity conditions. Recommended procedures for determining the thermal aging characteristics of a material at a series of temperatures and humidity conditions for the purpose of estimating time to a defined property change at some lower temperature are also

[1] This practice is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.96 on Environmentally Degradable Plastics and Biobased Products.

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described. This practice does not predict thermal aging characteristics where interactions between stress, environment, temperature, and time control failure.

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

1.10 *The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are mathematical conversions to SI units that are provided for information only and are not considered standard.*

NOTE 1—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D618 Practice for Conditioning Plastics for Testing
D883 Terminology Relating to Plastics
D1870 Practice for Elevated Temperature Aging Using a Tubular Oven (Withdrawn 1998)[3]
D2436 Specification for Forced-Convection Laboratory Ovens for Electrical Insulation (Withdrawn 1994)[3]
D3045 Practice for Heat Aging of Plastics Without Load
D3593 Test Method for Molecular Weight Averages/ Distribution of Certain Polymers by Liquid Size-Exclusion Chromatography (Gel Permeation Chromatography GPC) Using Universal Calibration (Withdrawn 1993)[3]
D3826 Practice for Determining Degradation End Point in Degradable Polyethylene and Polypropylene Using a Tensile Test
D5032 Practice for Maintaining Constant Relative Humidity by Means of Aqueous Glycerin Solutions
D5338 Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures
D5510 Practice for Heat Aging of Oxidatively Degradable Plastics (Withdrawn 2010)[3]
D6954 Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation
E104 Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions
E145 Specification for Gravity-Convection and Forced-Ventilation Ovens

3. Terminology

3.1 *Definitions*—The definitions used in this practice are in accordance with Terminology D883.

4. Significance and Use

4.1 Since the correlation between the conditions specified in this practice and actual disposal environments (for example, composting, soil or landfill) has not been determined or established, the test results are to be used only for comparative and ranking purposes in the laboratory. No extrapolation to real world disposal expectations or predictions are to be made from results obtained by this procedure. Real world evaluations and correlations are needed for such claims.

4.2 Degradable plastics exposed to heat and humidity are subject to many types of physical and chemical changes. The severity of the exposures in both time, temperature and humidity level, determines the extent and type of change that occurs. For example, short exposure times at elevated temperatures generally serve to shorten the induction period of oxidatively degradable plastics during which the depletion of antioxidants and stabilizers occurs. Physical properties, such as tensile and impact strength and elongation and modulus, sometimes change during this induction period; however, these changes are generally not due to molecular-weight degradation, but are merely a temperature-dependent response, such as increased crystallinity or loss of volatile material, or both. The effects of humidity are less well understood and are more difficult to predict and depend on the degradable plastics characteristics such as hydrophilicity, polarity and composition.

4.3 Generally, short exposures at elevated temperatures drive out volatiles such as moisture, solvents, or plasticizers; relieve molding stresses; advance the cure of thermosets; increase crystallinity; and cause some change in color of the plastic or coloring agent, or both. Normally, additional shrinkage is expected with a loss of volatiles or advance in polymerization.

4.4 Some plastic materials such as PVC become brittle due to loss of plasticizers or to molecular breakdown of the polymer. Polypropylene and its copolymers tend to become very brittle as molecular degradation occurs, whereas polyethylene tends to become soft and weak before it embrittles with resultant loss in tensile strength and elongation.

4.5 Embrittlement of a material is not necessarily commensurate with a decrease in molecular weight. Test Method D3593 is used to characterize any molecular-weight changes that are suspected to have occurred during thermal exposure.

4.6 The degree of change observed will depend on the property measured. Different properties do not change at the same rate. In most cases, ultimate properties, such as break strength or break elongation, are more sensitive to degradation than bulk properties such as modulus.

