



Standard Guide for Studying Fire Incidents in Oxygen Systems¹

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1. Scope

1.1 This guide covers procedures and material for examining fires in oxygen systems for the purposes of identifying potential causes and preventing recurrence.

1.2 This guide is not comprehensive. The analysis of oxygen fire incidents is not a science, and definitive causes have not been established for some events.

1.3 The procedures and analyses in this guide have been found to be useful for interpreting fire events, for helping identify potential causes, and for excluding other potential causes. The inclusion or omission of any analytical strategy is not intended to suggest either applicability or inapplicability of that method in any actual incident study.

NOTE 1—Although this guide has been found applicable for assisting qualified technical personnel to analyze incidents, each incident is unique and must be approached as a unique event. Therefore, the selection of specific tactics and the sequence of application of those tactics must be conscious decisions of those studying the event.

NOTE 2—The incident may require the formation of a team to provide the necessary expertise and experience to conduct the study. The personnel analyzing an incident, or at least one member of the team, should know the process under study and the equipment installation.

1.4 *Warning*—During combustion, gases, vapors, aerosols, fumes, or combinations thereof, are evolved, which may be present and may be hazardous to people. *Caution*—Adequate precautions should be taken to protect those conducting a study.

1.5 *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

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.

E 620 Practice for Reporting Opinions of Scientific or Technical Experts

E 678 Practice for Evaluation of Scientific or Technical Data

E 860 Practice for Examining And Preparing Items That Are Or May Become Involved In Criminal or Civil Litigation

E 1020 Practice for Reporting Incidents that May Involve Criminal or Civil Litigation

E 1138 Terminology for Technical Aspects of Products Liability Litigation

E 1188 Practice for Collection and Preservation of Information and Physical Items by a Technical Investigator

E 1459 Guide for Physical Evidence Labeling and Related Documentation

E 1492 Practice for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Science Laboratory

G 63 Guide for Evaluating Nonmetallic Materials for Oxygen Service

G 88 Guide for Designing Systems for Oxygen Service

G 93 Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen-Enriched Environments

G 94 Guide for Evaluating Metals for Oxygen Service

G 114 Practices for Evaluating the Age Resistance of Polymeric Materials Used in Oxygen Service

G 124 Test Method for Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres

G 126 Terminology Relating to the Compatibility and Sensitivity of Materials in Oxygen Enriched Atmospheres

G 128 Guide for Control of Hazards and Risks in Oxygen Enriched Systems

2.2 ASTM Adjunct:

Video: *Oxygen Safety*³

2.3 Compressed Gas Association (CGA) Standards:⁴

G-4.4 Industrial Practices for Gaseous Oxygen Transmission and Distribution Piping Systems

³ Available from ASTM Customer Service, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959. Request PCN 12-700880-31.

⁴ Available from Compressed Gas Association (CGA), 4221 Walney Rd., 5th Floor, Chantilly, VA 20151-2923, <http://www.cganet.com>.

G-4.8 Safe Use of Aluminum Structured Packing for Oxygen Distillation

2.4 *National Fire Protection Association (NFPA) Standard*.⁵

NFPA 53 Fire Hazards in Oxygen Enriched Atmospheres

NFPA 921 Guide for Fire and Explosion Investigations

2.5 *Occupational Safety and Health Act*.⁶

OSHA Process Safety Management Compliance Manual

3. Terminology

3.1 *Definitions*—See Guides G 63, G 94, and G 128 for the terms listed in this section.

3.1.1 *oxygen compatibility, (also oxidant compatibility), n*—the ability of a substance to coexist with both oxygen and a potential source(s) of ignition at an expected pressure and temperature with a magnitude of risk acceptable to the user.

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

3.1.3 *oxygen-enriched, adj*—a fluid (gas or liquid) mixture containing more than 25 mole % oxygen.

3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *incident, n*—an ignition or fire, or both, that is both undesired and unanticipated or an undesired and unanticipated consequence of an ignition or fire that was anticipated.

3.2.2 *direct incident cause, n*—the mechanical or thermodynamic event (such as breakage of a component or near-adiabatic compression), the physicochemical property (such as heat of combustion), the procedure (such as a valve opening rate), or any departure(s) from the intended state of any of these items, that leads directly to ignition or fire, or both.

3.2.3 *fractional evaporation, n*—the continuous evaporation of a quantity of liquid that results in a progressive increase in the concentration of a less-volatile constituent(s).

3.2.4 *Contaminant, n*—unwanted molecular or particulate matter that could adversely affect or degrade the operation, life, or reliability of the systems or components upon which it resides.

3.2.5 *Contamination, n*—(1) the amount of unwanted molecular non-volatile residue (NVR) or particulate matter in a system; (2) the process or condition of being contaminated. Discussion—Contamination and cleanliness are opposing properties: increasing cleanliness implies decreasing contamination.

4. Summary of Guide

4.1 Following a fire incident in an oxygen-enriched atmosphere, the equipment, operating procedures, and area are considered in light of other incidents, potential contributing factors, suggested analytical strategies, and demonstrated laboratory results. The goal is to determine direct cause(s) of the incident in order to prevent a recurrence.

5. Significance and Use

5.1 This guide helps those studying oxygen system incidents to select a direct cause hypothesis and to avoid conclusions based on hypotheses, however plausible, that have proven faulty in the past.

6. Abstract

6.1 A series of possible causes and common scenarios are described to assist those seeking to understand incidents in oxygen-enriched atmospheres. Many easily misinterpreted factors are described to help avoid faulty conclusions. Several suspected but unproven incident scenarios are described. Select laboratory data are presented to support assertions about direct causes of incidents.

