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One Potential Approach to an Introductory Standard on Oxidants Other than Oxygen[2]

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ABSTRACT: ASTM G-4 has addressed oxygen-enriched mixtures and intends to address other oxidants but has published little to date. One approach for branching out might relate oxygen to other oxidants with an abstract standard patterned after the oxygen abstract standard (G 128) employing similar content which overviews other oxidants of interest and relates design of systems for them to oxygen practice and dedicated standards similar to G-4's body of work as they become available. A rough "not-intended-for-use" and therefore potentially seriously flawed draft is presented that suggests one potential starting point for such a standard but would need evaluation, correction, validation and pursuit of a consensus as a minimum.

KEY WORDS: oxygen, oxidant, fluorine, nitrogen trifluoride, nitrous oxide, ozone.

ASTM Committee G4 on Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres has adopted a compelling series of standards in its topic area. In recent years, success in achieving its primary goal, the demands of standards maintenance, and a spate of issues has resulted in a reduced rate of production of new standards. However, additional standardization would be worthwhile, is possible, and may someday come to pass. One area in which plans have often been forecast but is yet to obtain is in the area of oxidants other than oxygen.

G-4 has often forecast effort in this area, and has reviewed some of the available experimentation, has an active Task Force at present, but has not forecast (at least to the Committee at large) the way such effort should integrate into its current body of work. The writer proposes coordination as is shown in Fig 1. This approach employs a standard "G XXX" that "introduces" other oxidants and compares similarities and differences that might encourage or discourage the use of oxygen safety practices as a starting point for safety with these other materials. It is positioned to support the G-4 Abstract Standard G 128, has extensive parallel structure to G 128, and is configured to be in turn supported by individual sub-abstract standards[3]. Sub-abstract standards would then complete the overview materials of G 128 that were not highlighted in the introduction standard for each nonoxygen oxidant and

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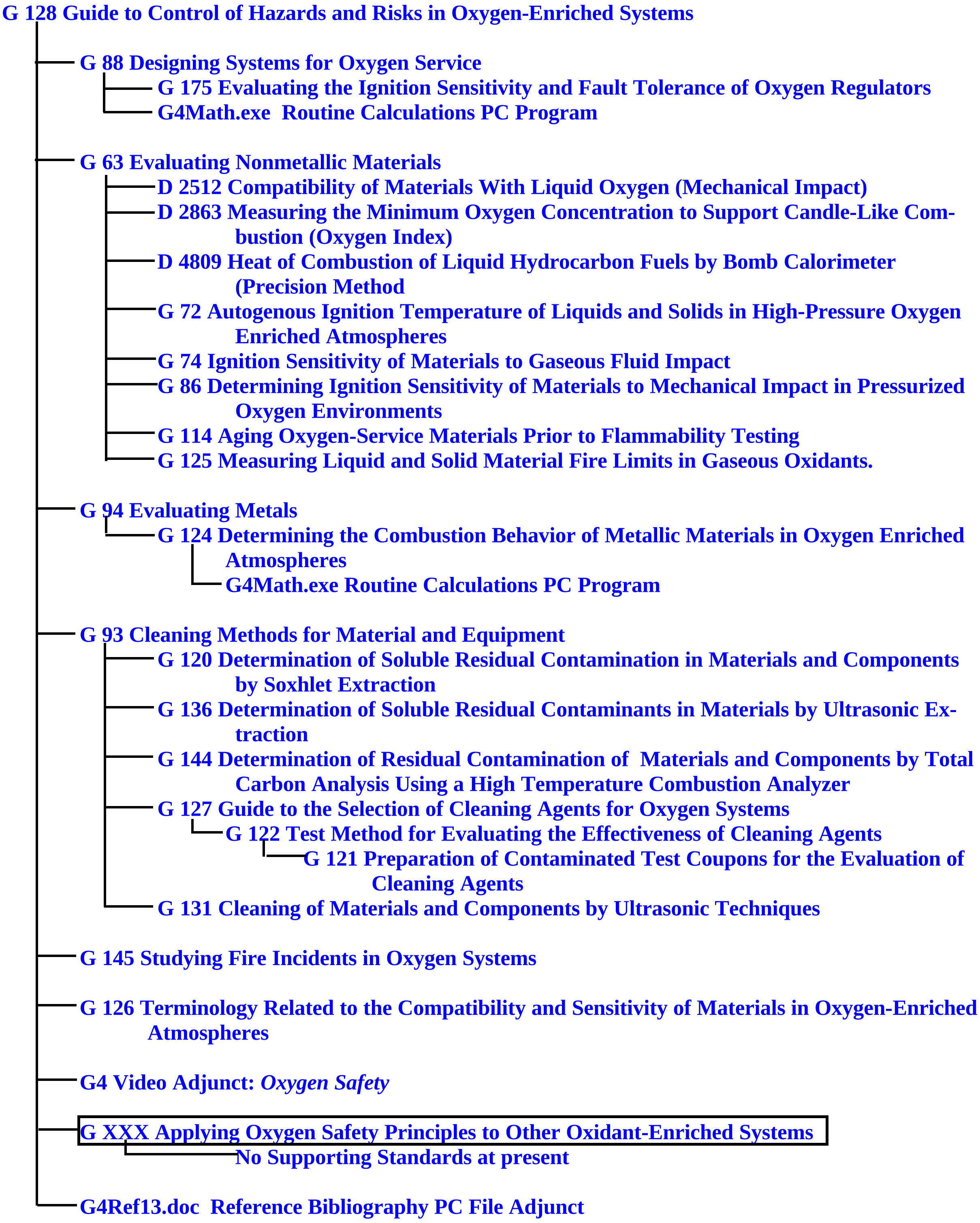
[2] This paper was self-published for the writers oxygen safety-opinion web site.
[3] The Chairman of G-4's Oxidants Other than Oxygen Task Force, Barry Newton, has indicated a particular desire to create a standard analogous to G 88 that would fit in this category.



- G 128 Guide to Control of Hazards and Risks in Oxygen-Enriched Systems
  - G 88 Designing Systems for Oxygen Service
    - G 175 Evaluating the Ignition Sensitivity and Fault Tolerance of Oxygen Regulators
    - G4Math.exe Routine Calculations PC Program
  - G 63 Evaluating Nonmetallic Materials
    - D 2512 Compatibility of Materials With Liquid Oxygen (Mechanical Impact)
    - D 2863 Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion (Oxygen Index)
    - D 4809 Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method
    - G 72 Autogenous Ignition Temperature of Liquids and Solids in High-Pressure Oxygen Enriched Atmospheres
    - G 74 Ignition Sensitivity of Materials to Gaseous Fluid Impact
    - G 86 Determining Ignition Sensitivity of Materials to Mechanical Impact in Pressurized Oxygen Environments
    - G 114 Aging Oxygen-Service Materials Prior to Flammability Testing
    - G 125 Measuring Liquid and Solid Material Fire Limits in Gaseous Oxidants.
  - G 94 Evaluating Metals
    - G 124 Determining the Combustion Behavior of Metallic Materials in Oxygen Enriched Atmospheres
      - G4Math.exe Routine Calculations PC Program
  - G 93 Cleaning Methods for Material and Equipment
    - G 120 Determination of Soluble Residual Contamination in Materials and Components by Soxhlet Extraction
    - G 136 Determination of Soluble Residual Contaminants in Materials by Ultrasonic Extraction
    - G 144 Determination of Residual Contamination of Materials and Components by Total Carbon Analysis Using a High Temperature Combustion Analyzer
    - G 127 Guide to the Selection of Cleaning Agents for Oxygen Systems
      - G 122 Test Method for Evaluating the Effectiveness of Cleaning Agents
        - G 121 Preparation of Contaminated Test Coupons for the Evaluation of Cleaning Agents
    - G 131 Cleaning of Materials and Components by Ultrasonic Techniques
  - G 145 Studying Fire Incidents in Oxygen Systems
  - G 126 Terminology Related to the Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres
  - G4 Video Adjunct: *Oxygen Safety*
  - G XXX Applying Oxygen Safety Principles to Other Oxidant-Enriched Systems
    - No Supporting Standards at present
  - G4Ref13.doc Reference Bibliography PC File Adjunct

