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Standard Practices for Evaluating the Age Resistance of Polymeric Materials Used in Oxygen Service[1]

This standard is issued under the fixed designation G114; 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 These practices describe procedures that are used to determine the age resistance of plastic, thermosetting, elastomeric, and polymer matrix composite materials exposed to oxygen-containing media.

1.2 While these practices focus on evaluating the age resistance of polymeric materials in oxygen-containing media prior to ignition and combustion testing, they also have relevance for evaluating the age resistance of metals, and nonmetallic oils and greases.

1.3 These practices address both established procedures that have a foundation of experience and new procedures that have yet to be validated. The latter are included to promote research and later elaboration in this practice as methods of the former type.

1.4 The results of these practices may not give exact correlation with service performance since service conditions vary widely and may involve multiple factors such as those listed in subsection 5.8.

1.5 Three procedures are described for evaluating the age resistance of polymeric materials depending on application and information sought.

1.5.1 *Procedure A: Natural Aging*—This procedure is used to simulate the effect(s) of one or more service stressors on a material's oxygen resistance, and is suitable for evaluating materials that experience continuous or intermittent exposure to elevated temperature during service.

1.5.2 *Procedure B: Accelerated Aging Comparative Oxygen Resistance*—This procedure is suitable for evaluating materials that are used in ambient temperature service, or at a temperature that is otherwise lower than the aging temperature, and is useful for developing oxygen compatibility rankings on a laboratory comparison basis.

1.5.3 *Procedure C: Accelerated Aging Lifetime Prediction*—This procedure is used to determine the relationship between aging temperature and a fixed level of property change, thereby allowing predictions to be made about the effect of prolonged service on oxidative degradation.

1.6 The values stated in SI units are to be regarded as the standard, however, all numerical values shall also be cited in the systems in which they were actually measured.

1.7 *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 precautionary statements are given in Section 10.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D395 Test Methods for Rubber Property—Compression Set
D412 Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension
D638 Test Method for Tensile Properties of Plastics
D1349 Practice for Rubber—Standard Conditions for Testing
D1708 Test Method for Tensile Properties of Plastics by Use of Microtensile Specimens
D2240 Test Method for Rubber Property—Durometer Hardness
D2512 Test Method for Compatibility of Materials with Liquid Oxygen (Impact Sensitivity Threshold and Pass-Fail Techniques)
D2863 Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)
D3039 Test Method for Tensile Properties of Polymer Matrix Composite Materials
D3045 Practice for Heat Aging of Plastics Without Load
D4809 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method)

[1] These practices are under the jurisdiction of ASTM Committee G04 on Compatibility and Sensitivity of Materials in Oxygen Enriched Atmospheres and is the direct responsibility of Subcommittee G04.02 on Recommended Practices.

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[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.

G63 Guide for Evaluating Nonmetallic Materials for Oxygen Service
G72 Test Method for Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen-Enriched Environment
G74 Test Method for Ignition Sensitivity of Nonmetallic Materials and Components by Gaseous Fluid Impact
G86 Test Method for Determining Ignition Sensitivity of Materials to Mechanical Impact in Ambient Liquid Oxygen and Pressurized Liquid and Gaseous Oxygen Environments
G125 Test Method for Measuring Liquid and Solid Material Fire Limits in Gaseous Oxidants
G126 Terminology Relating to the Compatibility and Sensitivity of Materials in Oxygen Enriched Atmospheres

2.2 *CGA Standard:*

CGA G-4.3 Type I QVL E Commodity Specification for Oxygen[3]

2.3 *Military Standard:*

MIL-PRF-27210 Amendment 1—Oxygen, Aviator's Breathing, Liquid and Gas[4]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *aging*—see Terminology G126.

3.1.2 *accelerated aging*—a type of artificial aging whereby the effect of prolonged exposure during service is simulated by aging at elevated temperature.

3.1.3 *artificial aging*—see Terminology G126.

3.1.4 *oxidative degradation*—physical or mechanical property changes occurring as a result of exposure to oxygen-containing media.

3.1.5 *oxygen-containing media*—air media containing greater than 21 mole % oxygen, or oxygen-enriched media containing greater than 25 mole % oxygen.

3.1.6 *oxygen resistance*—resistance of a material to ignite spontaneously, propagate by sustained combustion, or undergo oxidative degradation.

3.1.7 *oxygen service*—applications involving the production, storage, transportation, distribution, or use of oxygen-containing media.

3.1.8 *natural aging*—see Terminology G126.

3.1.9 *physical aging*—aging that occurs during normal storage and which is a function of time after molding or curing.

4. Summary of Practice

4.1 These practices can be used to evaluate systematically the effect of natural aging (Procedure A) or accelerated aging (Procedures B and C) on oxygen resistance. To apply its principle, the user first characterizes the material, then subjects the material to an aging stressor or stressors, followed by re-characterizing the material. Caution must be taken in interpreting results because interactions occurring in service may be different from those simulated during aging.

4.2 It is always more accurate, although not always practical, to determine the effect of natural aging (Procedure A) without resorting to accelerated aging (Procedures B and C). Accelerated aging procedures are more useful for determining material rankings (Procedure B) or for making lifetime predictions (Procedure C).

4.3 *Summary of Practice for Evaluating the Effect of Aging in Incident Studies:*

4.3.1 In incident studies, in which initial characterization data are not available, historical or average property data may be used to draw coarser conclusions about the effect of aging on oxygen resistance.