7. Direct-Cause Analysis

7.1 In this guide, the direct cause of an incident is the mechanical or thermodynamic event (such as breakage of a component or near-adiabatic compression), the physicochemical property (such as heat of combustion), the procedure (such as a valve opening rate), or any departure(s) from the intended state of any of these items, that leads directly to ignition or fire, or both. A fire might also be the result of a financial decision, worker skill, or manufacturing process—all of which can be viewed as causes—but such factors are addressed more properly in a system hazard review. It is noteworthy that some fires are anticipated and the risks (whether human or economic) are addressed by such things as shielding (for example to control human risk) or acceptance (for example to address economic risk). In these cases, a fire is not an “incident” unless some aspect of the event exceeded expectations the initial parameters (for example, the shielding did not provide the expected containment, or the cost exceeded projections). This guide seeks to identify the material choice, equipment design, assembly procedure, or other factor that led directly to the fire—and more specifically, to distinguish the physical object or action that caused the fire to start, to continue, or to be injurious or destructive. Remedial actions are found in other documents such as Guides G 63, G 88, and G 94, and Practice G 93, as well as NFPA 53, CGA G-4.4, and G-4.8, OSHA *Process Safety Management Compliance Manual*, and others.

7.2 *Example*—The direct cause of an incident may be concluded to be the use of an incompatible material, for example, a polyacetyl component was installed when a material such as PTFE (polytetrafluoroethylene) or CTFE (chlorotrifluoroethylene) was preferred. The direct cause was not that the budget was inadequate to cover the cost of PTFE; nor that specific frictional properties of polyacetyl were required for mechanical purposes; nor that an incorrect part was installed in error. Note that in this example, PTFE and CTFE might be needed to prevent or cope with ignition and fire, but that they might introduce non-fire-related issues such as loss of mechanical strength or production of toxic decomposition products when exposed to heat of compression.

8. Elements of a Study

8.1 *Overview*—The study of an oxygen incident typically begins (preferably promptly) after the event has concluded.

⁵ Available from National Fire Protection Association (NFPA), 1 Batterymarch Park, Quincy, MA 02169-7471, <http://www.nfpa.org>.

⁶ Available from Occupational Safety and Health Administration (OSHA), 200 Constitution Ave., NW, Washington, DC 20210, <http://www.osha.gov>.

The fire is extinguished and any safety requirements or immediate needs are addressed (treating injuries, returning systems to a safe state, and so forth). Then the investigator can begin to document the event, to preserve the artifacts, and to detect how they may have been altered or compromised by the event and follow-up activities. Although many of these steps are itemized here, the intent of this guide is not to specify how or in what order they should be conducted. Rather, information is offered about certain procedures that have been effective in the past, as well as some that have led to faulty conclusions. Typically, good scientific and laboratory skills are useful and adequate. Forensic skills and procedures can be helpful in many cases, but may not be practical in all. For example, the forensic Guide E 1459 can assist with managing post-incident artifacts, and related Practices E 1492, E 620, E 678, E 860, E 1020, and E 1188, as well as Terminology E 1138, may have other uses. However, when a forensic approach is needed because a legal action is involved, the insights in this guide may effectively supplement it.

8.2 Documentation—Urgent post-incident efforts include: photographing or videotaping the site and any damaged equipment; obtaining system drawings, supporting design analysis, process hazards analysis, and any other hazard-evaluation materials; interviewing persons knowledgeable about the system, operating procedures and the events before, during, and after the fire; collecting specimens, operating logs, and related information; and preliminary formulation and testing of hypotheses.

8.3 Analysis—The principal effort in a study will be analysis of the data and artifacts. This may require further examination of the equipment and records, laboratory study of selected items, and perhaps even laboratory simulation of the incident.

8.4 Completion of Study—An incident study is complete when the qualified technical personnel involved in the study conclude that the event is understood.

8.4.1 An incident might be understood adequately when a conclusion has been drawn about the direct cause of the event. The following examples show the distinction between direct causes and causes that are not physicochemical or thermodynamic events.

8.4.1.1 Example 1—A substantial amount of hydrocarbon oil was introduced into a system just before an incident. This single factor may be identified as the direct cause of the fire. Any reasons for introducing the lubricant may be important to a new hazard review, but are not the direct cause of the fire. Prevention can focus on cleanliness. *Initiating Event*: ignition of an incompatible oil. *Direct Cause*: contamination of the system.

8.4.1.2 Example 2—Records may show that a component broke and produced a rub in a piece of machinery just before an incident. This factor alone can ignite a fire and could be identified as the direct cause. If the component broke because it contained a flaw, the flaw might be determined to be the direct cause. However, if the part was selected because it offered economy, then the direct cause is still the inadequate part—not a misguided effort to economize. Prevention in this

case can focus on component quality. *Initiating Event*: friction during the rub. *Direct Cause*: Mechanical failure.

8.4.1.3 Example 3—Deviation from an important operating practice, such as first equalizing downstream pressure with a bypass valve before opening a quick-opening valve, may be established as the direct cause of a fire. The reasons for departing from mandated practice are important, but they are not the direct cause. Here, prevention can focus on following standard operating procedures. *Initiating Event*: approximately adiabatic compression. *Direct Cause*: incorrect operation.

8.4.2 An incident might be understood adequately when a conservative tactic has been identified that would have prevented or safely managed the event.