Figure 1—*Role of G XXX*

would prescribe how to apply the body of oxygen safety practice to other oxidants where valid. In time, the sub-abstract standards would be supported by specific standards in those cases where the oxygen standards that support G 128 cannot be applied directly to other oxidant use through analogy.

This effort is intended to propose potential rough-draft wording and structure for the first link in this one possible overall scheme. The importance of the “rough-draft” appellation is worth stressing. This text has been produced using the text of G 128 as a model and skeleton that was adjusted using a stream of consciousness of the writer. This “stream” is based on experience and a recent cursory review of numerous pertinent related documents. But the review of available documentation has not been exhaustive. The writer is retired for nearly a decade but had extensive practical design experience and book learning on oxygen systems, substantial practical experience and book learning on fluorine and nitrous oxide systems, but only limited book learning and small amounts of practical experience on nitrogen trifluoride, and ozone. These limitations were not allowed to curtail efforts to generate text, even when there was a risk that the materials speculated upon might be seriously flawed, because even wrong text can flag where discussion is needed and provide not only the topic but the incentive to make it right. Much of the text must be considered speculative and in need of review, revision or validation by a wide audience of experts if this approach is taken or if any of this material is factored into an alternative. The goal here was to produce a starting point for discussion, not to produce a meticulously accurate product.

This draft covers four rather well-known oxidants and most, perhaps all, have been involved in incidents and have demonstrated the need for care in their use. The writer would have liked to include other instructive examples such as a weak oxidant to show how a molecule can be an oxidant in one case and a fuel (reductant) in another. Among molecules considered this way that might be worthwhile for future review are: carbon monoxide and nitric oxide. Although carbon monoxide is clearly a fuel in oxygen, it was not clear that it was a oxidant even in mixture with stoichiometric hydrogen. Although the writer is anecdotally aware of nitric oxide incidents and found resource material detailing it as an oxidant, he lacked the resource material and contacts to categorize it as either a strong or weak oxidant or to comment on the practical possibility of any explosive decomposition, ...or even to assess situational fuel behavior.

This draft is presented in ASTM format and proposes a context within the G-4 body of work as is shown in Fig 1 sans ASTM designation. This is ***not*** an ASTM effort and warrants the following strong warning:

PLEASE NOTE:

THIS DOCUMENT IS NOT A STANDARD; IT IS “BOILER PLATE LANGUAGE” REPRESENTING THE TECHNICAL OPINION AND SPECULATIONS OF ONE PERSON AND IS BEING PRESENTED ONLY TO ENCOURAGE AND ASSIST STANDARDS DEVELOPMENT WITHIN THE ASTM G-4 TECHNICAL COMMITTEES AND AS SUCH, IT HAS NOT RECEIVED ANY APPROVAL OR VALIDATION REQUIRED TO BECOME A STANDARD. IT SHALL NOT BE USED FOR SYSTEM DESIGN OR ANALYSIS EXCEPT FOR THE SOLICITATION OF COMMENTARY ON ITS TECHNICAL CONTENT. ASTM G-4 MAY CHOSE TO USE ALL, SOME OR NONE OF THIS MATERIAL, AND MAY NEED TO CORRECT ERRORS OR FLAWED RECOMMENDATIONS IF/WHEN IT PRODUCES A STANDARD IN THIS AREA

This proposal parallels the structure of G 128 in many ways and as such adopts and modifies and supplements some of the text present there in order to comment. It struggles to provide corresponding commentary on each element of G 128, and some of these efforts to comment may be seriously flawed. A Closure/Reconciliation is provided at the end. To avoid attribution issues, where wording is boilerplate and does not change, the corresponding sections from G 128 will be cited instead of replicated. Where changes are relatively small, the original portions will be shown in black text. New or modified proposals will be shown in blue text. The most speculative and potentially flawed material, as well as blank spaces that need to be filled in will appear in red.

The shear size of this draft may tend to be daunting. However, the reader should be aware of two things. The first thing is that this draft employs larger text and indenting for clarity that are not used with published ASTM standards. This is essentially four sequential revised copies of G 128. G 128-95 is fourteen pages long in the Committee's compilation. Those pages replicated and revised are about 24 pages each in this draft. Therefore the published length of this standard as it currently exists would be about half the number of pages of this draft.

The second thing is that although this, like G 128, is an "abstract" standard, and abstracts are thought of as terse overviews of larger works, one should recall that G 128 and each segment of this draft abstracts the entire body of G-4 standards and other known material from other sources. Therefore, even though G 128 is one of G-4's longer standards, and even though this draft represents four revised clones of G 128, it is indeed brief and terse with respect to the quantity of material it is "abstracting". However, there may be a desire within G-4 to attempt to condense all four of these segments into one by addressing all four oxidants together. The writer has considered that and even tried to do it but considered the result confusing. However, if G-4 were able to competently accomplish that feat it would be worthwhile. Alternatively, G-4 might consider splitting it into four separate sub-abstract standards, or even forgoing the use of the abstract-standard function for these other oxidants. Regardless of the ultimate course of action, seeing this draft should help facilitate that decision.

Designation G XXX

Standard Guide for
Applying Oxygen Safety Principles to Other Oxidant Systems

This standard is issued under the fixed designation G XXX; 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 ($^{\varepsilon}$) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide is analogous to the ASTM Committee G4 abstract standard *G 128 Control of Hazards and Risk in Oxygen Enriched Systems* that it supports. Whereas, G 128 is the starting point for those asking "Are there safety problems associated with my use of oxygen?", this guide tackles the question "Are there any safety problems associated with my use of oxidants other than oxygen?" Most oxidants present similar hazards to those of oxygen but in varying degrees greater or lesser, and in a few cases there are additional hazards beyond those of oxygen. As with oxygen, this is an introduction to the unique concerns that must be addressed in the handling of these materials. The principal hazard is again the prospect of ignition with resultant fire, explosion or both. This hazard requires design considerations beyond those that apply to all systems such as adequate strength, corrosion resistance, fatigue resistance, and pressure safety relief.

Note 1- [ASTM Boilerplate Note 1 from G 128]

1.2 This guide draws coarse comparisons between selected oxidants in listing causes of system fires and methods to prevent them. Sources of information about each oxidant are listed and often summarized. In many cases, the focus is on oxygen guides whenever they are reasonably applicable, but in time a series of specific guides may support this guide much as the body of oxygen practice guides support G 128.

