Standard Guide for Evaluating Metals for Oxygen Service[1]

This standard is issued under the fixed designation G94; 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 guide applies to metallic materials under consideration for oxygen or oxygen-enriched fluid service, direct or indirect, as defined in Section 3. It is concerned primarily with the properties of a metallic material associated with its relative susceptibility to ignition and propagation of combustion. It does not involve mechanical properties, potential toxicity, outgassing, reactions between various materials in the system, functional reliability, or performance characteristics such as aging, shredding, or sloughing of particles, except when these might contribute to an ignition.

1.2 This document applies only to metals; nonmetals are covered in Guide G63.

NOTE 1—The American Society for Testing and Materials takes no position respecting the validity of any evaluation methods asserted in connection with any item mentioned in this guide. Users of this guide are expressly advised that determination of the validity of any such evaluation methods and data and the risk of use of such evaluation methods and data are entirely their own responsibility.

NOTE 2—In evaluating materials, any mixture with oxygen exceeding atmospheric concentration at pressures higher than atmospheric should be evaluated from the hazard point of view for possible significant increase in material combustibility.

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

1.4 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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)

D4809 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method)

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

G86 Test Method for Determining Ignition Sensitivity of Materials to Mechanical Impact in Ambient Liquid Oxygen and Pressurized Liquid and Gaseous Oxygen Environments

G88 Guide for Designing Systems for Oxygen Service

G93 Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen-Enriched Environments

G124 Test Method for Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres

G126 Terminology Relating to the Compatibility and Sensitivity of Materials in Oxygen Enriched Atmospheres

G128 Guide for Control of Hazards and Risks in Oxygen Enriched Systems

2.2 *ASTM Special Technical Publications (STPs) on the Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres:*

ASTM STPs in this category are listed as: 812, 910, 986, 1040, 1111, 1167, 1197, 1319, 1395, and 1454

2.3 *Compressed Gas Association Documents:*

Pamphlet G-4.4-2003 (EIGA Doc. 13/02) Oxygen Pipeline Systems[3]

Pamphlet G-4.8 Safe Use of Aluminum Structured Packing for Oxygen Distillation[3]

Pamphlet G-4.9 Safe Use of Brazed Aluminum Heat Exchangers for Producing Pressurized Oxygen[3]

[1] This guide is 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.

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

Pamphlet P-8.4 (EIGA Doc. 65/99) Safe Operation of Reboilers Condensers in Air Separation Plants[3]

2.4 *ASTM Adjuncts:*

Test Program Report on the Ignition and Combustion of Materials in High-Pressure Oxygen[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *autoignition temperature*—the lowest temperature at which a material will spontaneously ignite in oxygen under specific test conditions (see Guide G126).

3.1.2 *direct oxygen service*—in contact with oxygen during normal operations. Examples: oxygen compressor piston rings, control valve seats (see Guide G126).

3.1.3 *exemption pressure*—the maximum pressure for an engineering alloy at which there are no oxygen velocity restrictions (from CGA 4.4 and EIGA doc 13/02).

3.1.4 *impact-ignition resistance*—the resistance of a material to ignition when struck by an object in an oxygen atmosphere under a specific test procedure (see Guide G126).

3.1.5 *indirect oxygen service*—not normally in contact with oxygen, but which might be as a result of a reasonably foreseeable malfunction, operator error, or process upset. Examples: liquid oxygen tank insulation, liquid oxygen pump motor bearings (see Guide G126).

3.1.6 *maximum use pressure*—the maximum pressure to which a material can be subjected due to a reasonably foreseeable malfunction, operator error, or process upset (see Guide G63).

3.1.7 *maximum use temperature*—the maximum temperature to which a material can be subjected due to a reasonably foreseeable malfunction, operator error, or process upset (see Guide G126).

3.1.8 *nonmetallic*—any material, other than a metal, or any composite in which the metal is not the most easily ignited component and for which the individual constituents cannot be evaluated independently (see Guide G126).

3.1.9 *operating pressure*—the pressure expected under normal operating conditions (see Guide G126).

3.1.10 *operating temperature*—the temperature expected under normal operating conditions (see Guide G126).