8.4.2.1 Example 1—If an item of machinery cannot employ oxygen-compatible materials because they compromise its operating economy, and it becomes the site of a fire and injures someone, then the event may be understood adequately (regarding preventing recurrence of injury rather than fire) when inadequate shielding or inadequate mechanical design or some other comparable factor is identified singly or in combination as the direct cause.

8.4.3 The study is complete when the direct cause has been determined. Preventing the repetition of an event is the function of a hazard review using well-established techniques, including the use of related standards from ASTM Committee G-4. The hazard review may be integral to the incident study and may involve some or all of the same people, but it is a separate activity for the purpose of this guide.

9. Factors Affecting an Incident Study

9.1 Missing Components—Following some oxygen incidents, components have appeared to be absent, leading to speculation that the component was not installed or that its mechanical failure and passage through the system were at fault. Sometimes, the damage is so negligible that the possibility that there was no fire is considered. These conclusions can be in error. In an oxygen-enriched atmosphere, combustion can be remarkably clean. A simple polymer may be converted totally into carbon dioxide and water, leaving no trace of its prior presence. If the component is small or if it has a low heat of combustion, there may be no evidence of heat damage. For example, PTFE seats in ball valves (which are large and have low heat of combustion) and nylon seats in cylinder valves (which are small and have high heat of combustion) have burned completely in some incidents with no melting of metal components, no appearance of residual carbon, and no remains of the polymer itself.

9.2 Contamination:

9.2.1 When contamination is present in an oxygen system, the contaminant may serve to start the incident. The ensuing fire involving the polymers, metals, and contaminant may consume the contaminant fully, leaving no indication of its original presence.

9.2.2 When contaminant levels are high, they may produce so large an explosive event that the system integrity can be breached, and the fire can be extinguished without complete combustion of the contaminant. Therefore, some of the contaminant may be found after an incident in the same regions of the system where the fire occurred. In these instances, the

flammability of the contaminant can be so much greater than that of the metals and polymers that there may be only scant damage to the system materials.

9.2.3 Example—In laboratory tests of an oxygen system component, hydrocarbon lubricating oil was introduced and ignited. When the amount of lubricant was small, a fire may or may not have resulted, but there was usually no trace of the oil after the test. When the amount of lubricant was large, the component was blown apart. Threads on the component parts were stripped. A pressure gage was in fragments. After the event, neither melting nor consumption of the components was observed, and the parts had an obvious coating of the oil.

9.2.4 Carbon or Black Dust—In many incidents, a black powder will be present on many surfaces. The powder could be unreacted carbon from incomplete combustion of organic materials either inside or outside the component. However, some powders that look like carbon are not. For example, fires involving aluminum in gaseous or liquid oxygen may produce a black (and in some cases gray) powder that is largely unreacted aluminum. Indeed, such dust may be present as a result of a fire involving aluminum or it may be present because of fabrication processes. In metal inert gas (MIG) welding, aluminum is vaporized and condenses as a black dust in the region of the bead. If this powder is present in an oxygen system, it may be a cause of ignition, because it is very flammable and has been observed burning even in air.

9.2.5 Oil—Oil in oxygen systems can be a severe hazard (1).⁷ Many oils, hydrocarbons in particular, are relatively volatile in comparison to metals and polymers. Their auto-ignition temperatures are much lower than those of most other materials (metals and nonmetals) used to fabricate oxygen systems, including many materials not generally regarded as oxygen compatible. Therefore, heat of compression can ignite oils much more easily. Furthermore, many oils burn very rapidly, even explosively, and they are always a strong candidate as the cause of an oxygen incident.

9.2.5.1 Simple ultraviolet black light inspection of a site and incident artifacts is a convenient way to identify the presence of some oils. Many oils do not fluoresce. Therefore, the discovery of oil-like fluorescence suggests oil as a potential cause, but the absence of fluorescence does not necessarily rule out contamination with oil as a cause.

9.2.5.2 The use of ultraviolet light has other limitations. Many materials besides oil fluoresce. For example, there is a fluorescent constituent in blood that might be mistaken for oil contamination if injuries occurred and components became wetted with blood.

9.2.5.3 The absence of an oil residue cannot rule out oil contamination as a potential cause of an incident. The need to avoid oil contamination is often ignored by system users/operators who are not well trained or knowledgeable about oxygen compatibility issues. There is a general view that lubrication is beneficial, and there are few convenient sources of oxygen-compatible lubricants.

9.3 Particle Impact:

9.3.1 Impact and subsequent ignition of particles in oxygen systems has been demonstrated to have been the cause of several fires. This ignition mechanism is especially likely at and just downstream of locations where the velocity of the oxygen is sonic (any location across which there is about a 2:1 absolute pressure drop), and has been demonstrated at velocities as low as 150 ft/s (50 m/s) (2).

9.3.2 References 3-5 describe incidents thought to have been affected by particle impact.

9.4 Debris Sumps—Many systems contain regions where debris tends to collect. Particle debris can accumulate at low points or stagnant side branches. If the piping for a bypass valve is connected to the bottom region of a horizontal run of pipe, debris that passes through the system may drop into the stagnant upstream legs of the bypass run. If this valve is then opened, accumulated debris is injected into the high-velocity valve and may cause a fire either in the bypass run or further downstream.

9.5 Heat of Compression:

9.5.1 When a gas is compressed rapidly, its temperature rises. The pressurization of a system tends to produce the greatest temperatures within the gas initially in the system. The increase in temperature can cause autoignition of some system components. This compression is nearly adiabatic and typically occurs at system end points or trapped volumes. In extreme cases, heat of compression has produced some of the most explosive (rupturing and fragmenting components) and most probable mechanisms of oxygen fires. In severe cases, a heat of compression fire may occur on the very first pressurization of a system. Every incident should be examined for a mechanism that may have enabled rapid gas compression and for where the compressed gas may have been located relative to the fire damage.