1.3 [ASTM Boilerplate Paragraph 1.3 from G 128]

2. Referenced Documents

2.1 *ASTM Standards*

G 63 Guide for Evaluating Nonmetallic Materials for Oxygen Service[4]
G 88 Guide for Designing Systems for Oxygen Service[4]
G 93 Practice for Cleaning Methods for Material and Equipment Used in Oxygen-Enriched Environments[4]
G 94 Guide for Evaluating Metals for Oxygen Service[4]

2.2 *ASTM Adjuncts:*

Video: *Oxygen Safety*[5]
G-4 Reference Bibliography[6]
Technical and Professional Training course textbook: *Fire Hazards In Oxygen Systems*[6]

2.3 *ASTM CHETAH Program:*

CHETAH: Chemical Thermodynamic Data and Energy Release Computer Program[7]

2.4 *Compressed Gas Association (CGA) Standards*:

G-4.1 Cleaning Equipment for Oxygen Service[8]
G-4.4 Oxygen Pipeline Systems (EIGA DOC 13/02)[8]
G-4.4 Industrial Practices for Gaseous Oxygen Transmission and Distribution

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[4] *Annual Book of ASTM Standards*, Vol. 14.02.
[5] Available from ASTM Headquarters. Order ADJG0088..
[6] ASTM Textbook and G4Math Utility software, available from ASTM International Technical & Professional Training Course *Fire Hazards in Oxygen Systems*.
[7] Available from ASTM Customer Service, 1916 Race ST., Philadekphia PA, 19103, order 0505189015 (3.5-in. media) and 0505189115 (5.25-in. media)..
[8] Available from Compressed Gas Assocaition, 1725 Jefferson Davis Highway, Suite 1004, Arlington, VA, 22202.

Piping Systems (Superceded by CGA G-4.4/EIGA 13/02)[8]

European Industrial Gas Association (EIGA) Standards:

13/02/E Oxygen Pipeline Systems (CGA G-4.4)[9]

33/86/E Cleaning of Equipment for Oxygen Service[9]

92/03/E IGC Code of Practice—Nitrogen Trifluoride[9]

116/07/E IGC Code of Practice—Nitrous Oxide[9]

???/07/E IGC Code of Practice—Fluorine (Pending)[9]

2.6 *National Fire Prevention Association (NFPA) Standards:*

50 Bulk Oxygen Systems at Consumer Sites[10]

51 Oxygen-Fuel Gas Systems for Welding, Cutting and Allied Processes[10]

53 Fire Hazards in Oxygen-Enriched Atmospheres[10]

99 Health Care Facilities[10]

2.7 *Praxair Documents:*

GS-38 Cleaning[11]

L-5110N Guidelines for Design and Installation of Industrial Gaseous Oxygen Distribution Piping Systems[11]

2.8 *Military Specifications*:

MIL-G-27617 Military Specification, Grease, Aircraft, Fuel and Oil Resistant[12]

MIL-G-47219 (MI) Military Specification Grease, Lubricating, Halogenated[12]

DOD-L-24574 (SH) Military Specification, Lubricating Fluid for Low and High Pressure Oxidizing Gas Systems[12]

2.9 *NASA Documents:*

KSC 79K22280 Specification for 1,000-GPM LO_2 Pump Bearings[13]

3. Terminology

3.1 *Definitions*—See Guides G 63, G 94, and G128 for the terms listed in this section.

3.1.1-3.16 [ASTM Boilerplate Paragraphs 333.11-3.16 from G 128-95]

3.2 *Description of Terms Specific to This Standard:*

3.2.1-3.2.3.1 [ASTM Boilerplate Paragraphs 3.2.1-3.2.3.1 from G 128-95]

3.2.4 *oxidant, n*—a chemical that experiences the gain of one or more electrons during a reaction.

[9] Available from European Industrial Gas Association, Publication de la Soudure Autogene, 32 Boulevard de la Chapelle, 75880 Paris Cedex 18, France..

[10] Available from the National Fire Protection Association, 1 Batterymarch Park, Box 9101, Quincy, MA 02269-9101.

[11] Available from Praxair., Linde Division Communications Dept., P.O. Box 44, Tonawanda, NY 14151-0044.

[12] Available from Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS.

[13] Available from NASA, Engineering Documentation Center, John F. Kennedy Space Center, FL 32899.

3.2.5 *fuel, n*—a chemical that experiences the loss of one or more electrons during a reaction.

4. Significance and Use

4.1 *Purpose of Guide XXX*--[ASTM Boilerplate Paragraph 4.1 from G 88-05].

4.2 *Role of Guide XXX*-- ASTM G04's abstract standard is Guide G 128, and it introduces the overall subject of oxygen compatibility and the body of related work and related resources including standards, adjuncts such as research reports and a video G04 has developed and adopted for use in coping with oxygen hazards. The interrelationships among the standards are shown in Figure 1. Guide G 128 is supported by a series of standards that cover (1) the selections of materials (both metals and nonmetals) which are supported by a series of standards for testing materials of interest and for preparing materials for test; (2) the cleaning for of oxygen hardware which is supported by a series of standards on cleaning procedures, cleanliness testing methods and cleaning agent selection and evaluation; (3) the study of fire incidents in oxygen systems; (4) a computer algorithm, (5) related terminology, and (6) Guide XXX. G XXX is similar in intent and structure to G 128 and deals with the similarities and differences between oxygen and other selected oxidants, details about the other oxidants and the coarse details of relating oxygen system safety by comparing and contrasting them to systems for these other oxidants including existing oxygen practices that might be applicable without extensive modification. In time it is expected that more detailed standards to specific oxidants structured similarly to those that support G 128 will be developed and they will support G XXX and in turn, when needed, will be supported by selected detailed standards similar to others which support G 128.

4.3 *Use of Guide XXX*--Guide G XXX is used to become familiar with the gross features of nonoxgen oxidants that are known to pose potential safety hazards. G XXX seeks to identify which hazards are of greater and which are of lesser importance. And it especially seeks to identify which hazards are characteristically different or are aggravated to differing degree by other properties of individual oxidants. In time the number of non-oxygen oxidants covered may increase beyond the series that are initially overviewed.

6. Key Oxidants

6.1 This version of this guide compares oxygen to the selected oxidants: fluorine, nitrogen trifluoride, nitrous oxide, and ozone. This series has been chosen based upon the commercial impact of the oxidants, the scale of the hazard they reflect and in their ability to exhibit an educational range of severity. Future revision may add other oxidants to the text based on any of these factors.

7. Key Hazards

7.1 The hazards of oxygen of interest here resulted from its ability to react with other materials to produce fire and/or explosion. System materials of construction and contaminants can all react. Ignition results from heat of compression, mechanical or particle impact, friction, acoustic resonance, thermal sources, arcs, sparks and perhaps from other less well established mechanisms such as flow friction.

7.2 Oxidants other than oxygen often exhibit all of the hazards exhibited by oxygen but often to greater or lesser extent and in addition they can be endothermic molecules which may exhibit explosive reaction or decompositions even in the absence of a second material or contamination.

8. Noteworthy Incidents

8.1 Incidents—Incidents are the most significant driving factor in the development of oxidant compatibility practices. Incidents provide the justification and urgency in identifying hazards. Incidents involving oxidants have ranged from minor inconveniences to some of the most serious and costly events that have been experienced in industry. Many have also caused a significant number of fatalities. Incidents are seldom publicized widely and so this list is not comprehensive.