4.7 Effects of exposure can be quite variable, especially when samples are exposed for long intervals of time. Factors that affect the reproducibility of data are the degree of temperature control of the enclosure, humidity level of the oven, air velocity over the specimen, and exposure period which are evaluated by this practice. Errors in exposure are cumulative with time; for example certain materials have the potential to be degraded due to the influence of humidity rather than oxidation in long-term tests and thus give misleading results. Materials susceptible to hydrolysis (that is, hydrolytically degradable plastics) undergo degradation when subjected to long-term thermal tests due to the presence of moisture rather than oxidation.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

4.8 Do not infer that comparative material ranking is undesirable or unworkable. On the contrary, this practice is designed to provide information that can be used for such comparative purposes after appropriate physical property tests are performed following exposure. However, since it does not account for the influence of stress or environment that is involved in most real life applications, the information obtained from this practice must be used cautiously by the designer, who must inevitably make material choices using additional information, such as moisture, soil-type and composition, and mechanical-action effects that are consistent with the requirements of the particular application.

4.9 It is possible for many temperature indices to exist, in fact, one for each failure criterion (time to reach failure is dependent on the exposure temperature and humidity). Therefore, for any application of the temperature index to be valid, the thermal-aging program must duplicate the intended exposure conditions of the end product. If the plastic material is exposed in the end use in a manner not evaluated in the aging program, the temperature index thus derived is not applicable to the use of the plastic material.

4.10 In some situations, a material can be exposed to one temperature and humidity, for a particular period of time, followed by exposure to another temperature at the same humidity, for a particular period of time. This practice can be used for such applications. The heat-aging curve of the first temperature and humidity is derived, followed by derivation of the heat-aging curve for the second temperature at the same humidity, after exposure of samples to the first temperature and humidity.

4.11 There can be very large errors when Arrhenius plots or equations based on data from experiments at a series of temperatures and humidity are used to estimate time to produce a defined property change at some lower temperature. This estimate of time to produce the property change or failure must always be accompanied by a 95 % confidence interval for the range of times possible based on the calculation or estimate.

5. Apparatus

5.1 *Provisions for Conditioning,* at specified standard conditions.

5.2 *Oven Type:*

5.2.1 *Gravity-Convection Oven*—Recommended for film specimens having a nominal thickness not greater than 0.25 mm (0.010 in.).

5.2.2 *Forced-Ventilation Oven*—Recommended for specimens having a nominal thickness greater than 0.25 mm (0.010 in.). When it is necessary to avoid contamination among specimens or materials, it is possible that a tubular-oven procedure, such as that specified in Practice D1870, will be desirable. Oven apparatus shall be in accordance with Specifications D2436 and E145, Type 1A and Type IIB, with 50 ± 10 air changes/h and the requirements for uniformity extended to include the range of test temperatures. Recording instrumentation to monitor the temperature and humidity of exposure is recommended.

5.3 *Specimen Rack*—A specimen rack or frame of suitable design to allow ready air circulation around the specimens.

5.4 *Relative Humidity Control:*

5.4.1 The chamber shall be able to control relative humidity to within ±5 % when the set point temperature has an operational tolerance of ±1°C.

5.4.2 Relative humidity at different temperatures can be controlled within a narrow range by using saturated aqueous solutions in accordance with Practice E104 or Practice D5032.

6. Test Specimen

6.1 The number and type of test specimens required shall be in accordance with the ASTM test method for the specific property to be determined; this requirement must be met at each time and temperature and humidity selected. Unless otherwise specified or agreed upon by all interested parties, expose a minimum of three replicates of each material at each time and temperature and humidity selected.

6.2 The specimen thickness is to be comparable to but no greater than the maximum thickness of the intended article in its application, and its method of fabrication must be the same as that for the intended application.

6.3 All test specimens for a series of temperatures must be of the same age, preferably from the same manufacturing run and date.

7. Conditioning

7.1 Conduct initial tests in the standard laboratory atmosphere as specified in Practice D618, and with the specimens conditioned in accordance with the requirements of the test method for determining the specific property or properties required.

7.2 When required, the conditioning of specimens following exposure at elevated temperature and prior to testing, unless otherwise specified, shall be in accordance with Practice D618.

8. Procedure

8.1 Select oven type depending on thickness of the specimens being tested (5.2).

8.2 Select the exposure procedure to be used, depending on whether only temperature, or temperature and humidity will be controlled.