NOTE 3—Oxygen system fires require an energy source to trigger ignition, as do most fires. Particle impact and compression heating were briefly described above since they are very often implicated in oxygen system fires; however, several other ignition mechanisms are known to occur. The most common ignition mechanisms are discussed in greater depth in Guides G 88 and G 128.

9.5.2 References 6-10 describe theory and experimental work on heat of compression.

9.6 Overpressure:

9.6.1 A fire in an oxygen system can produce overpressure damage from pressures increasing beyond the system's physical containment capabilities. It also can result from damage or erosion that reduces system pressure containment capabilities to below normal pressure exposure levels. Among the characteristics that may be seen are bulging, bursting, venting, explosion, and fragmentation.

9.6.2 Bulging—Bulging or swelling of components can occur at the site of an explosion or at weak regions of the system, or both. In brazed copper systems, it is common to see overpressure effects at annealed regions, such as just outside brazed joints, where hardened tubing will be annealed and therefore of lower strength. The presence of such bulging in brazed copper joints in a local region only suggests a localized explosive event. Bulging at many such joints may also indicate a systematic pressure increase.

⁷ The boldface numbers in parentheses refer to the references listed at the end of this guide.

9.6.3 *Bursting*—Vessels that burst into several large pieces typically have failed along weak regions or flaws and have been exposed to either a small or slow explosive event (such as deflagration) or to a general systematic pressure rise that has been relatively slow. Common gas phase combustion, or deflagration, often proceeds with a propagation velocity of the reacting zone of up to about 30 ft/s (10 m/s), well below the speed of sound.

9.6.3.1 Cylindrical vessels designed properly and pressurized slowly to failure often fail in a characteristic way a tear starts at a weak point in the wall of the cylinder and propagates longitudinally in both directions until it reaches the head, where it propagates along the edge of the head. Sometimes the head may be torn totally free, while the vessel often remains as one piece. Fig. 1 shows how a ruptured cylindrical vessel might look if flattened fully.

9.6.3.2 In some metal alloys such as aluminum, alloys, piping is extruded with dies and mandrels in a way that can produce weak longitudinal seams. Overpressure, either slow or fast, can cause tears along these seams, yielding several similar pieces. This can occur at pressures much lower than those normally expected to cause fragmentation.

9.6.4 *Fragmentation*—When a vessel is fragmented into many small pieces of dissimilar shapes and sizes, it usually suggests a very fast combustion that produced pressures well above the burst pressure of the vessel, before the vessel actually fails. This type of failure is also commonly known as a “brittle” failure.

9.6.4.1 Vessels that burst into many small pieces are often associated with a detonation. Whereas deflagration is relatively slow (see 9.6.3), in some very flammable conditions, called high-explosive, the velocity may achieve 3000 to 9000 ft/s (much faster than the speed of sound). In the latter instance, relief valves and vents are ineffective in limiting system pressures, and fragmentation often results with the production of small fragments. However, it is not always possible to infer that fragments resulted from a detonation. In recent times, the

testing of flammable metals in liquid oxygen has produced two-phase combustion and vessel fragmentation, and it is not certain at present that the combustion rates were in excess of the speed of sound. This has led to the description of these events as “violent explosive reactions (VERs)” rather than detonations.

9.7 *Time Delays*—Most oxygen fire incidents are associated with a prior transient event, usually operation of a valve, that often is causal to the event. Most of the time the fire occurs almost simultaneously with the transient event, but there can be appreciable delays.

9.7.1 *Example 1*—An oxygen system is pressurized when a valve is opened. About 30 min later, a large leak develops in a closed PTFE-seated ball valve downstream, or the ball valve downstream is found to be hot. It is possible that the pressurization produced heat-of-compression temperatures above the ignition point of the PTFE valve seat. Because the valve was closed, the inert combustion products could accumulate and slow combustion to the point where it may have taken 30 min or more to breach the seat or to make the valve hot enough to detect. In pressurized oxygen index tests of PTFE rod burning in flowing oxygen/nitrogen mixtures near the end point, 30 min or more were required to burn a 75-mm (3-in.) long rod.

9.7.2 *Example 2*—Liquid oxygen flow to a waste vaporizer is interrupted, and the waste line clears itself. Several hours later, an explosion breaches a vertical run of piping where liquid could collect. In this case, liquid with a low level of contaminants can fill a sump and slowly evaporate while concentrating flammable constituents (see 10.2 on fractional evaporation). When a flammable mixture is developed, an ignition source can produce the delayed event.

9.8 *Crevices*—A crevice can be a potential ignition cause in liquid oxygen (LOX) systems if it fills with liquid, especially through a narrow passage or pore. When the vessel is drained and warmed, high pressure and high velocity will develop in the liquid, if the passage is small, as it tries to escape. If the crevice is in a weld of a metal that produced MIG weld dust,