8.1.1 Supply vessel fires. Supply vessel fires have occurred for oxygen, fluorine, and nitrous oxide. Vessel explosions have been particularly serious when oxygen became contaminated with fuel gasses. Nitrous oxide vessel explosions have been particularly serious even in the absence of contamination. Fluorine vessel fires have been less explosive and less destructive than for oxygen and nitrous oxide (perhaps due in part to its lower pressures) but there have been toxicity issues. No supply vessel fires are known of for nitrogen trifluoride. Ozone is not typically sold or stored as a bulk gas but, owing to relatively short half life for its decay, is usually produced at the point of use.

8.1.2 Hardware. Hardware fires have occurred in oxygen, fluorine, and nitrogen trifluoride systems. Hardware fires have been few if any in nitrous oxide and ozone services to date. Fluorine fires have differed from many oxygen fires in that the lower pressure does not produce as powerful a flame jet and in many cases of valve fires, the fire often occurs in the valve being operated as much as down stream.

8.1.3 Explosions. Explosions have occurred when oxygen came in contact with large amounts of contamination or when it was in contact with very reactive metals such as aluminum. Liquid nitrous oxide and liquid ozone decomposition explosions have occurred in the absence of a fuel.

8.1.4 Environmental Fires. Oxygen has often been involved in environmental fires when leakage occurred. Nitrous oxide produced several in-door fires when leakage into storage rooms (typically closets) occurred. In many cases fluorine and nitrogen trifluoride have been shielded (in gas cabinets or other containers) in a way that prevents environmental exposure.

9. Fluorine (F_2)

9.1 *Overview*—Fluorine is often cited as the strongest oxidant. Table 1 lists the heats of combustion or formation of several materials in the series of oxidants of interest here. Fluorine is so aggressive that it reacts with many materials even at room temperature. Room-temperature reaction may be far too fast to call normal corrosion, yet too slow to

TABLE 1—Example Heats of Combustion

call normal combustion. Fluorine supports combustion and explosion, causes metals and many other materials to corrode (slow oxidation similar to rusting), and reacts with most chemicals. It can react violently with water and most normally used fire-extinguishing agents. There are even compounds of fluorine with the noble gas argon reported. It is a diatomic molecule slightly heavier than oxygen with similar specific heat (ratio of specific heats of 1.364). It is similarly and slightly less prone to compression heating and expansion cooling than is oxygen (ratio of specific heats of 1.397). Pure fluorine gas is reported as colorless by some (**1**)[14] and pale yellow by others (**2**), and has a pungent burning smell. Liquid fluorine is yellow (**2**) and boils at -188°C (-306°F) (**2**). Fluorine has a melting point of –219.62°C (-363.32°F) (**2**). Upon release into air, fluorine will tend to form hydrofluoric acid with humidity in the air, a weak but highly corrosive acid that attacks most materials and will etch glass.

9.1.1 *Commercial Uses of Fluorine:*

9.1.1.1

9.1.2 *Chemical Processes:*

9.1.2.1

9.2 *Production and Distribution*—Fluorine cannot be reacted with other chemicals as a practical production method, but there are exotic reactions reported that release fluorine gas. Today, it is exclusively produced commercially by electrolysis of hydrogen fluoride acid. Through the years, a large fraction of the produced fluorine has not been marketed commercially. In several important major applications, the fluorine was produced with proprietary or even secret technology at the site of its use to produce other compounds of fluorine (PCTFE, refrigeration fluids) as products, and fluorine has always been used to

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[14] The boldface numbers in parenthesis refer to the list of references at the end of this standard.

react uranium into a gaseous state for the diffusion separation of fissile isotopes for use in atomic energy and atomic weapons. As a result, a major fraction of the experience and expertise in the production and handling of fluorine is not common knowledge. However there is a commercial industry that has marketed fluorine in lower pressure gas cylinders (to 400 psig) and fluorine-gas mixtures (10-15 % F_2 in nitrogen or argon at up to 2400? psig in gas cylinders and tube trailers).

9.3 *Hazards and Risks*

9.3.1 Unlike oxygen, the hazards of fluorine are obvious. It is toxic, and corrosive and quickly exhibits it fire tendencies to the unwary. The odor and irritation experienced on contact with the gas serve as a strong warning.

9.3.2 Fluorine delivers on its warning. It attacks most materials and makes them easy to ignite, and produces an intense combustion.

9.3.3 Like oxygen, fluorine is considered to be nonflammable (which means that when it reacts it gains rather than loses an electron).

Note 2: The property of "flammability" can be rather arbitrarily defined by whether a material gains or loses an electron(s) in a chemical reaction, and not whether it will react and participate and even cause a fire. Fuels (chemical reductants) are considered to burn (to lose an electron) and be "flammable", while oxidants (which gain the electron) are considered to be "nonflammable". However, the oxidant's contribution to the production of fire and heat is comparable to that of the fuel. If there is no fuel, there is no fire. If there is no oxidant, there is no fire. A material may gain one or more electrons and, therefore, be an oxidant under this definition when it is reacted with one material (for example, a hydrocarbon) and lose an electron and therefore be a fuel when reacted with another material (for example, oxygen). This can be especially misleading because some materials considered nonflammable in air, can produce reactions that evolve heat and light and explosion, but because they neither gain nor lose an electron are neither considered to be "flammable' nor "nonflammable" and some are called "unstable". Their hazard can be just as great or even greater than would present in ordinary combustion.

9.3.4 The ability of a fluorine-enriched atmosphere to support and enhance combustion after ignition occurs is its fire hazard. The risk to people and property that accompanies this hazard is variable. Sometimes the human risk is grave; sometimes the economic risk is severe. In these instances, the need to prevent combustion is strong. Occasionally, the risk is small enough that it can be accepted—and other tactics may be used to minimize the risk. The overall concept of hazard and risk have been lumped into the term "oxidant compatibility".

9.3.4.1 The ASTM Committee G-4 first codified its interpretation of the concept of "Oxygen Compatibility" in its Standards Technology Training (now Technical and Professional Training) course textbook *Fire Hazards in Oxygen Systems*. By analogy, the concept extends to oxidants, like fluorine, as follows:

> "The ability of a substance to coexist with both oxidant and a potential sources(s) of ignition within the acceptable risk parameter of the user [at an expected pressure and temperature]."

9.3.4.2 In this definition, a system is oxidant compatible if it cannot or is unlikely to burn, if the occurrence of fires is adequately infrequent, or even if potential fires can be isolated and their effects can be tolerated

9.3.4. Other organizations have a similar respect for the hazards of oxidants in general and fluorine in particular. Oxygen is the most widely used oxidant and is thoroughly overviewed in ASTM G 128, and much of the material there is repeated here for comparison and contrast. Fluorine is much less extensively addressed, but there is significant material published by the European Industrial Gases Association (EIGA) in its Coed of Practice ???/07/E, ASTM Committee G4 (**3**), the National Institute for Standard and Technology (NIST) (**4**), various vendor Material Safety Data Sheets (MSDS) (**1**), encyclopedia (**2**), and in assorted technical papers (**5-31**). In many of the latter papers, corrosion is addressed more so than fire related properties, and not every paper was examined in preparing this document.