4.4 *Practices for Natural Aging (Procedure A) and Accelerated Aging for Comparative Oxygen Resistance (Procedure B):*

4.4.1 The effect of aging is reported as positive or negative depending upon whether the property used to evaluate oxygen resistance increases or decreases, and the magnitude of the effect is reported as the degree to which the measured property changes relative to that of the unaged material.

4.5 *Practice for Accelerated Aging for Lifetime Prediction (Procedure C):*

4.5.1 The time necessary to produce a fixed level of property change is determined at a series of elevated aging temperatures, and the time necessary to produce the same level of property change at some lower temperature is then determined by linear extrapolation.

4.5.2 A practice for evaluating the effect of accelerated aging on physical and mechanical properties under conditions of variable time and temperature has been validated for significance and is described in detail. This practice is similar to that given in Practice D3045 but is specific to aging in oxygen-containing media.

4.5.3 A practice for evaluating the effect of accelerated aging on ignition and combustion properties under conditions of variable time and temperature has not been validated for significance, but may yield meaningful results. The practice described is included to promote research and possible development into an established method.

4.5.4 There can be very large errors when accelerated aging Arrhenius approaches are used to estimate the time necessary to produce a fixed level of property change at some lower temperature. This estimated time to produce a fixed level of property change or "failure" at the lower temperature is often called the "service life." Because of the errors associated with these calculations, this time should be considered to be the "maximum expected" rather than "typical."

NOTE 1—Errors in accelerated aging Arrhenius approaches arise from changes in this oxidative degradation mechanism at elevated temperature.

5. Significance and Use

5.1 This practice allows the user to evaluate the effect of service or accelerating aging on the oxygen resistance of polymeric materials used in oxygen service.

[3] Available from Compressed Gas Association (CGA), 4221 Walney Rd., 5th Floor, Chantilly, VA 20151-2923, http://www.cganet.com.

[4] Available from Standardization Documents Order Desk, DODSSP, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA 19111-5098, http://www.dsp.dla.mil.

5.2 The use of this practice presupposes that the properties used to evaluate the effect of aging can be shown to relate to the intended use of the material, and are also sensitive to the effect of aging.

5.3 Polymeric materials will, in general, be more susceptible than metals to aging effects as evidenced by irreversible property loss. Such property loss may lead to catastrophic component failure, including a secondary fire, before primary ignition or combustion of the polymeric material occurs.

5.4 Polymers aged in the presence of oxygen-containing media may undergo many types of reversible and irreversible physical and chemical property change. The severity of the aging conditions determines the extent and type of changes that take place. Polymers are not necessarily degraded by aging, but may be unchanged or improved. For example, aging may drive off volatile materials, thus raising the ignition temperature without compromising mechanical properties. However, aging under prolonged or severe conditions (for example, elevated oxygen concentration) will usually cause a decrease in mechanical performance, while improving resistance to ignition and combustion.

5.5 Aging may result in reversible mass increase (physisorption), irreversible mass increase (chemisorption), plasticization, discoloration, loss of volatiles, embrittlement, softening due to sorption of volatiles, cracking, relief of molding stresses, increased crystallinity, dimensional change, advance of cure in thermosets and elastomers, chain scissioning, and crosslinking.

5.6 After a period of service, a material's properties may be significantly different from those when new. All materials rated for oxygen service should remain resistant to ignition and combustion (primary fire risk). Furthermore, all materials rated for oxygen service should be resistant to oxidative degradation and retain relevant physical and mechanical properties during service, because part failure can indirectly lead to an unacceptable ignition or combustion risk (secondary fire risk).

5.7 In cases where aging makes a material more susceptible to fire or causes significant oxidative degradation, aging tests may be used to evaluate whether the material will become unacceptable during service. In cases where aging makes a material less susceptible to fire, aging tests may be used to evaluate whether a material can be conditioned (artificially aged) to prolong its service lifetime.

5.8 Oxygen resistance as determined by this practice does not constitute grounds for material acceptability in oxygen service. Determination of material acceptability must be performed within the broader context of review of system or component design, plausible ignition mechanisms, ignition probability, post-ignition material properties, and reaction effects such as are covered by Guide G63.

5.9 The potential for personnel injury, facility damage, product loss, or downtime occurring as a result of ignition, combustion, or catastrophic equipment failure will be least for systems or components using air and greatest for systems or components using pure oxygen.

5.10 In terms of physical and mechanical properties, aging is expected to have a greater influence on a polymer's ultimate properties such as strength and elongation, than bulk properties such as modulus.

5.11 In terms of fire properties, aging is expected to have a greater influence on a polymer's ignition properties (for example, autogenous ignition temperature (AIT), mechanical and pneumatic impact) than its propagation properties (for example, upward and downward flame propagation). To date, the only background on aging influences is that of the Bundesanstalt für Materialforschung und -prüfung (BAM) which has assessed the effect of aging at elevated pressure and temperature on a material's AIT. BAM has used the AIT test results to establish maximum constraints on the use of materials at elevated pressure and temperature.[5]

6. Rationale for Aging Tests

6.1 The body of information on the effect of natural aging on oxygen resistance under conditions of multiple stressors is small, and so, this practice is intended to promote testing towards the goal of developing better practices to evaluate the competing effects of multiple stressors.

6.2 The body of information on the effect of accelerated aging on ignition and combustion is small, and so, this practice is intended to promote testing towards the goal of developing potential practices to evaluate the effect of accelerated aging on ignition and combustion.

7. Apparatus

7.1 *General Considerations:*

7.1.1 The apparatus used for aging can vary widely. Aging in ambient pressure air, gravity-convection ovens or forced-ventilation ovens may be used. When aging in pressurized oxygen-enriched media, pressure-rated cell-type ovens or oxygen pressure chambers that provide a greater margin of safety must be used because of the increased risk of ignition or combustion.