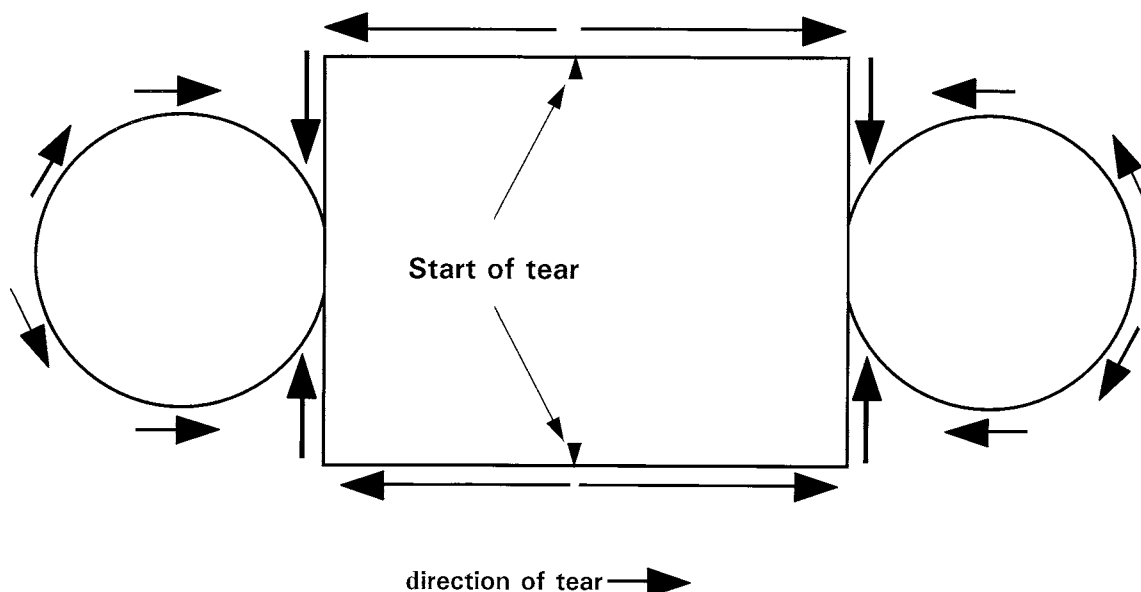


FIG. 1 Illustration of How A Ruptured Cylindrical Vessel Might Look if Fully Flattened

it may contain fine, easily ignited particles that may become entrained in the flow and impact a piping intersection or valve seat, causing ignition. If the liquid contains a low level of contaminants, the liquid in the crevice may concentrate contaminants as it evaporates (see 10.2 on fractional evaporation), and may inject sensitive hydrocarbon contaminants through the passage. These events have been crudely demonstrated in laboratory tests and are believed to have resulted in some metal ignitions.

9.9 Surface Discoloration:

9.9.1 *Pink Brass*—During a fire, brass alloys may be exposed to brief, intense temperature or to corrosive chemicals, resulting in a surface depletion of the volatile zinc constituent. The result can be a pink hue on the brass surface that is not contamination and that is also not likely to be associated with the cause of the incident.

9.10 Flash Fire:

9.10.1 There are often two distinct phases in an oxygen incident: an initial flash fire of the most flammable portion of the system followed by slower, more enduring general combustion.

9.10.2 In laboratory tests employing igniters or contaminants, there often is a pressure spike only several milliseconds in duration that signals the start of the event.

9.10.2.1 *Example 1*—In the 1960s, tests of animal carcasses showed that when the carcass was ignited in oxygen, the fire spread first over the carcass surface, burning away very fine hair. This flash fire occurred in a split second, even under snug cloth wrappings that simulated clothing. In the second stage, a widespread fire of the cloth and carcass fat often developed that appeared to be nearly simultaneous over the entire surface (11).

9.10.2.2 *Example 2*—In a hospital operating room, oxygen is used to improve a patient's oxygenation during surgery. On occasion the oxygen may accumulate under the surgical drapes in sufficient quantities to substantially increase the local oxygen concentration. Subsequent ignition produced a rapid fire of the very fine nap of the bedding (so fast that it was described as a spark), followed by a general fire of the cloth. This flash fire of the nap of material and clothing has been demonstrated experimentally (12,13).

9.10.3 The prospect of an initial flash fire involving surface contaminants is one reason that low levels of oil in an oxygen system may not be discoverable after an incident, despite the possibility of having played a crucial causal role either in ignition or in the related kindling chain.

9.11 Explosive Decompression:

9.11.1 When a gas permeates or dissolves into a material at high pressure and the surrounding pressure is released at a rate faster than the gas can diffuse out of the material, then the material becomes a sort of pressure vessel. If the material is an elastomer, it can swell like a balloon, sometimes more than doubling its apparent size (14,15). The internal pressure can cause the elastomer to exceed its tensile strength, and it can burst. This is explosive decompression.

9.11.1.1 Some O-ring design handbooks have described explosive decompression as a potential source of ignition in oxygen systems. The events believed to occur during explosive decompression (tearing, friction, high gas velocities, and so

forth) are all plausible elements of ignition. However, Committee G-4 has not located any original data supporting this potential mechanism, nor is Committee G-4 aware of any laboratory tests that have produced ignition in this way, or any incidents believed to have been caused by this mechanism.

9.12 *Intimate Mixture*—Intimate mixing can lead to increased flammability. Materials that dissolve in liquid oxygen tend to be high explosives. Among the factors that lead to increased flammability in intimately mixed (homogeneous) fuel and oxidant systems are adiabaticity, accessibility to oxidants, and so forth.

9.13 High Surface Area to Volume Ratio:

9.13.1 Systems with a high surface area-to-volume (SAV) ratio exhibit intimate mixture that leads to great flammability. It is well demonstrated that the finer a metal powder is ground, the more rapid will be its reaction with oxygen. High SAV ratio systems include sintered filter media, packed columns, powders, and dusts.