8.2.1 *Procedure A,* single exposure temperature at constant relative humidity.

8.2.2 *Procedure B,* various exposure temperatures and constant relative humidity at each temperature.

8.2.3 *Procedure C,* various exposure temperatures with various relative humidity conditions.

8.2.4 *Procedure D,* single exposure temperature with no humidity.

8.2.5 *Procedure E,* various temperatures with no humidity.

8.2.6 *Procedure F,* single exposure temperature with various relative humidity conditions.

NOTE 2—Procedures D and E, in the absence of moisture, are not mandatory for this procedure as no disposal system has zero humidity, but are included as a means for identifying effects of moisture on degradation of a plastic where needed. They can be neglected if this information is not needed or obtained by using Practice D5510.

8.3 Any specimens being exposed to any single condition described by procedures A (8.2.1) through E (8.2.5) must be exposed at the same time in the same device. Use a sufficient number of replicates of each material for each exposure time so that results of tests used to characterize the material property can be compared by analysis of variance or a similar statistical data analysis procedure.

8.4 For procedure B (8.2.2) or procedure E (8.2.5), use a minimum of four exposure temperatures to define the property change as a function of temperature:

8.4.1 The lowest temperature at a selected humidity must produce the desired level of property change or product failure in approximately six months. (This can be done by preliminary testing or range finding to estimate property changes under the conditions to be evaluated thoroughly.) The next higher temperature at the same selected humidity must produce the same level of property change or product failure at approximately one month.

8.4.2 The third and fourth temperatures at the selected humidity must produce the desired level of property change or product failure in approximately one week and one day, respectively.

8.4.3 Select the exposure temperatures from Table 1 (and an appropriate humidity level) when possible. If the suggested heat aging times in 8.4.1 and 8.4.2 are followed, the exposure time Schedules A, B, C, D, and E shall be used.

8.4.4 The purpose of Table 1, giving time schedules at specific temperatures, is to show a typical heat aging schedule for a particular property of some material. In practice, it is often difficult to estimate the effect of heat aging before obtaining the test data. It is therefore usually necessary to start only the short-term heat aging at one or two temperatures until data are obtained to be used as a basis for selecting the remainder of the heat aging temperatures. Since the temperature dependency of oxidatively degradable plastics can vary considerably, Table 1 is to be used only as a starting guide. To obtain more accurate data, exposure times and temperatures intermediate to those given in Table 1 can be used.

NOTE 3—It is possible that the activation energy of certain materials at higher temperatures will be different than the activation energy of the material at lower temperatures. Caution is needed when developing Table 1 relationships on the basis of data from only the highest aging temperature.

8.5 Test one set of non-exposed specimens for the selected property in accordance with the appropriate test method, including provisions for conditioning.

8.6 Mount the test specimens in specimen racks or frames, and place the frames in the oven such that both sides of the specimens are exposed to air flow. In order to minimize any effects from temperature variation within the oven, it is recommended that the frames or specimens be repositioned periodically.

8.7 Expose the remaining sets of specimens for the selected time intervals at the selected temperatures and humidity level. Following exposure, condition these specimens in accordance with established procedure, and then test. If an effect of aging without heat is anticipated, condition and test a parallel set of aged unexposed specimens.

8.8 It is possible to establish effects at a given temperature by first running tests in the absence of moisture and then repeating the dry tests at a desired humidity level. Humidity levels must be selected in the range 20 % to 80 % for a given temperature.

8.9 Humidity effects to correlate with disposal environments such as soil, compost and landfill shall be in the ranges of 15-40 %, 35- 70 %, and 35-60 %, respectively.