7.1.2 This practice focuses on small-scale aging methods involving a requisite number and type of specimens in accordance with the ASTM test method for the specific property being determined. The scale of the aging procedure can be increased in numerous ways, provided care is taken to ensure safety.

7.1.3 A provision shall be made for suspending specimens vertically without touching each other or the sides of the aging chamber. If possible, maintain at least a 5 cm (2 in.) separation between specimens and the sides of the aging oven, cell, or chamber.

7.1.4 The temperature, and pressure if different than ambient, should be recorded.

7.1.5 Temperatures shall be measured in close proximity to the test piece.

[5] Wegener, W., Binder, C., Hengstenberg, P., Herrmann, K. P., and Weinert, P., "Tests to Evaluate the Suitability of Materials for Oxygen Service," *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Third Volume, ASTM STP 986*, D. W. Schroll, Ed. ASTM, 1988, pp. 268–278.

7.1.6 Uniform heating shall be accomplished by mechanical agitation or forced circulation whenever possible or practical. Baffles or other design features shall be used to ensure uniform heating is attained in all parts of the chamber and to prevent local overheating or dead spots.

7.1.7 In cases where circulated air is used, increasing the air flow rate, will improve temperature uniformity. However, while low air speed will promote accumulation of degradation products and volatilized ingredients, as well as oxygen depletion, high air speed will increase the rate of deterioration due to reduced oxygen depletion, higher oxygen diffusion or mass transport rates, and increased volatilization of plasticizers and antioxidants.

7.1.8 Specimen preparation for larger scale experiments or unique combinations of stressors that qualify as research may utilize other hardware that allows safe aging. Safety must be carefully evaluated for any aging arrangement.

NOTE 2—The effects of aging may be quite variable, especially when specimens are aged for long intervals. Factors that may affect reproducibility of data include temperature uniformity and control and humidity within the aging apparatus. For example, materials susceptible to hydrolysis may undergo degradation not directly attributable to the effects of oxygen.

NOTE 3—Aging apparatuses must be designed so that specimens, especially vulcanized elastomers, do not come in contact with copper or copper-containing alloys, which can accelerate aging.

7.2 *Gravity-Convection Air Ovens:*

7.2.1 Gravity convection ovens are recommended for film specimens having a nominal thickness not greater than 0.25 mm (0.010 in.). In order to maintain a constant, evenly distributed temperature throughout the heating interval, automatic temperature control by means of thermostatic regulation shall be used. Aluminum chamber or cell walls will help maintain temperature consistency. The air shall circulate at not less than 3 or more than 10 changes per hour.

7.3 *Forced-Ventilation Air Ovens:*

7.3.1 Forced ventilation ovens are recommended for specimens having a nominal thickness greater than 0.25 mm (0.010 in.). The source of heat is optional, but shall be located outside the aging chamber proper. The air shall be preheated to the target aging temperature. The air shall circulate at not less than 3 or more than 10 changes per hour, and the flow shall be as laminar and uniform as possible. Specimens shall be placed with the smallest surface facing the air flow so as to avoid disturbing the air flow.

NOTE 4—During forced-ventilation air aging and in cases where a motor driven fan is used, in order to avoid ozone contamination, the aging media must not come into contact with the fan motor brush discharge in order to avoid ozone contamination. Accordingly, it is not permissible to use motor-driven fans inside the oven, for example.

7.4 *Cell-type Air Ovens:*

7.4.1 Cell-type ovens shall consist of one or more unconnected cylindrical cells having a minimum height of 300 mm (12 in.) in which the temperature can be kept constant and the air circulates at not less than 3 or more than 10 changes per hour. Cells shall be surrounded by a good heat transfer medium (aluminum block, liquid bath, or saturated vapor). The air passing through one cell shall not enter into other cells. Cells are especially useful when aging dissimilar types of polymers (see Note 7).

7.5 *Pressure Chambers:*

7.5.1 A pressure chamber shall consist of a vessel made of stainless steel or other suitable material. When aging in oxygen-containing media, both the chamber and the heat transfer medium surrounding the chamber shall be made of materials that do not react with oxygen.

7.5.1.1 The chamber shall be equipped with a burst disk to prevent the maximum allowable water pressure (MAWP) for the chamber from being exceeded in the case of an extreme reaction between the test material and oxygen. Additionally, an engineering design safety factor can be used to further reduce the possibility of catastrophic over-pressurization.

7.5.1.2 The size of the chamber is optional, but shall be such that *(1)* the total volume of the specimens does not exceed 10 percent of the free space in the chamber, and *(2)* the maximum expected operating pressure (MEOP) produced by a worst-case combustion to form completely oxidized gaseous by-products does not exceed eighty percent of the MAWP for the chamber. For example, in a typical isothermal combustion in 100 percent oxygen, and assuming oxygen is the limiting reactant (that is, all oxygen originally present is consumed), the MEOP can be estimated as:[6]

$$MEOP = \frac{n_{gas} \cdot R \cdot T_f}{V_c} \leq 0.8\ MAWP \tag{1}$$

where:

n_{gas} = number of moles of gas produced by the combustion (assumes all moles of gas originally present in the aging medium were consumed),
R = ideal gas constant, and
V_c = pressure chamber volume.