9.4 *Sources of Information*

9.4.1 Even though fluorine is more oxidizing than oxygen, the much smaller market for it and the great care taken with it due to its toxicity and corrosivity results in a low number of incidents (though at a system-for-system rate higher than for oxygen). For these same reasons the body of standards and publications that are available that deal with the fire hazard are all small in number. This section will overview what is available, but to a large extent the standards that come to be published to support this abstract standard may well prove to be the first public documents of their kind.

9.4.2 Designing equipment for use with fluorine-enriched gases relies to a much greater extent than for oxygen on the experience base of what has worked in the past. All of the hazard mechanisms that apply to oxygen also apply to fluorine but correlating the practices is still a challenge. Still, whereas book-learning is highly worthwhile and practical in coping with the oxygen hazard, hands-on experience is relatively much more important and possibly even vital in coping with the fluorine hazard. And this is unlikely to change even when the quantity of book-learning resources increases.

9.4.3 This standard is the first in the ASTM system to overview the fluorine hazard. But there are experimental data available in a limited number of technical papers cited here, many of which were under government contracts and are listed along with the vastly larger body of oxygen papers in the ASTM Committee G-4 Reference Bibliography.

9.4.4 Since most fluorine is produced by its principal users who maintain in-house expertise, for years there has been only a small number commercial sources of fluorine known and their MSDSs are available, and two were consulted in preparing this standard (**1**).

9.5 *Causes of Fires in Fluorine*

9.5.1 Although published documents and accident investigations for fluorine incidents are scant (nearly nonexistent), anecdotally such events have happened. Virtually every fire mechanism known to exist for oxygen applies also to fluorine in theory, and there are some additional mechanisms that are known to apply for fluorine that do not affect oxygen. The mechanisms cited for oxygen in the current G 128 and G 88 are also cited here along with others and elaborated upon. The order cited is slightly different than those used in G 88-05 and G 128-95.

9.5.2 Kindling Chain. Ignition often starts with a small generation of heat, that grows and amplifies itself and shifts from one behavior to another and another, involving other materials and mechanisms, until it is in a runaway condition— a self-sustaining fire. The material that is most flammable that initially responds to the first heating in this sequence of events or “chain” is the “tinder” or “kindling’. Numerous mechanisms, specifically ignition mechanisms, can provide for the first small (and some times not so small) generation of heat.

9.5.3 Ignition Mechanisms. Fires in fluorine require an initial source of energy (sometime self produced) as is also the case with fires in oxygen. Incident histories are not adequately documented or numerous to reliably rank ignition causes for the many potential ignition mechanisms.

9.5.3.1 Autogenous Ignition (Autoignition). Ignition temperatures have been measured for several metals in fluorine (**16**). Curiously the most time honored metal (Alloy 400) for safe use in fluorine exhibited one of the lowest results. However, no data are known for ignition temperatures of polymers in fluorine. Some papers refer to this type of ignition that occurs when a material is heated in oxidant to be “thermal ignition”, but that is not the most common usage of the term.

9.5.3.2 Thermal (Spontaneous) Ignition. Thermal ignition is commonly taken to be when a material reacting at a low rate is capable of heating itself to the autogenous ignition point of 9.5.3.1. In oxygen the most commonly cited cases of thermal ignition are the spontaneous fires that occur (1) when linseed oil soaked rags are piled up, and (2) when machinery such as compressors are run in on nitrogen or other nonreactive gas producing wear-dust debris and then converted to oxygen service. In each case, there is a high surface-area-to-volume insulating situation that allows low level reactions to self-heat and produce a kindling chain. Similar effect obtains in much more reactive fluorine, however, even in this case laboratory data are few and anecdotal data indicate that whereas metal-fines piles may react and heat to the melting or sintering point, outright fires and explosions in fluorine are not always a certainty. However, where carbon-fines are being fluorinated, sudden violent explosions can be common. In these cases, the difference is likely exacerbated by the fact that for many metals, the reaction products in the pile are inert solid fluorides of low vapor pressure, while for carbon the reaction products are gaseous (for example, carbon tetrafluoride) of high vapor pressure. The volatility of the reaction products in fluorine is a key factor in the hazard of fluorine in comparison to other oxidants.

9.5.3.3 Particle Impact. Particles present or generated in fluorine systems carry the same risk of ignition as in oxygen systems. Upon impact (and perhaps due to spontaneous self-reaction) these particles can ignite and serve as tinder in a kindling chain.

9.5.3.3.1 Fluorine systems commonly generate particles/powder during service. There are typically metal fluorides and as such are nonreactive in fluorine and pose little risk of self-ignition or of promoting ignition despite their high surface-area-to-volume. Their role as abrasives and debris may be otherwise detrimental.

9.5.3.4 Pneumatic Impact or Compression Heating. Because fluorine has greater heat capacities than oxygen, it does not heat as much in rapid (near-adiabatic) compression for comparable starting and finishing pressures (**4**), and because pure fluorine is shipped and used commercially at much lower pressures (400 versus 3000-4000 psig), peak temperatures during compression are much less, as is the maximum heat transfer that occurs to polymers (**4**). Fluorine mixtures that are sold (at 10-30% in nitrogen or argon and pressures of at least 2400 psig) are capable of peak compression temperatures and heat transfers to polymers approaching those of oxygen.

9.5.3.4.1 Adiabatic compression processes for fluorine in relation to other gases is reviewed in a recent tutorial (**32**), and NIST software (**4**) allows for estimation of peak adiabatic (isentropic) compression temperatures and heat transfers of numerous real (as opposed to ideal) gases including fluorine.

9.5.3.5 Mechanical Impact. There are few experimental data or anecdotal experience to assess mechanical impact in either pure or dilute fluorine service. Because impact heats, abrades, scrapes, and otherwise upsets metals, all processes more likely to initiate reactions than for oxygen, mechanical impact should be a more serious risk in fluorine than in oxygen.

9.5.3.6 Friction and Galling. Friction and galling should both be important mechanisms in a theoretical regard. Both should yield particles of metal and expose fresh surface area that would begin to react with fluorine and immediately result in the transfer of heat. Furthermore, among incidents known in fluorine there is a greater tendency for the fire to affect the valve being operated more so than for oxygen which more often affects the system farther downstream. However, there is still a random nature operating in that anecdotal experimentation has shown that substantial friction, fresh metal exposure and heating can all also occur together without *necessarily* producing ignition and fire.

9.5.3.6 Owing to the large amount of scrupulously clean nickel alloy and stainless steel alloy that is used with fluorine, it is not uncommon for galling to occur. Valves have often locked up on their first operation. This may be a cause of some fires in fluorine service, however, lab testing that has ruptured and rubbed these metal in high pressure fluorine does not confirm this possibility to date.

9.5.3.7 Resonance. Resonance tends to produce the most intense heating at high flows, something that only occurs in well designed fluorine systems during failures. However, resonance temperatures have been magnified by the presence of particles which are common occurrences in older fluorine systems.

9.5.3.8 Static Electric Discharge. There are no static electricity measurements known in the literature for fluorine flows. However, in some oxygen systems static electricity has been greatest in insulating systems (polymer-lined hoses) rather than in conductive systems. In most of the severe fluorine service systems, polymers are nearly totally avoided. However, here again, particles can magnify the formation of charge separation and older fluorine systems tend to have numerous metal fluoride fines present.