9.13.2 *Porosity*—Porous systems exhibit high SAV. Often, the flammability of a high SAV ratio system may not be obvious due to the small amount of oxidant present. For example, a small amount of LOX spilled onto a porous asphalt surface can be viewed as an intimately mixed, high SAV ratio system (see 9.13.1) (16). Other examples would include LOX impregnating a powder, fines ground in a system, an open-cell foam, or any spongy material.

9.14 Fresh Metal Exposure (FME):

9.14.1 Fresh metal exposure is an often-considered ignition source. In theory, the surface of a system is damaged by two parts rubbing together, by spalling of an oxide, by development of a small crack, and so forth. The model proposes that fresh metal is exposed and begins to react with oxygen. This oxide formation releases heat that initiates a chain reaction of oxide formation and heat release until ignition and a potential fire occur. This mechanism is suspected most commonly in metals that have very protective oxides whose formation is highly exothermic.

9.14.2 Titanium has exhibited FME ignition in numerous laboratory tests (17).

9.14.3 The FME effect does not appear to have been demonstrated with metals other than titanium. Although aluminum has many physical and thermodynamic properties that should be important to FME ignition, and although FME ignition has been speculated for aluminum, numerous attempts to produce this effect in the laboratory have failed (18).

9.14.4 Fresh metal is believed to have been a factor causing several fires in multi-gas compressors or in compressors that have been initially broken in with inert gases prior to conversion to oxygen use. In these cases, it is believed there may have been accumulations of small particles with fresh metal surfaces, high surface-area-to-volume ratios and intimate mixture with the oxygen. In addition, many of the fresh metal rubbing surfaces that form in inert gases may exhibit greater friction resulting from the lack of a hard oxide film (passive oxide layer). Standard practice in cases where compressors are being changed over to oxygen service after inert gas use is often to operate the compressor with gases that contain progressively

greater levels of oxygen to passivate the particles and rubbing surfaces and reduce their flammability.

10. Common Incident Scenarios

10.1 Several types of incidents have happened so often that any event must be evaluated to determine whether it is of this type. The key to these events appears to be attributable to basic human nature: common actions taken for granted so often that, even though their risks in oxygen systems are well known, they are likely to happen despite efforts and procedures to prevent them.

10.2 *Fraction Evaporation of Liquid Oxygen:*

10.2.1 Liquid oxygen (LOX) has a solubility for many flammable chemicals, and many of these can exist as particles in the liquid. These include hydrocarbons (especially acetylene), ozone, nitrous oxide, metal dusts, and others. Normally, very low levels of such materials do not pose a fire hazard. However, if a substantial portion of liquid is contained in an enclosed, “dead-ended,” region of a system (including vaporizers) and allowed to evaporate, the oxygen will distill preferentially, leading to a progressively increasing concentration of these flammable materials until a flammable mixture occurs. Further evaporation will ultimately lead to stoichiometric mixtures that ignite quite easily. Solutions of liquid oxygen and colloids of liquid oxygen with flammable materials are highly explosive and can fragment the vessels that contain them, even if the vessels vent to atmosphere. This scenario has happened frequently in industry (19-22).

10.2.2 Residue that is left when LOX is boiled to dryness may be a source for ignition. When ignition occurs, it is due to a specific ignition event. The ignition mechanism(s) that affect fractional-evaporated LOX have not been demonstrated in the laboratory, but the presence of shock-sensitive materials such as copper acetylides (19) and the development of electrostatic discharge from frozen particles of matter in the liquid have been suggested. These ignition sources are plausible, but many remain speculative.

10.2.3 Direct causes of events involving fractional evaporation of LOX relate to its ultimate achievement of the lower explosive limit and have been taken to be: (1) allowing the initial liquid to contain a level of contamination that is too high; (2) allowing the liquid to be mixed with other streams (gas, solid, or liquid) that contain flammable materials; and (3) allowing contaminated liquid to evaporate in volumes so large that an appreciable amount of liquid still remains while its trace flammable contaminants concentrate into the flammable region.

10.3 *Condensation of Air*—Air exposed to very low temperatures condenses. When air condenses, the first drops appear at a concentration of about 50 mol % oxygen (23), a level that already presents a significant fire hazard. If enough of this oxygen-enriched “liquid air” is formed, it can enrich even more during vaporization, further aggravating the hazard. Liquid air has a boiling point lower than that of liquid oxygen, so liquid air will not form on liquid oxygen lines. Similarly, liquid air has a boiling point lower than that of high-pressure liquid nitrogen, and so would not form on these lines. However, liquid air forms easily on low-pressure liquid nitrogen lines and on lines of liquids with still lower boiling points (such

as liquid hydrogen or liquid helium). Oxygen enriched liquid air can condense within the porous structure of insulations used on the piping itself and represent an explosion hazard (24). Liquid air draining onto asphalt pavement can present a significant explosion risk (16). In one instance, a large amount of liquid nitrogen condensed air onto fatty meat products, and an explosion resulted upon later mechanical grinding of the meat (25).

10.4 *Fractional Evaporating of Liquid Air*—Air that initially condenses and runs off a cold surface can yield a pool or puddle having about 50 mol % oxygen (23). The oxygen level of the pool increases as the pool evaporates and can approach pure oxygen levels in its final stage. The explosive risk of a puddle of liquid air on asphalt increases with time, just as it occurs with fractional evaporating mechanisms.