And where T_f is the final temperature inside the chamber after 100 % combustion as determined by:

$$T_f = T_i + \left(\frac{\Delta H_c \cdot m_{sample}}{C_p \cdot m_{chamber}} \right) \tag{2}$$

where:

T_i = initial aging temperature,
ΔH_c = heat of combustion of the specimen as determined under isothermal conditions per Test Method D4809,
m_{sample} = mass of the combusted specimens,
C_p = heat capacity of the metal or metal alloy used to construct the pressure chamber, and
$m_{chamber}$ = mass of pressure chamber.

NOTE 5—**Warning:** The pressure chamber shall be constructed of materials that are known to be resistant to ignition and combustion in the aging medium used, and at the aging temperatures and pressures used.

NOTE 6—**Warning:** Precautions must be taken to ensure that the pressure chamber is not overloaded, or aging temperatures and pressures used that would cause the safety margins for the chamber to be exceeded.

7.5.2 In cases where the effect of aging on ignition or combustion properties is being examined, the vessel used to

[6] ASME, 2004, *Boiler and Pressure Vessel Code*, Section VIII, Division 1, New York, New York.

perform the ignition test (AIT reaction vessel and mechanical impact test chamber, or pneumatic impact test chamber subassembly) or combustion test (calorimeter bomb) may also serve as the apparatus for the aging procedure.

7.5.2.1 To examine the effect of aging on the autogenous ignition sensitivity, specimens would be placed into the AIT reaction vessel of Test Method G72, and aged at the desired pressure(s) and temperature(s).

7.5.2.2 To examine the effect of aging on gaseous pneumatic impact ignition sensitivity, specimens should be placed in the test chamber subassembly of Test Method G74, and aged at the desired pressure(s) and temperature(s).

7.5.2.3 To examine the effect of aging on pressurized oxygen mechanical impact ignition sensitivity, specimens should be placed in the test chamber of Test Method G86, and aged at the desired pressure(s) and temperature(s).

7.5.2.4 To examine the effect of aging on heat of combustion, specimens should be placed in the calorimeter bomb Test Method D4809, and aged at the desired pressure(s) and temperature(s).

7.6 *Specimen Rack,* of suitable design to allow ready circulation around the specimens during aging.

7.7 *Test Equipment,* in accordance with appropriate ASTM test method(s) to determine the selected property(ies).

8. Reagents

8.1 *Gaseous Oxygen*—Conforming to MIL-PRF-27210, Amendment 1, Type 2, CGA-4.3 Type I, or oxygen of 99.5 % minimum purity is used. Oxygen of other purities or in mixture with other materials may be necessary depending upon the intent of the study.

8.2 *Diluent Gases*—Gases other than oxygen used to prepare atmospheres other than pure oxygen should have purities at least equal to that specified for the gaseous oxygen.

9. Specimens, Test Articles, and Sampling

9.1 The number and type of specimens required shall be in accordance with the ASTM test method for the specific property being determined.

9.2 The form of all specimens shall be such that no mechanical, chemical, or heat treatment will be required after aging.

9.3 Aging shall be carried out on materials conditioned in accordance with the ASTM test method for the specific property to be determined. Further provisions should be made to ensure whenever possible that the specimen thickness is comparable to but no greater than the minimum thickness in the intended application. Specimens shall be free of blemishes or other flaws.

9.4 Comparison of results shall be limited to specimens having similar dimensions and approximately the same exposed area.

9.5 Comparison of results shall be limited to specimens having comparable cure dates (elastomers and thermosets) or mold dates (plastics).

9.6 Size permitting, aging of representative hardware or components containing the softgood of interest is preferred. However, the form of test article shall be such that negligible heating due to machining to remove the softgood of interest will be required after aging and prior to property evaluation.

9.7 The method of specimen fabrication should be the same as that of the intended application.

9.8 Different specimens for mechanical and physical property tests than those used for ignition tests shall be used. Mechanical and physical testing may prestress, crack, or otherwise change the specimens in ways that would not occur in actual service, and therefore may bias ignition test results.

9.9 Whenever possible, marking (such as application of gage lines used for measuring elongation) shall be carried out after aging as inks can affect aging.

9.10 The same cleaning methods used in service will be used for specimen preparation. Lubricants that would be used with the material should be applied in similar amounts. If the material is used in intimate contact with other materials, then it is preferable to age the material in contact with these same materials.

NOTE 7—If possible, it is recommended that only the following types of polymers be aged together:

(a) polymers of the same general type

(b) elastomers with similar amounts of sulfur

(c) elastomers with similar sulfur:accelerant ratios

(d) polymers with similar types and loading of accelerants, antioxidants, peroxides, and plasticizers

10. Safety Precautions

10.1 *Oxygen:*

NOTE 8—**Warning:** Gaseous oxygen vigorously accelerates combustion. Adequate safety precautions are important when heating organic materials in oxygen under pressure, since the rate of oxidation may, in some cases, become very rapid, particularly if a large surface area of material is aged.

Keep oil and grease away. Do not use oil or grease on regulators, gages or control equipment.

Use only with equipment conditioned for oxygen service by careful cleaning to remove oil, grease and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator. Release the regulator tension before opening the cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from the cylinder in which it is received to any other cylinder.

Do not drop the cylinder. Make sure the cylinder is secured at all times.

Keep the cylinder valve closed when not in use.

Stand away from the outlet when opening the cylinder valve.

The oxygen shall be for technical use only. Do not use for inhalation purposes.

Keep the cylinder out of the sun and away from heat.

Keep the cylinder away from corrosive environment(s)
Do not use unlabeled cylinders.
Do not use dented or damaged cylinders.

10.1.1 See Compressed Gas Association Pamphlets G-4 and G-4.1[7] for details on the safe use of oxygen.

10.2 Refer to the safety precautions sections of referenced standards for further safety information applicable to the use of each standard and therefore applicable to this practice when used in conjunction with it.