TABLE 1 Suggested Temperatures and Exposure Times for the Determination of Heat Aging of Oxidatively Degradable Plastics[A,B]

NOTE 1—Ensure that humidities are in the ranges indicated earlier and appropriate for disposal environments of interest

Suggested Exposure Temperature (°C)	Logarithm Temperature (°C)	Estimated Failure Time (h) at 90°C				
		1-10	11-24	25-48	49-96	97-192
30	1.477	A				
40	1.602	B	A			
50	1.699	C	B	A		
60	1.778	D	C	B	A	
70	1.845	E	D	C	B	A
80	1.903		E	D	C	B
90	1.954			E	D	C
100	2.000				E	D
110	2.041					E

[A]Suggested exposure times: A-2, 4, 8, 16, 24, 32 weeks; B-3, 6, 12, 24, 36, 48 days; C-1, 2, 4, 8, 12, 16 days; D-8, 16, 32, 64, 96, 128 h; and E-2, 4, 8, 16, 24, 32 h.

[B]It is important that suggested exposure humidities for the chosen temperatures be in the ranges mentioned in 1.2, depending on the expected disposal site. For compost, 45-70 %; for landfill, 35-60 %; for soil, 15-40 %.

9. Calculation

9.1 When materials are compared at a single temperature and humidity level, use analysis of variance to compare the mean of the measured property data for each material at each exposure time. Use the results from each replicate of each material being compared for the analysis of variance. It is recommended that the F statistic for 95 % confidence be used to determine significance for the results from the analysis of variance calculations.

9.2 When materials are being compared using a range of different temperatures and selected humidities, use the following procedure to analyze the data and to estimate the exposure time necessary to produce a predetermined level of property change at some temperature lower than the test temperature used. This time can be used for general ranking of materials for temperature and humidity stability or as an estimate of the maximum expected service life at the temperature selected.

9.2.1 Prepare plots of the measured property as a function of exposure time for all temperatures and humidities used. Prepare plots in accordance with Fig. 1 where the abscissa is a logarithmic time scale and the value of the measured property is the ordinate.

9.2.2 Use regression analysis to determine the relationship between the logarithm of exposure time and measured property. Use the regression equation to determine the exposure time necessary to produce a predetermined level of property

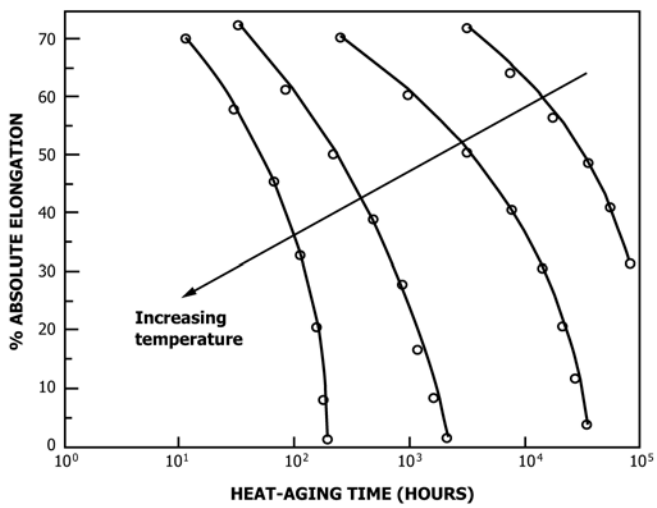

FIG. 1 Typical Heat-Aging Curves—% Absolute Elongation Versus Time (for Example only)

change. An acceptable regression equation must have an r^2 of at least 80 %. A plot of the residuals (value of property retention predicted by regression equation minus actual value) versus aging time must show a random distribution. Use of graphical interpretation to estimate the exposure time necessary to produce the predetermined level of property change is not recommended.

9.2.3 Plot the logarithm of the calculated times to produce the predetermined level of property change (determined by the acceptable regression equation) as a function of the reciprocal of the absolute temperature (1/T in °K) of each exposure used. A typical plot of this type (known as an Arrhenius plot) is shown in Fig. 2. Use regression analysis to determine the equation defining the log time/reciprocal temperature relationship. An acceptable regression equation must meet the requirements described in 9.2.2.

NOTE 4—It is acceptable to use exposure humidities at chosen temperatures to generate curves similar to those in Fig. 1 and Fig. 2.