10.5 *Gage Swapping:*

10.5.1 Perhaps the most common type of oxygen fire occurs when gages that are not adequately cleaned are installed on oxygen systems. The worst of these situations appears to be when the gage installed was previously used on a system used with an oil or hydraulic fluid. A similar risk is present when gages are tested or recalibrated using a flammable oil that is not removed prior to returning the gage to service. These events have happened so often and have been demonstrated in the laboratory with such reliability that heat of compression is well established as the direct cause of these incidents. Often, the gage will explode and fragment on the first pressurization or an early pressurization after installation. If the system is not exposed to rapid pressurization initially, the oil may migrate from the gage and contaminate much of the system and thus put other parts of the system at risk from compression, particle impact, resonance, or other ignition mechanisms.

10.5.2 Any incident study should include an examination of gages for damage, for consistency with the kind of gage that should have been in use, and for possible oil contamination. Finding any of these suggests gage swapping.

10.5.3 Gages usually are used in a near-vertical position. Oils and particles do not tend to migrate upward and so do not migrate readily into gage elements. Therefore, any oil in the gage is likely to be due to gage swapping. Conversely, because gages are installed vertically, any pressurization cycling is likely to pump oil out of the gage and back into the system. Indeed, one mechanism that might prevent ignition of the oil in the first pressurization cycle is that the gage may be completely full of oil, thereby allowing only trivial contact with oxygen. As the gage undergoes pressure cycling, oil can be displaced, allowing room for oxygen that can result in a heat-of-compression event.

10.6 *Oxygen Substitution:*

10.6.1 A severe hazard may occur when oxygen is introduced into systems normally operated with other non-oxidant gases. In these instances, all four of the precaution levels described in Guide G 128 are likely to be absent: cleanliness, compatible lubricants, compatible polymers, and compatible metals. See Test Method G 124.

10.6.2 Oxygen introduced into a mechanic’s impact wrench is very likely to produce a potentially fatal explosion.

10.6.3 Oxygen introduced into air compressors or vacuum pumps may be exposed to incompatible lubricating oils, and friction and may lead to severe explosions.

10.7 *Oxygen Mixtures*—Oxygen (liquid or gas) that is introduced into flammable gases or liquids or flammable gases or liquids that are introduced into oxygen (liquid or gas) represent an extreme risk. These mixtures may be highly explosive and may cause fragmentation of high-pressure cylinders, despite the installation of a pressure relief valve or rupture disk. In events such as these, there may be a reaction of the oxygen with the flammable material that is so fast and so explosive that recovered components do not exhibit ignition or heat damage, having been thrown clear of the combustion site before even the rapid ignition event can occur.

10.8 *Oxygen Used for Cooling*—There have been several instances in which welders purged oxygen from their torches into their clothes to cool themselves. Ignition often produced deadly fires.

10.9 *Improper Repair and Lubrication:*

10.9.1 Oxygen equipment often is repaired by persons unfamiliar with the oxygen hazard. When equipment is difficult to operate or when there are rubbing parts, there is a common tendency among repair technicians and users alike to consider lubricating it. Further, some types of hardware are virtually identical in design to oxygen systems that typically use lubricants, but few lubricants available in the commercial marketplace are oxygen compatible. When someone fails to notice or is unaware of the “Use No Oils” practice with oxygen equipment, fires in oxygen often result. This possibility must be considered in the study of any incident. Also, the time period under consideration must be the component’s entire prior service life, while hydrocarbons introduced into an oxygen system may produce a fire on the very next use; in some circumstances they may not cause the fire for more than a decade. Consequently, the service and repair record of every affected component should be studied.

10.9.2 *Thread Sealants*—Repair of oxygen hardware often requires disassembly. Reassembly requires the use of fresh pipe-thread sealant materials (often called luting or dope). Because thread sealants also serve as lubricants, there is a tendency for repair persons to select a sealant for its convenience, and the typical oxygen-compatible sealants are not conveniently available. Therefore, repair persons often will substitute a sealant of greater flammability than was used originally. Even when PTFE tape is being used as a sealant, repair persons tend to apply additional grease or oil to ease assembly. People often view more as better, so sealant pastes and added greases often are applied in large amounts. This typically results in extrusion of a bead of sealant/lubricant ahead of the fitting into the oxygen system, which is a very undesirable practice. This bead of flammable paste may be at a dead end, where heat of compression is most able to produce ignition, or it may migrate to other vulnerable regions. In every incident, fittings should always be inspected for evidence of non-oxygen-compatible lubricants within the threads.

10.9.3 *Cylinder-Valve-Outlet Fittings*—There is a pervasive tendency to use lubricants and sealants (including hydrocarbon-based greases and PTFE tape) on cylinder-valve-

outlet (CGA, EIGA, or DIN, and so forth) fittings, despite efforts to discourage such use. These fittings are intended to rely on a metal-to-metal seal or on an installed O-ring. Lubricants and sealants applied here may migrate throughout a downstream system and are known to have caused incidents. Tape may also cause mechanical damage to the fitting. There is a similar tendency to apply PTFE tape or other sealants to other types of compression fittings (ferrules, flares, and so forth) that also are intended to rely upon metal-to-metal sealing.

10.10 *Porous Materials and LOX*—Some paving surfaces (asphalt, macadam, blacktop) can be explosive when in contact with LOX. The LOX spills or condensation of air onto road surfaces (and fractional evaporation) can lead to an explosive result if an ignition source is present. The ignition source can be as little as a wrench dropped onto the surface, creating mechanical impact. It can also be the force heavy objects exert on a surface yielding compression or friction. The minimum ignition energy and autogenous ignition temperature of these surfaces are among the lowest known (16).