9.5.3.9 Electric Arc. Electric arcing is a highly effective method of igniting materials in oxygen and has when welding is attempted on pressurized oxygen systems. It should be similarly hazardous on fluorine systems.

9.5.3.10 Flow Friction. Flow friction is a speculative mechanism used to explain incidents that resist all other forms of explanation. It is analyzed as waves of motion/oscillation that occur during gas flow over polymers that produce internal friction processes that might heat polymers to the ignition point (**33)**. Lab experiments to date to demonstrate it in oxygen systems have not been successful. They have produced heating but not ignition. However, any tendency for polymers to heat under cyclic stress and strain would tend to be more significant in fluorine systems where reaction rates are much more affected by temperature.

9.5.3.10.1 Although “flow friction” should be more aggressive in fluorine than in oxygen, far fewer polymers are used in fluorine systems, especially in high velocity regions such as valve seats, and the pressures are much lower. Therefore it is difficult to say whether flow friction is a more valid or greater concern. However, anecdotal experience in fluorine systems would seem to indicate a greater frequency of gasket and packing fires (two areas where polymers find use in fluorine) than for oxygen systems.

9.5.3.11 Fresh Metal Exposure. Many believe that every surface that is exposed to fluorine will develop a very thin coating of fluoride that is protective (see 9.12). Whenever this protective “passive” layer is violated a new reaction should begin with associated heating. However, as for fresh-metal exposure tests of materials in oxygen, there are few if any demonstrated cases of fresh metal exposure ignition in fluorine except for cases of accumulated high surface-area-to-volume fines which tend to be fairly adiabatic, especially near the pile centers. Fresh metal exposure in fluorine is by no means a certain ignition source. Abrupt exposure of heated metal (heated with internal friction during twisting) resulting in torsional rupture is possible and has been demonstrated in cylinder pressure fluorine without ignition.

9.5.3.12 Decomposition. Neither literature nor the anecdotal record cite any common endothermic molecules for fluorine and its trace compounds formed in systems. There are no citations of molecules with other elements that correspond to the endothermic molecule nitrous oxide (reviewed elsewhere in this standard) and none that would correspond to the endothermic molecule ozone, (also reviewed elsewhere in this standard).

9.5.3.13 Other Ignition Mechanisms. Other mechanisms can not be ruled out, but none are speculated upon in the available literature.

9.6 **Hazards**

9.6.1 *Recognized hazards.* Fluorine is extremely dangerous because of it toxicity and corrosion hazards but they will not be covered here except as they affect the fire hazard. Because of the great reactivity of fluorine in comparison to oxygen, every fire hazard known to oxygen use (with only rare exception) is a similar or greater hazard to fluorine use, although individual features of these hazards may not always be more severe than for oxygen. Further, even potential hazards of oxygen use that have *not* been observed may be realized in corresponding fluorine systems. These include (1) fluorine concentration and associated diluents, (2) pressure, (3) temperature, (4) phase, (5) velocity. (6) time and age, (7) mechanical failure.

9.6.1.1 *Fluorine Concentration and Associated Diluents.* Higher fluorine concentrations increase the hazards of ignition and fire intensity because more fluorine is present to mix with the fuel. Diluents are as important as they are for oxygen systems. Nonreactive diluents that have large molecular size are more effective at attenuating flammability. In oxygen systems even tenths of a percent of diluents can be important, but whether a similar extreme effect for trace diluents is operative in fluorine is not certain but is likely. There are a number of volatile metal fluorides that may form and inhibit the rate of relative combustion in fluorine relative to oxygen for some materials but can also therefore magnify the potential pressures produced.

9.6.1.2 *Pressure.* Higher pressures also increase the hazards of ignition and fire intensity. Pressure increases the density of the gas, with the same effect as increasing the concentration: more fluorine is available to the fuel, so materials ignite easier and burn faster. Pressure also increases the gas velocity at restrictions such as valves, regulators, and intersections—which increases friction, particle impact, and compression heating.

9.6.1.3 *Temperature.* Unlike oxygen, practical use temperatures have a significant affect on the reactivity of fluorine, and therefore its ignition tendencies and potentially even the intensity of combustion and resulting damage. Elevated temperatures are even more risky than for oxygen and more likely to induce autogenous or thermal (self-induced temperature) ignition—and they may enable combustion to occur in a system that is not otherwise flammable, even if it is made of some of the most normally fire-resistant metals and polymers in oxygen. As for oxygen, any high temperature can accelerate aging of polymers and thereby reduce their compatibility with fluorine.

9.6.1.4 *Phase.* Fluorine liquid may be used in distillation processes to purify the products, but fluorine is not stored, used nor sold as a liquid. The base of liquid phase experience is small. Its behavior and risks as a liquid should mirror or exceed the same behaviors of liquid oxygen.

9.6.1.5 *Velocity*. Increased fluorine velocities in flowing systems lead to higher particle velocities, which increase the likelihood of ignition by particle impact. Particles in fluorine systems tend be far more numerous than in oxygen systems, but they tend to be overwhelmingly of lower-risk metal fluorides and very seldom of higher risk reactive materials and contaminants. “Flow friction” which is speculated but unproven as an ignition mechanism in oxygen should be equally or more viable in fluorine systems owing to the much lower temperatures required for ignition. The consequences on flow friction of the heavier fluorine molecule in increasing flow momentum but perhaps also shifting resonant frequencies is not known but anecdotal incident experience suggests fluorine systems experience a much greater ratio of fires in operated valves than downstream relative to oxygen experience.

9.6.1.6 *Time*. Time and age are important hazards. Even more so than for oxygen, fires and explosions in fluorine-enriched atmospheres sometime occur the first time fluorine is introduced into a system and often appear to be spontaneous without an easily identifiable “trigger”. However, unlike oxygen, the rate of system fires does not seem to increase similarly with age, perhaps owing to the tendency of fluorine to react contaminants that may be introduced in service thus preserving the system cleanliness. However, other age-related mechanisms (embrittlement, porosity, abrasion, rubs, and mechanical failure) are still operative and so aged fluorine systems are not immune from fire.

9.6.1.7 *Mechanical Failure*. The same mechanical failures that jeopardize oxygen systems also threaten fluorine systems. These include impact of broken parts, rubbing, particle generation, failed seals, etc. Friction and galling are a particular risk in fluorine, both in tendency to occur and consequence when they do occur. Many of these also violate the “passivation” (see 9.12) of the fluorine system and are therefore suspected to be of even greater risk in fluorine than they are in oxygen. Indeed, in oxygen service, the components (namely oxygen compressors and pumps) most at risk of failure and therefore most likely to experience fires are often placed behind barriers, because their reliability can not be made sufficiently high to address the risk to life and injury otherwise. In many (especially pure) fluorine systems, much of the more mundane hardware also can not be made sufficiently reliable to cope with the risk of fire and so many valves and other components are placed behind barriers and are remotely operated.

9.7 *Fire Prevention*

9.7.1 G 128 patterns the approaches to preventing fires in oxygen to those used for preventing fires in air. This standard will pattern the approach for fluorine fire to those for oxygen fires. In each there is a gradation of steps taken with greater numbers and more extensive use depending on the severity of the situation.