11. Testing of Specimens

11.1 To minimize repeatability errors, it is recommended that properties of the unaged sample be determined within 96 h of the start of the aging interval. Results on specimens which are found to be imperfect shall be discarded and retests shall be made.

11.2 The material should be in the exact condition for use prior to aging. Any cleaning should be consistent with cleaning required for the application of interest.

11.3 Test the material as specified in the test method(s) chosen: Test Methods D395 (compression set), D412 (tension—rubbers), D638 (tension—plastics), D1708 (microtension—plastics), D3039 (tension—composites), D2240 (Durometer hardness), D2512 (liquid oxygen impact), D2863 (oxygen index), D4809 (heat of combustion), G72 (AIT), G74 (gaseous oxygen impact), G86 (mechanical impact), G125 (fire limit), or other method as described in Note 9. If time is suspected to be a key aging parameter, retain some of the material in its original condition for later testing in concert with the aged material.

NOTE 9—Other property indicators that can be used to determine the age resistance of plastic, thermosetting, elastomeric, and polymer matrix composite materials to oxygen-containing media include exothermicity testing using an Accelerated Rate Calorimeter, friction/rubbing testing, particle impact, promoted and hot wire ignition, electric arc testing, resonance, or internal flexing.

11.4 If desired, and to increase the data base obtained, the material may be further characterized prior to aging by weighing it, recording dimensions, or checking other mechanical properties related to application (Charpy or Izod mechanical impact strength, tear resistance, flexibility, fracture toughness, etc.).

12. Aging Procedures

12.1 *General Considerations:*

12.1.1 To evaluate accurately the effect of aging on oxygen resistance, the property being evaluated must be relevant to the service application.

12.1.2 Use a sufficient number of replicates of each material for each aging condition so that results can be compared by analysis of variance or similar statistical data analysis procedure.

12.1.3 Use aging temperatures and times such that the deterioration will not be so great as to prevent determination of final properties.

12.1.4 The minimum interval between curing (elastomers, thermosets, thermosetting matrix composites) or molding (plastics, thermoplastic matrix composites) and the start of aging shall be 24 h.

12.1.5 The maximum interval between curing or molding and the start of aging shall also be controlled so that comparison of results is limited to materials with similar production dates. It is especially important to maintain a consistent production date—aging date interval when comparing like materials, or when dealing with materials that are known to undergo significant physical aging. If the production date of a material is unknown, aging shall begin within two months of delivery to the customer.

12.1.6 When conducting aging at a single temperature, it is usually desirable to age all materials at the same time in the same apparatus as long as mixing of polymers of dissimilar type (see Note 7) can be avoided.

12.2 *Choosing Aging Conditions:*

12.2.1 The user must first identify the stressors most likely to contribute to aging of the material (for example, time, temperature, pressure, erosion due to flow friction, or chemical exposure), and the test method that is most likely to measure the property change.

12.2.2 *Time*—Time may be the most elemental aging factor. Time alone may age a material (for example, physical aging of elastomers and glassy polymers). It is always more accurate, although not always practical, to determine the effect of time without resorting to accelerated aging. The effect of natural aging can be determined by testing materials that have been in service or in storage and comparing results with data obtained on new material. Time may affect any properties, and hence characterization by any of the test methods referenced herein may be worthwhile.

12.2.3 *Temperature*—For materials used in elevated temperature service, aging at the same elevated temperature will simulate natural aging. In this case, the effect of temperature is determined directly. For materials used in ambient temperature service, exposure to elevated temperatures will simulate accelerated aging. In this case, an Arrhenius method is used to convert the effect of temperature to that of time, thereby allowing predictions to be made about the effect of time (prolonged service) on a given property. Aging at elevated temperature often leads to an increased AIT as determined by Test Method G72. Oxidation caused by chemisorption of oxygen may cause a decrease in the heat of combustion as determined by Test Method D4809, or may increase the fire limit or oxygen index (see Test Method G125 or D2863 respectively.) Aging may lead to a cracking, loss of resiliency, and other physical and mechanical property loss (see Test Methods D395, D412, D638, D1708, D2240, D3039). Aging may also lead to an increase in surface area that can produce easily ignitable edges, hence ambient temperature mechanical impact ignition tests per Test Method D2512 or Test Method G86, or pneumatic impact ignition tests per Test Method G74 may be worthwhile. If specific information about the effect of temperature up to 280°C (540°F) on impact ignition properties is desired, heated gaseous oxygen mechanical impact ignition

[7] Available from Compressed Gas Association, 1235 Jefferson Davis Highway, Arlington, VA.

tests per Test Method G74, or heated gaseous oxygen pneumatic impact ignition tests per Test Method G86 may be worthwhile.

NOTE 10—**Caution:** For every 10°C increase in temperature, the oxidation rate may be approximately double. When testing rapidly aging materials, or materials containing or contaminated with oxidizing chemicals, or during aging of materials with a large surface area, the oxidation rate may be catalyzed to such as extent as to become violent with increasing temperature.

12.2.4 *Pressure*—Pressure may cause physisorption of oxygen, which in the case of elastomers may cause swelling, and in the case of rapid pressure cycling, fatigue and mechanical failure. Therefore, tests to ascertain dimensional changes and mechanical property retention may be of interest. Also, variable pressure AIT tests run from 2.1 to 20.7 MPa (300 to 3000 psi) per Test Method G72, variable pressure gaseous oxygen mechanical impact ignition tests run at 0 to 68.9 MPa (0 to 10 000 psi) per Test Method G86, or pressurized gaseous oxygen pneumatic impact ignition tests run at 0 to 68.9 MPa (0 to 10 000 psi) per Test Method G74 may be worthwhile.