10.11 *Quick-Opening Valves*—Any quick-opening valve introduces an element of risk in an oxygen system. Among quick-opening valves, ball valves are among the most convenient, least expensive, and, therefore, most likely to be involved in misuse. Ball valves used with large differential pressures (greater than several hundred pounds per square inch) may produce sufficient heat-of-compression temperatures and energies to ignite polymers or oils downstream. There have even been reports of ball valves themselves igniting upon being opened. Every incident should be examined to identify valves that may have been opened quickly at or upstream of the damage zone.

11. Analytical Techniques

11.1 There are numerous analytical methods that can help identify the causes of incidents in oxygen. A few are identified here and described in brief terms. This list is not complete.

11.2 *Mathematics*—Meaningful calculations often may be performed to estimate compression temperatures, pressure rise expectation during combustion, comparison of heat released to materials consumed, and other variables. Correlations are available to calculate the energy released by examining the extent of the damage from an explosion.

11.3 *SEM*—Scanning electron microscope testing can identify the presence of elements with atomic numbers greater than carbon that are present, surface features characteristic of fatigue failures, and many other pertinent factors.

11.4 *Solvent Extractions*—Solvent extraction can help identify whether there are flammable residues present either on the damaged surfaces or in other portions of the same system that were not exposed to fire, giving insight into whether contamination might have played a role. The residue removed can be further analyzed chemically to discern its possible origins.

11.4.1 Sometimes, the presence and amount of contamination in a system before an incident can be determined by solvent extracting regions of the system that were valved off (closed) at the time of the incident. If oil is found, it is a strong indicator of contamination.

11.4.2 The isolated section is flushed carefully with an aggressive solvent. Then the solvent is collected and dried. An

oily residue suggests contamination. The amount is an indicator of the degree of contamination, and one can calculate an approximate contamination per unit area based on the area flushed. It is relatively easy to identify many oils by subjecting the extracted oil to an IR (infrared) scan.

11.5 Fatigue Failure Chevrons—The edges of broken metals can be examined under a microscope to determine whether they failed due to cyclic stress exposure, which often produces a characteristic chevron appearance.

11.6 Metal Alloy Identification—There are instruments that can conveniently identify a metal alloy, allowing insight into whether an inappropriate metal may have been substituted for a more compatible metal. This analysis may be important when damage to a metal was greater than expected in an incident.

11.7 Polymer Identification—Polymers are difficult to identify conveniently. Most PTFE has a characteristic white appearance. The CTFE plastic and FKM (poly(hexafluoropropylene-co-vinylidene fluoride)) rubber have high density. Silicone often has a characteristic red color, but is not the only red elastomer. Unless deliberately color-coded, most rubbers are black. Therefore, most polymers are difficult to identify.

11.8 Black Light—Black light is a convenient method to indicate the presence of potentially incompatible surface films that are present. A positive result is a strong indication of an incompatible material being present. However, one often does not know whether the material is compatible. Further, a negative test typically is inconclusive because many incompatible contaminants (such as pure hydrocarbon oils) do not fluoresce.

12. Simulations

12.1 It is desirable to simulate (reproduce) an incident in the laboratory. A successful laboratory simulation of an oxygen fire incident can be a very convincing indicator that the incident is understood. One might seek to show that ignition is possible under the terms of any explanatory hypothesis. One might also seek to demonstrate the extent of damage, or any other features that were observed. However, conducting a meaningful simulation can be very difficult, especially simulating the ignition source. Sometimes, a component is operated for decades before an event occurs. One can attempt to accelerate the aging of a new component before testing (see Practice G 114), but accelerated aging is not necessarily comparable to real service. Sometimes a component is too complex or costly to subject to testing. Therefore, often only individual key features of an incident will be simulated. For example, even if one does not know how ignition occurred, one can introduce an ignition source and determine whether the resulting damage is consistent with that observed in real-world incidents.

12.2 Example—If heat of compression is suspected to be the cause of a gage failure, it is desirable to contaminate a similar gage with an oil similar to that suspected to have been present, and then to pressurize rapidly to the levels suspected to have been present in the incident. An incident with similar resulting damage is a strong indication that the direct cause of the incident may have been found.

12.3 Warning—Do not attempt any type of simulation until the proposed experiment has undergone a hazard review and all necessary precautions have been taken.

13. Report

13.1 The initial versions of this guide have not addressed a report structure nor in which cases a report is required. When a report is produced, those conducting the study should consider a description of the event and background data, a list of hypotheses and the arguments for or against each, and any conclusion(s) as to the direct cause. Additional material is at the discretion of the authors, however, if recommendations to prevent recurrence are formulated, based on the direct cause(s) as well as any identified root cause(s), it is desirable to list them in the report, also. In many cases, it is worthwhile to complete and report on a study while the facts are “fresh,” but diligence should not be compromised in the pursuit of haste. Due to the uncertainty in such studies, many incident-study reports state categorically that the results of the study are, at best, technical judgment and not necessarily a definitive explanation of the actual event.

14. Collegiality

14.1 Incidents in oxygen occur infrequently and are seldom described in the open literature. Most incidents appear to occur either very early or rather late in a system’s service life. This guide is an effort of ASTM Committee G-4 to describe techniques known to help understand the unique features of these events. It is also a listing of these events. In the spirit of collegiality, anyone who experiences or studies an oxygen incident using the techniques here or any others that show merit is encouraged to share the experience, new approaches, new interpretations, or new hypothesis and speculation with Committee G-4 for potential inclusion in this guide. Such submission may be in the form of letters, but the preferred method would be submission of a paper to any G-4 International Symposia on Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres or its less formal seminar series at each regular Committee meeting. For more information contact ASTM Committee G-4 Staff Manager, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, (610) 832-9726.

15. Keywords

15.1 accident; cause; fire; incident; investigation; oxygen

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