9.7.2 In oxygen systems there is always an oxidant (oxygen) present, often there is fuel present (in the materials of the system itself), and sometimes there are ignition mechanisms present (heat of compression, particle impact, etc). So in oxygen there is effort to pick the best materials possible and to minimize the number and intensity of ignition sources. In fluorine there is again oxidant present and there is a smaller number of materials that will resist fire, and more sources of ignition present.

9.7.3 As for oxygen, depending on the fluorine or fluorine mixture system, there are progressively stringent measures applied in the order cleaning/passivation, compatible lubricants, compatible polymers and other nonmetals, and compatible metals. However, unlike oxygen systems in which some of these steps may be unnecessary, in fluorine and fluorine-mixture systems all of these steps are usually required.

9.7.4 In many fluorine systems, not only will all four of the previous tactics be applied but there will often be additional protective measures taken in terms of barriers, ventilation, and the like.

9.7.5 Recognizing, identifying and controlling potential sources of ignition and possible causes of fires in fluorine is not simple. Present knowledge does not enable us to identify all possible ignition sources. Hence few fluorine systems can enjoy a certainty that fires are not possible. There is a strong empirical influence in the approach to oxygen safety that is even greater for fluorine safety. To a large extent, one does what has been successful in the past, provided it has been successful often for long periods of time, and is based on sound principle. For this reason ASTM G-4 standards take a multi-pronged approach that attempts to align as many factors as possible toward reducing the likelihood of ignition and fire.

9.7.6 This approach is based on using the extensive body of information available on the ignition and flammability of materials and methods with demonstrated ability to reduce the number and severity of fires in oxygen with adjustments to it based on the known properties and behavior of fluorine. Guides G 63, G 88 and G 94 as well as Practice G 93, describe the many factors affecting oxygen and oxygen-enriched systems and describe how to reduce the hazards associated with these systems. These same guides are often taken as a starting point for fluorine and fluorine-enriched systems and are then expanded upon. Only rarely would any less stringent practices be followed.

9.7.8 ASTM G-4 and other resources correlate control of oxidant system hazards with special attention to (1) system design; (2) component selection; (3) operating procedures; (4) cleaning; (5) passivation; (6) compatible lubricants; (7) compatible polymers and other nonmetals; (8) compatible metals; and (9) isolation and shielding. Each of these approaches is discussed in more detail below.

9.8 *System Design*

9.8.1 Oxygen and especially fluorine system design should not be undertaken casually—these systems require careful and specialized design considerations. The first and most important rule is: Consult an expert! Guides G 63, G 88, Practice G 93 and Guides G 94 and G 128 define “Qualified technical personnel” and provide vital information for use by these experts. Indeed, in many companies, individuals are designated as specialists to acquire the expertise and assist others in oxidant system design.

9.8.2 System design for any oxidant should begin with the same mechanical principles as conventional air or gas system design and follow the same nationally recognized codes and standards—there are no special codes that mandate how to design oxidant systems.

Keep in mind that when portions of systems are barricaded, as is done often with fluorine components, in such a way that they do not travel in commence and are not used as ordinarily specified in codes, they may not fall under the legal mandates of the codes, and this may allow latitude and flexibility in coping with the fluorine hazard. The added hazards inherent in the use of oxidants should then be evaluated to modify conventional practices while still conforming to appropriate requirements. In general that leads to a more—not less—conservative design. Fluorine system designs can usually be approached as more careful modifications of similar oxygen system designs that (unless barricaded or isolated) also meet or exceed the compatibility measures that would be taken with oxygen.

9.8.3 The severity of system operating conditions is defined similarly to those for oxygen. Concentration, pressure, temperature, phase, and time are all crucial (however, except at the manufacturing and purification stage, the liquid phase is not typically encountered in today's commercial fluorine practices). As these factors increase, the risk increases, and the system design must be modified to a greater extent. Fluorine concentration and phase are established by the system function. But the others can be influenced by the system design. For example pressure can be reduced with a regulator as close to the gas source as possible to minimize the hazard (and most fluorine systems have a regulator right on the source cylinders, often shielded for the most severe services). Temperatures can be limited, for example by including protection from runaway heaters. The effects of time and age can be mitigated by designing for effective preventive maintenance.

9.8.3.1 Velocity is a hazard that is controlled primarily by overall system design. Line sizes should be selected to limit fluorine gas velocity. There are no adopted velocity criteria for fluorine systems but existing guides for oxygen systems may suggest an upper limit and may be adjusted downward when needed and when possible. Rules applied to oxygen systems as to abrupt line size changes, locations of intersections and risk of particle impingement and compression heating in certain geometries are all applicable to fluorine systems near polymers and perhaps elsewhere, as well. As for oxygen, one reduces velocity and upgrades the fire resistance of fluorine-system materials wherever needed to cope with velocity and particle hazards. However, more often with fluorine, it is not always possible to upgrade to a nonflammable metal.

9.8.4 Additional considerations as reviewed in the remaining sections are integrated into the design of a fluorine system. Again in many cases, care beyond that normally accorded oxygen systems can be required. For example, the initial cleanliness of an oxygen system is established as the components are built and the system fabricated, and it is crucial to prevent contamination during the systems life. However, the reactivity of fluorine would act to “clean” low rates of organic chemicals introduction, but in the case of fluorine exposure of the system, even to moist air, can pose a hazard that would not obtain with most oxygen systems.

9.8.5 The only specific guidance on fluorine system design itself is found in the various vendor’s Material Safety Data Sheets and a pending EIGA Code of Practice on Fluorine. However, oxygen design materials such as Guide G 63, CGA G-4.4, EIGA 13/02/E, NFPA 50 and 51, and many others provide excellent guidelines for system design that can be considered by analogy in the design of fluorine systems, although these references are not handbooks. This includes material in the ASTM G-4 Committee Technical and Professional

Training Course *Controlling Fire Hazards in Oxygen Systems* which teaches the fundamentals of oxygen safety for oxygen process designers and equipment specifiers and includes a textbook.

9.8.5.1 Many references on oxygen hazards are cautious and explicit about the use of their data, and this caution is worthwhile to apply to other data and other oxidants such as fluorine. For example, Praxair Publication L-5110N warns:

> "This publication is not a design handbook and does not relieve the user from exercising competent engineering judgment or using qualified professional personnel who can tailor your design to your specific situation.
>
> "In situations where qualified people are not available locally to design the system, obtain professional assistance from a competent source. If the oxygen supplier can not offer assistance, he should be able to direct you to a consultant who can provide the necessary service. Remember that design of oxygen systems requires specialized knowledge. Liability problems associated with improperly designed systems can far outweigh the cost of professional services."

9.9 *Component Selection*

9.9.1 ASTM Committee G-4 standards do not recommend specific products. Indeed, they are disclaimed as specifications. Further, their nature is not such that products can be marketed under a blanket claim of meeting any of the four applicable oxygen standards (G 63, G 88, G 93, or G 94) and this applies even more so to fluorine systems as well. Clearly the thrust of these standards is to enable evaluation of system needs in the context of a particular application. As the application changes, such as exposure to higher pressure, a host of conditions change—or hazard thresholds are crossed—that may render previously accepted products unacceptable for further use. Therefore, although there may be a few products that are acceptable in any and all oxygen applications, one can not consider products to be "approved for oxygen or any other service" under the procedures of these standards without also specifying the conditions for which the approvals are intended.