NOTE 11—Depending on component design and application, the ignition probability due to adiabatic compression may be greater than the ignition probability due to autogenous ignition. In such cases, pneumatic impact (adiabatic compression) ignition tests per Test Method G74 may be more appropriate than AIT tests per Test Method G72.

NOTE 12—If oxygen pressure or concentration is low during aging, and oxidation is rapid, oxygen may not diffuse into the specimen fast enough to allow uniform oxidation. Conversely, higher oxygen pressure or concentration will promote rapid diffusion and more uniform oxidation. Care, however, must be exercised to ensure that the oxidation rates achieved during aging closely resemble the rates occurring in service.

12.2.5 *Loading*—The effects of oxygen exposure may be exacerbated by dynamic and static loading effects occurring during service. However, duplication of these effects during testing can be a challenge. Constructing mock fixtures or testing partially dissembled or intact components may be necessary.

12.2.6 *Friction/Erosion*—Friction erosion tends to increase the specific surface area of smooth surfaces and decrease the specific surface area of rough surfaces. Increased surface area suggests AIT tests per Test Method G72, or gaseous oxygen mechanical impact ignition tests per Test Method D2512 or Test Method G86, or pneumatic impact ignition tests per Test Method G74, since increased surface roughness is currently thought to increase ignition sensitivity. Conversely, to the extent that surface erosion does not affect the bulk specimen or bulk properties, the user would not expect to see great changes in the heat of combustion as determined by Test Method D4809, or tensile strength as determined by Test Methods D412, D638, D1708, or D3039.

12.2.7 *Chemical Exposure*—In addition to oxygen, aggressive chemical media encountered during service (for example, solvents and cleaning agents) can also cause aging. Aggressive chemical media may extract additives, can permeate into the material, attack the surface, alter the specific surface area, passivate the surface, or change a material's mechanical properties, turning it hard, gummy or otherwise. Surface properties may be affected preferentially compared to bulk properties, and changes can either be reversible or irreversible. The wide assortment of prospects suggests that many of the test methods referenced herein may be worthwhile.

12.3 *Procedure A: Natural Aging:*

12.3.1 This procedure is used to simulate the effect(s) of one or more service stressors on a material's oxygen resistance, and is suitable for evaluating materials that experience continuous or intermittent exposure to elevated temperature during service.

NOTE 13—As long as the properties of interest can be shown to be invariant from lot to lot, and time-dependent physical aging can be neglected or accounted for, the effect of natural aging can also be estimated by testing materials removed from service and comparing results with data obtained on new material.

12.3.2 During natural aging, all aging conditions must approximate service conditions, for example, time, temperature, pressure, loading, friction/erosion, and chemical exposure.

12.3.3 The material is subjected to the selected stressor(s). For example, to conduct time/pressure/temperature aging, place the material in the pressure chamber, pressurize it as specified in Test Method G72, raise the temperature to the level of interest, and allow it to soak for the chosen time. By using elements of Test Method G72 for this procedure, the safety measures of Test Method G72 and the historical experience adds confidence in the margin of safety present, provided the amount of material involved is not in excess of the amount the vessel of Test Method G72 is capable of containing in an inadvertent ignition.

12.3.4 Specimens are placed in the aging apparatus only after it has been preheated to operating temperature. The aging interval starts when the specimens are placed in the aging apparatus.

12.3.5 Further instruction is given in Annex A1.

12.4 *Procedure B: Accelerated Aging for Comparative Oxygen Resistance:*

12.4.1 This procedure shall be used to evaluate the relative oxygen resistance of different materials and develop oxygen compatibility rankings on a laboratory comparison basis.

12.4.2 The procedure is suitable for evaluating materials that are used in ambient temperature service, or at a temperature that is lower than the aging temperature. The aging temperature may be any elevated standard temperature such as are given in Practice D1349.

12.4.3 The aging interval will depend on the rate of deterioration of the particular material being tested. Intervals frequently used are 3, 7, and 14 days.

12.4.4 Unless otherwise indicated, the pressure of the aging apparatus prior to heating shall be 1 atmosphere (14.7 psi, 101 kPa).

12.4.5 Specimens shall be placed in the aging apparatus only after it has been preheated to the operating temperature. The aging interval starts when the specimens are placed in the aging apparatus.

12.5 *Procedure C: Accelerated Aging for Lifetime Prediction:*

12.5.1 When using this procedure, all aging conditions used must approximate service conditions, except for time,

temperature, and pressure. For example, aging times and temperatures will be selected from Table 1 of Practice D3045. Unless otherwise indicated, the pressure of the aging apparatus prior to heating shall be 1 atmosphere (14.7 psi, 101 kPa).

12.5.2 This procedure is used to determine the relationship between aging temperature and fixed level of property change. When using this procedure, a minimum of four aging temperatures shall be used. When possible, follow the procedures given in Practice D3045, Table 1 when selecting aging times and temperatures (follow Schedules A, B, C, and D), namely:

12.5.2.1 The lowest temperature (Schedule A) should produce the desired level of property change or product failure in approximately nine to twelve months. The next highest temperature (Schedule B) should produce the same level of property change or product failure in approximately six months.

NOTE 14—The lowest temperature (Schedule A) is typically 15 to 25°C above the maximum expected service temperature, or alternatively, the estimated limiting temperature as described in Practice D3045.

12.5.2.2 The third and fourth temperatures (Schedules C and D) should produce the same level of property change or product failure in approximately three months and one month, respectively.