3.1.11 *oxygen-enriched*—applies to a fluid (gas or liquid) that contains more than 25 mol % oxygen (see Guide G126).

3.1.12 *qualified technical personnel*—persons such as engineers and chemists who, by virtue of education, training, or experience, know how to apply physical and chemical principles involved in the reactions between oxygen and other materials (see Guide G126).

3.1.13 *reaction effect*—the personnel injury, facility damage, product loss, downtime, or mission loss that could occur as the result of an ignition (see Guide G126).

3.1.14 *threshold pressure*—there are several different definitions of threshold pressure that are pertinent to the technical literature. It is important that the user of the technical literature fully understand those definitions of threshold pressure which apply to specific investigations being reviewed. Two definitions for threshold pressure, based on interpretations of the bulk of the current literature, appear below.

3.1.14.1 *threshold pressure*—in a promoted ignition-combustion test series conducted over a range of pressures, this is the maximum pressure at which no burns, per the test criteria, were observed and above which burns were experienced or tests were not conducted.

3.1.14.2 *threshold pressure*—the minimum gas pressure (at a specified oxygen concentration and ambient temperature) that supports self-sustained combustion of the entire standard sample (see Guide G124).

4. Significance and Use

4.1 The purpose of this guide is to furnish qualified technical personnel with pertinent information for use in selecting metals for oxygen service in order to minimize the probability of ignition and the risk of explosion or fire. It is intended for use in selecting materials for applications in connection with the production, storage, transportation, distribution, or use of oxygen. *It is not intended as a specification for approving materials for oxygen service.*

5. Factors Affecting Selection of Materials

5.1 *General:*

5.1.1 The selection of a material for use with oxygen or oxygen-enriched atmospheres is primarily a matter of understanding the circumstances that cause oxygen to react with the material. Most materials in contact with oxygen will not ignite without a source of ignition energy. When an energy-input exceeds the configuration-dependent threshold, then ignition and combustion may occur. Thus, the material's flammability properties and the ignition energy sources within a system must be considered. These should be viewed in the context of the entire system design so that the specific factors listed in this guide will assume the proper relative significance. In summary, it depends on the application.

5.2 *Relative Amount of Data Available for Metals and Nonmetals:*

5.2.1 Studies of the flammability of gaseous fuels were begun more than 150 years ago. A wide variety of applications have been studied and documented, including a wide range of important subtleties such as quenching phenomena, turbulence, cool flames, influence of initial temperature, etc., all of which have been used effectively for safety and loss prevention. A smaller, yet still substantial, background exists for nonmetallic solids. In contrast to this, the study of the flammability of metals dates only to the 1950s, and even though it has accelerated rapidly, the uncovering and understanding of subtleties have not yet matured. In addition, the heterogeneity of the metal and oxidizer systems and the heat transfer properties of metals, as well as the known, complex ignition energy and ignition/burning mechanisms, clearly dictate that caution is required when applying laboratory findings to actual

[4] Available from ASTM International Headquarters. Order Adjunct No. ADJG0094. Original adjunct produced in 1986.

applications. In many cases, laboratory metals burning tests are designed on what is believed to be a worst-case basis, but could the particular actual application be worse? Further, because so many subtleties exist, accumulation of favorable experience (no metal fires) in some particular application may not be as fully relevant to another application as might be the case for gaseous or nonmetallic solids where the relevance may be more thoroughly understood.

5.2.1.1 ASTM Symposia and Special Technical Publications on these symposia have contributed significantly to the study of the flammability and sensitivity of materials in oxygen-enriched atmospheres. See section 2.2 for listing of STP numbers and the References Section for key papers.

5.3 *Relationship of Guide G94 with Guides G63, G88, and G93:*

5.3.1 This guide addresses the evaluation of metals for use in oxygen systems and especially in major structural portions of a system. Guide G63 addresses the evaluation of nonmetals. Guide G88 presents design and operational maxims for all systems. In general, however, Guides G63 and G88 focus on physically small portions of an oxygen system that represent the critical sites most likely to encounter ignition. Guide G93 covers a key issue pertinent to actual operating oxygen systems; cleaning for the service.