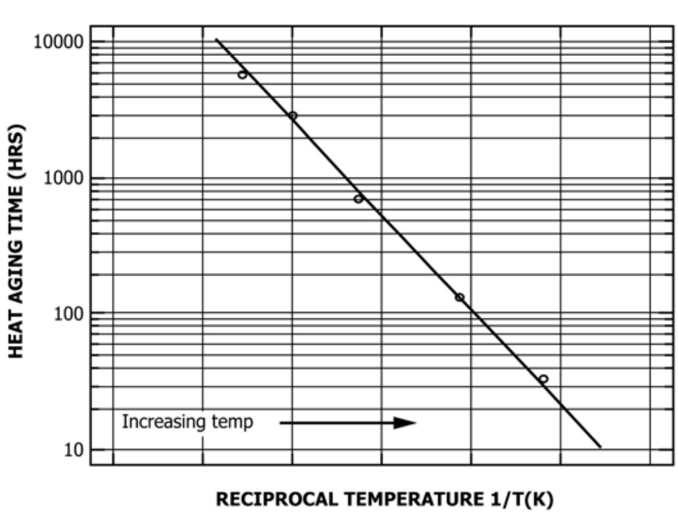

FIG. 2 Typical Arrhenius Plot—Heat Aging Time Versus Reciprocal Temperature (for Example only)

9.2.4 Use the equation for the log of the time to produce the defined property change as a function of the reciprocal absolute temperature to determine the time to produce this property change at a preselected temperature agreed upon by all interested parties.

9.2.5 Calculate the 95 % confidence interval for the time to produce the defined property change using the "standard error" from the regression analysis for the estimated time for the selected temperature. This is readily available from most software packages that do regression analysis. This 95 % confidence interval can be determined by taking the calculated time ± (2 × standard error for estimated time).

10. Report

10.1 Include the following in the test report:

10.1.1 Material, type, and thickness of plastic subjected to exposure, along with specimen preparation procedure;

10.1.2 Pre-conditioning and post-conditioning procedures followed;

10.1.3 Test methods used for evaluation of each measured property change; (for example, Practice D3826 for 95 % loss of elongation at failure);

10.1.4 Observations of any visible changes in the test specimens;

10.1.5 Procedure oven type used;

10.1.6 Exposure temperatures used, and times of exposure at each temperature;

10.1.7 Relative humidity of oven during exposures and the anticipated correlation with proposed disposal environments;

10.1.8 Linear velocity of air flow within the oven(s);

10.1.9 Results from analysis of variance, comparing the results for each material for each exposure time when a single temperature and humidity is used; and

10.1.10 When a series of temperatures and humidities is used to expose materials, the following shall be reported for each material tested:

10.1.10.1 Graphs derived in accordance with 9.2.1 and 9.2.3;

10.1.10.2 Regression equations for property change as a function of exposure time for each temperature at the humidity used;

10.1.10.3 Regression equation for time to produce a defined property change as a function of reciprocal absolute temperature;

10.1.10.4 Estimated time to produce the defined property change at the selected temperature and humidity for each material tested; and

10.1.10.5 The 95 % confidence interval for times to produce the defined property change at the selected temperature and humidity (calculated in accordance with 9.2.5) for each material tested.

NOTE 5—The aged specimen can be subjected to other tests. However, since there are a large number of potential samples from this experimental design, the exact aging conditions of the tested samples shall be part of the report and any subsequent claims. For example degradation products obtained in this procedure can be used in biodegradation tests as indicated in Guide D6954-04 (Tier 2) to develop further evidence that environmental degradation and biodegradation is ultimately possible. However, since there are a large number of potential samples from the experimental design here, care must be taken to record samples used and conditions exposed to in this procedure and no claim for oxidation and biodegradation occurring simultaneously is to be made without testing in the appropriate method for disposal, for example Test Method D5338 for composting.

11. Precision and Bias

11.1 No statement of precision and bias is applicable to this practice. However, the precision and bias associated with different test methods and analytical procedures used to study exposed samples must be taken into account in interpreting the data obtained from methods used in conjunction with this practice.

12. Keywords

12.1 age; degradable; embrittlement; humidity; oven; oxidation; property change