NOTE 15—The use of high aging temperatures during accelerated aging may result in degradation mechanisms different from those occurring during service, thus invalidating results. Also, avoid aging at known transition temperatures since aging rates or mechanisms, or both, may change significantly.

12.5.3 The maximum expected service temperature or estimated limiting temperature may be based on prior knowledge of similar material, and may subsequently be amended on the basis of data acquired using Procedure B.

12.5.4 It is often difficult to estimate the effect of accelerated aging before obtaining test data. Therefore, it is usually necessary to start only the short-term data at one or two temperatures (Schedules C and D) until data are obtained to be used as a basis for selecting the remaining aging temperatures.

NOTE 16—Lifetime prediction studies have shown that because of diffusion limited (heterogeneous) oxidation, bulk properties such as strength may not be amenable to Arrhenius approaches, while surface sensitive properties such as elongation are.

12.6 *Re-characterizing the Aged Material:*

12.6.1 At the end of the aging interval, remove the specimens from the aging apparatus, cool to room temperature, and allow them to rest not less than 16 h nor more than 96 h before determination of the physical, mechanical, ignition, or combustion properties selected in 11.3. For specimens to be used in tensile elongation tests, apply gage lines at this point.

12.6.2 Following return to normal (or other chosen) conditions perform the same characterization tests of Section 11. For example, if the selected method is Test Method G72 (AIT), begin the temperature ramp immediately after the aging soak at temperature is complete.

13. Calculation

13.1 *Procedure A: Natural Aging, and Procedure B: Accelerated Aging Comparative Oxygen Resistance:*

13.1.1 For properties such as tensile strength and ultimate elongation, the aging results shall be expressed as a percentage change for the given property:

$$P = [(A - O)/O] \times 100 \quad (3)$$

where:

P = percentage change in property,
A = value after aging, and
O = original value.

13.1.2 For properties like Durometer hardness, the aging results shall be expressed as an absolute change:

$$P = A - O \quad (4)$$

13.2 *Procedure C: Accelerated Aging Lifetime Prediction:*

13.2.1 When materials are compared at a single temperature, use analysis of variance to compare the mean of the measured property data for each material at each aging interval. Use the results from each replicate of each material being compared for analysis of the 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.

13.2.2 When materials are being compared using a series of temperatures, use the following procedure to analyze the data and to estimate the aging time needed to produce a fixed level of property change at some temperature lower than the actual test temperatures. This time can be used for general ranking of material in terms of oxygen age resistance, or as an estimate of the upper service limit at the temperature selected.

13.2.3 Prepare plots of the measured property as a function of the aging interval for all the temperatures used. Plots should be prepared in accordance with Figure 1 of Practice D3045 (reproduced as Fig. 1) where the x-axis is the logarithm of the aging time and the y-axis is the value of the measured property.

13.2.4 Use nonlinear regression analysis to determine the relationship between the logarithm of the aging time and the measured property. Based on the nonlinear regression analysis results, determine the aging time necessary to produce a fixed level of property change. An acceptable regression equation must have an r^2 of at least 80 %. A plot of residuals (value of property retention predicted by regression equation minus actual value) versus aging time must show a random distribution. The use of graphical interpretation to estimate the exposure time necessary to produce the fixed level of property change is not recommended.

13.2.5 Plot the logarithm of the calculated aging time to produce the fixed level of property change as a function of the reciprocal temperature ($1/T$ in K) for each aging temperature used in accordance with Fig. 2 (Arrhenius plot) of Practice D3045 (reproduced). Use linear least squares regression analysis to determine the log time/reciprocal temperature relationship:

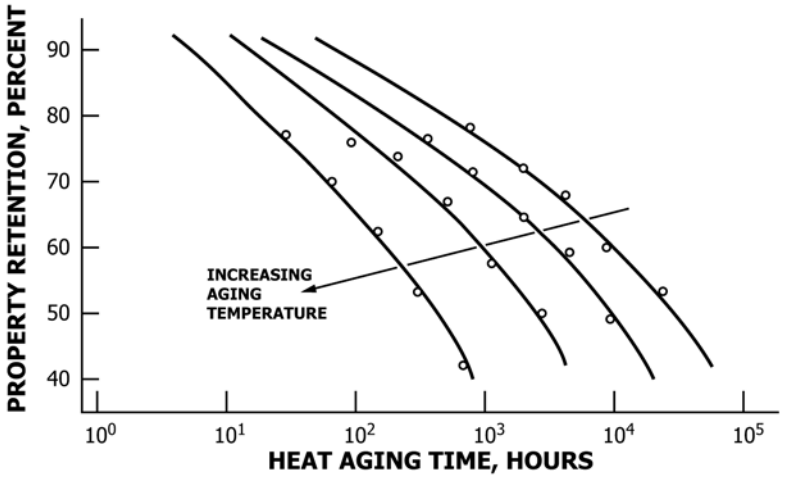

FIG. 1 Heat Aging Curves—Property Retention versus Aging Time

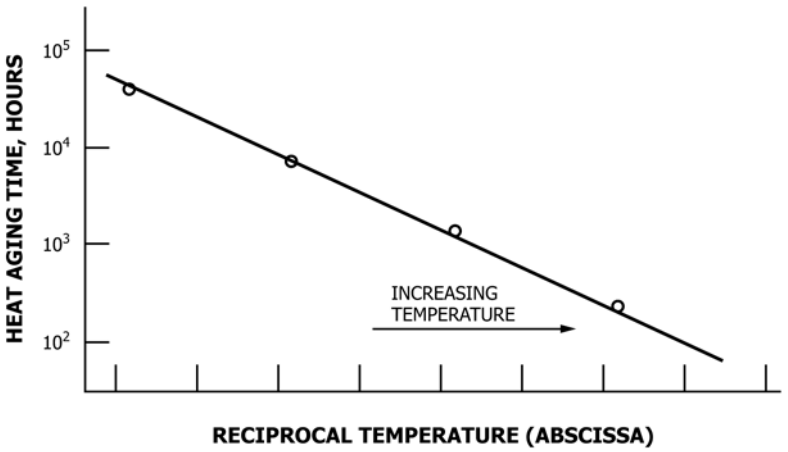

FIG. 2 Arrhenius Plot—Time of 50 % Property Retention versus Reciprocal of Absolute Temperature