5.3.2 The nonmetals in an oxygen system (valve seats and packing, piston rings, gaskets, o-rings) are small; therefore, the use of the most fire-resistant materials is usually a realistic, practical option with regard to cost and availability. In comparison, the choice of material for the major structural members of a system is much more limited, and the use of special alloys may have to be avoided to achieve realistic costs and delivery times. Indeed, with the exception of ceramic materials, which have relatively few practical uses, most nonmetals have less fire resistance than virtually all metals. Nonmetals are typically introduced into a system to provide a physical property not achievable from metals. Nonmetals may serve as "links" in a kindling chain (see 5.6.5), and since the locations of use are typically mechanically severe, the primary thrust in achieving compatible oxygen systems rests with the minor components as addressed by Guides G63 and G88 that explain the emphasis on using the most fire-resistant materials and Guide G93 which deals with the importance of system cleanliness.

5.3.3 Since metals are typically more fire-resistant and are used in typically less fire-prone functions, they represent a second tier of interest. However, because metal components are relatively so large, a fire of a metal component is a very important event, and should a nonmetal ignite, any consequential reaction of the metal can aggravate the severity of an ignition many times over. Hence, while the selection of nonmetals by Guide G63 and the careful design of components by Guide G88 are the first line of defense, optimum metal selection is an important second-line of defense.

5.3.4 Contaminants and residues that are left in oxygen systems may contribute to incidents via ignition mechanisms such as particle impact and promoted ignition-combustion (kindling chain). Therefore, oxygen system cleanliness is essential. Guide G93 describes in detail the essential elements for cleaning oxygen systems.

5.4 *Differences in Oxygen Compatibility of Metals and Nonmetals:*

5.4.1 There are several fundamental differences between the oxygen compatibility of metals and nonceramic nonmetals. These principal differences are summarized in Table 1.

5.4.2 Common-use metals are harder to ignite. They have high autoignition temperatures in the range 900 to 2000°C (1650 to 3600°F). In comparison, most combustible nonmetals have autoignition temperatures in the range 150 to 500°C (300 to 1000°F). Metals have high thermal conductivities that help dissipate local heat inputs that might easily ignite nonmetals. Many metals also grow protective oxide coatings (see 5.5) that interfere with ignition and propagation.

5.4.3 Once ignited, however, metal combustion can be highly destructive. Adiabatic flame temperatures for metals are much higher than for most polymers (Table X1.7). The greater density of most metals provides greater heat release potential from components of comparable size. Since many metal oxides do not exist as oxide vapors (they largely dissociate upon vaporization), combustion of these metals inherently yields coalescing liquid metal oxide of high heat capacity in the flame zone at the oxide boiling point (there may be very little gaseous metal oxide). In comparison, combustion of polymers yields gaseous combustion products (typically carbon dioxide and steam) that tend to dissipate the heat release.

5.4.4 Contact with a mixture of liquid metal and oxide at high temperature results in a massive heat transfer relative to that possible upon contact with hot, low-heat-capacity, gaseous combustion products of polymers. As a result, metal combustion can be very destructive. Indeed, certain metal combustion flames are an effective scarfing agent for hard-to-cut materials like concrete (**1**).[5]

5.4.5 Finally, because most polymers produce largely inert gas combustion products, there is a substantial dilution of the oxygen in the flame that inhibits combustion and if in a stagnant system, may even extinguish a fire. For many metals, combustion produces the molten oxide of negligible volume condensing in the flame front and, hence, oxygen dilution is much less.

5.5 *Protective Oxide Coatings:*

5.5.1 Oxides that grow on the surfaces of metals can play a role in the metal's flammability. Those films that interfere with ignition and combustion are known as protective oxides. Typically, an oxide will tend to be protective if it fully covers the exposed metal, if it is tenaciously adherent, and if it has a

TABLE 1 Comparison of Metals and Nonmetals Flammability

	Metals	Nonmetals
Combustion products	molten metal oxide	hot gases
Autoignition temperatures	900–2000°C	150–500°C
Thermal conductivities	higher	lower
Flame temperature	higher	lower
Heat release	higher due to density	lower
Surface oxide	can be protective	negligible

[5] The boldface numbers in parentheses refer to the list of references at the end of this guide.