$$\log t = \log t_o - \frac{E_a}{RT} \quad (5)$$

where:

t, t_o = time, initial time,
E = Arrhenius activation energy,
R = Universal gas constant, and
T = temperature.

An acceptable regression analysis must meet the requirements described in 13.2.4.

13.2.6 Using the values for log t_o and $-E_a/R$ determined in 13.2.5, calculate the time, t, to produce the fixed level of property change at the temperature of interest, T, for example room temperature or another agreed-upon temperature.

13.2.7 Calculate the 95 % confidence interval for the time to produce the defined property change using the "standard error" from the regression analysis performed in 13.2.5. This 95 % confidence interval can be determined by taking the calculated time ± (2 × standard error for the estimated time).

14. Report

14.1 In reporting the aging process, include the following data:

14.1.1 Type of material, manufacturer, composition, and batch/lot number, if known,

14.1.2 Material preparation and cure and molding information, if known,

14.1.3 Sample dimensions and condition,

14.1.4 Observations of any visible changes,

14.1.5 Type of aging apparatus used,

14.1.6 Aging temperature(s) used, and aging times at each aging temperature,

14.1.7 Pre-aged and post-aged physical, ignition, and combustion properties and the percent change,

14.1.8 Cross references to any original or final condition flammability test reports that may be available, and

14.1.9 Other applicable aging parameters (pressure, abrasion, chemical exposure, friction, etc.).

14.2 When a series of temperatures are used to age materials the following shall be reported for each material tested:

14.2.1 Plots analogous to Figs. 1 and 2,

14.2.2 Nonlinear regression equations to determine the relationship between the logarithm of the aging time and the measured property for each aging temperature used,

14.2.3 The linear regression (Arrhenius) equation used for predicting the time to produce a fixed level of property change as a function of reciprocal temperature,

14.2.4 Estimated time to produce a fixed level of property change at a selected temperature,

14.2.5 95 % confidence intervals for times to produce a fixed level of property change, and

14.2.6 The level of property change used in all calculations.

14.3 In reporting the change in flammability properties, use the following formats to cite the aging influence:

14.3.1 For use of Test Method G72, the change in the AIT should be reported, and a decrease in AIT shall be called a degradation and an increase shall be called an enhancement.

14.3.2 For use of Test Method G74, the change in reactive pressure should be reported, and a decrease in reactive pressure shall be called a degradation and an increase shall be called an enhancement.

14.3.3 For use of Test Method G86, the change in reactive threshold energy should be reported and a decrease in threshold should be called a degradation, and an increase should be called an enhancement.

14.3.4 For use of Test Method G125 or D2863, the change in the fire limit or oxygen index should be reported and a decrease should be called a degradation, and an increase should be called an enhancement.

14.3.5 For use of Test Method D2512, the change in reactive threshold energy should be reported and a decrease in threshold should be called a degradation, and an increase should be called an enhancement.

14.3.6 For use of Test Method D4809, the change in heat of combustion should be reported and an increase should be called a degradation and a decrease should be called an enhancement.

15. Precision and Bias

15.1 No statements of precision and bias are applicable to this standard; these are dependent upon the ASTM test method for the specific property(ies) to be determined.

16. Keywords

16.1 aging; accelerated aging; combustion; enriched air; flammability; ignition; lifetime prediction; natural aging; oxidative degradation; oxygen; oxygen compatibility

ANNEX

(Mandatory Information)

A1. EXAMPLE PROCEDURE FOR TIME/PRESSURE AGING

A1.1 Prepare specimens in as-used cleanliness.

A1.2 Weigh, and examine specimens for appearance and flexibility.

A1.3 Test the specimens using Test Method G72.

A1.4 Place in vessel of Test Method G72, pressurize, warm, and soak for 100 h, using the procedures and safety precautions of Test Method G72.

A1.4.1 The initial soak temperature should be selected as 100°C below the autoignition temperature. If testing demonstrates material degradation, then the test should be repeated at progressively lower temperatures in increments of 25°C until degradation is no longer observed, and the material should be reported as having a degradation threshold equal to the highest temperature tested at which degradation did not occur.

A1.5 At the end of the aging cycle, the vessel should be vented and cooled and the specimens again examined for qualitative changes in appearance, flexibility, etc.

A1.6 Retest the specimens in the aged condition.

A1.7 Report the difference, in weight, physical changes, and alteration of AIT.

A1.8 This example procedure is based upon the method used at BAM.

APPENDIX

(Nonmandatory Information)

X1. ADDITIONAL LITERATURE

X1.1 Waller, J. M., Hornung, S. D., and Beeson, H. D., "Fuel Cell Elastomeric Materials Oxygen Compatibility Testing: Effect of 450 and 6200 kPa Oxygen," *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres, ASTM STP 1319*, 1997.