9.9.2 Some products are marketed for fluorine service, but not every experienced designer agrees that every one of these products has adequate fluorine compatibility or even that a blanket approval is reasonable. Some companies do list materials that are approved across the board, but many others tie approval to specific applications and level of application hazard. It behooves the user to determine whether the properties of the particular products (whether or not they are marketed for fluorine service) actually meet the needs of the users application.

9.9.2.1 Performance tests conducted by hardware manufacturers generally do not simulate any specific application. Laboratory tests can not duplicate the endless variety of actual operating conditions; such tests only indicate a predicted result in a controlled laboratory setting and cannot assure the same result in a particular application or service.

9.9.2.2 Material qualification tests are also method specific and rarely afford blanket approval. The user should evaluate the material test results along with the test method to determine if they correspond to the way the material will be used in a specific design.

9.9.3 It is also important to note that most common industrial components—such as valves, fittings, filters, regulators, gages, and other instruments—are not designed for specific applications. Rather, they are versatile, general purpose products that can be used properly in many types of applications and systems. Hardware manufacturers in general have neither the experience nor expertise to select the most appropriate components for a specific use, such as a fluorine system. Only the fluorine system designer or user can have full knowledge of the entire system and each component's function, which must be considered when selecting the system components. Fluorine system designers and users both must be sensitive to product function, material compatibility, adequate ratings, and proper installation, operation, and maintenance.

9.9.4 Valve selection requires special attention by the system designer, because valves are one of the few mechanical items that are actuated routinely while the system is in use. The designer must determine the type of valve, its location, how it will be operated, and—often neglected— how it might be operated incorrectly.

9.9.4.1 Particular attention should be directed to valve pressure and temperature ratings, internal materials of construction, and how readily the valve can be cleaned and kept clean. Valves often are selected with higher ratings, greater wall thicknesses, and more fire resistant materials than the rest of the system because they are exposed to more severe service conditions. In some cases, oxygen valves of certain metals can be considered nonpropagating if they are sufficiently thick, but some test data suggest this approach may not be applicable to fluorine service (**3**).

9.9.5 As valves are opened and closed they almost always generate localized high velocities near the valve seat or immediately downstream. This creates a local increase in the hazard level at the valve location and often requires that special consideration be given to the selection of seat materials and potential impingement areas nearby.

9.9.5.1 Fluorine system valves also pose a more serious risk of personal injury, because many are opened and closed manually—so that at the very moment they are most susceptible to the conditions that can cause a fire, someone's hand is on them. Indeed, the fire-risk is so much greater with fluorine than with oxygen, despite the lower maximums of pressure in fluorine service, valve handles and sometime whole systems are commonly shielded and extended or remote operators used on severe service valves.

9.9.5.2 Oxygen Guides G 88, CGA G-4.4, EIGA 13/02/E and NFPA 51 unanimously emphasize that valves must be opened slowly. Opening speed is controlled by valve design, as well as by operating procedures. Ball, plug and butterfly valves are used in some low-pressure systems such as pipelines, because their straight-through design provides a lower pressure drop than a globe valve. However, ball and plug valves are quick-opening and create high velocity when opened, whereas needle valves are designed to open slowly (Fig. 3 of G 128). If a full-flow valve is used in a high pressure service, the piping system must be designed carefully to equalize the pressure across the valve before it is opened.

9.9.5.3 Even while closed, valves require extra consideration. Valves used in gas service often have seats or stem tips made of polymers that are exposed to the system fluid when the valve is closed. They can be subject to impingement from high velocity generated by another component upstream, and thus become a potential ignition point. For this reason, it is common in the more severe fluorine gas services to use metal-to-metal seated valves, even though the most severe fluorine services are at a fraction of the pressure used with severe oxygen services.

9.10. *System Operation*

9.10.1 Due to the greater hazard of fluorine, it is usually accorded much more care in both the system design and the cautions employed by system operators. Perhaps the most neglected aspect of controlling oxygen systems hazards involve system operation. Oxygen fires frequently are caused by systems whose safe operation depend so greatly on the operator's strict adherence to certain procedures that they can not tolerate simple human error. In these poorly designed systems, a single mistake—such as actuating one of a series of valves in the wrong sequence—can lead to a catastrophe. G 128 cites (in its sections 15.1.1 through 15.4) and reviews example events documented in the ASTM video adjunct entitled, *Oxygen Safety*, that illustrate several design errors that invited and then compounded operator errors, causing serious accidents in oxygen.

9.10.1.1 In both examples rapid compression led to ignition. In one an operator was supposed to open a ball valve, then slowly pressurize a downstream system with the valve on an adjacent cylinder, but instead left the ball valve closed until the cylinder valve was open, then shocked the downstream system. Other episodes with ball valves were similar. All of the events could have been prevented with more cautious system operation.

9.10.1.2 In fluorine systems the lower typical pressures and lesser adiabatic compression heating would have produced smaller temperature rises and reduced heat transfers, but due to the greater reactivity of fluorine and therefore lower autogenous ignition temperature and thermal ignition threshold, such ignition might still be possible. In addition other factors such as flow friction may demand specific operating practices.

9.10.2 Therefore, as noted in the *Oxygen Safety* video adjunct, thorough planning and careful monitoring of operating procedures and maintenance practices are important in oxidant fire prevention. However, safe operation should be engineered into the design of an oxygen system—by the selection and placement of components—and not rely solely on operator compliance with procedures to prevent oxygen fires. As noted in G 88 Section 7.19.4 "Avoid Overly Complicated Procedures" one must remember that complex and repetitive procedures are more prone to discrepancy than simple straightforward procedures. Since human error is difficult to prevent, in crucial systems, automation may be required to achieve reliable system operation.

9.11 *Cleaning.*

9.11.1 A fluorine system requires cleaning comparable to or greater than that of an oxygen system. Cleaning is the first measure required, even though it may be the last step accomplished in preparing a system for oxidant service. Any such system typically must be evaluated carefully for cleanliness, and most will be cleaned scrupulously. In fact, the extent of cleanliness used on a system exposed to only 10% fluorine (in nitrogen or argon) may be very similar to that applied to pure-fluorine, high pressure systems.

9.11.2 Organic particles and fine particles burn violently in concentrated oxidant and are often the beginning of the kindling chain that starts a fire. Hydrocarbon oil or grease contamination is particularly undesirable. In mild applications, inert particles may be removed less scrupulously. A mild fluorine exposure may not be subject to any other requirements, but its cleanliness should always be a concern.

9.11.2.1 The basis for determining the oxidant concentration and pressure at which more scrupulous cleaning is needed should be related to the flammability of the contaminants, lubricants, polymers, and metals. If the contaminants are unidentified, one must assume they may be flammable and therefore must be eliminated at even a small increase in oxidant concentration or pressure.

9.11.3 Cleaning methods used with oxygen systems are often applied to other oxidant systems including fluorine systems and should be evaluated and selected by analogy following the guidance contained in Practice G 93, CGA G-4.1, EIGA 33/86/E, and Praxair GS-39. Practice G 93 provides special guidance for cleaning components in its Section on Interferences.

9.11.3.1 *Disassembly:*

9.11.3.1.1 It is imperative that oxidant systems be cleaned as individual articles, preferably prior to assembly. Assembled systems must be disassembled for cleaning if construction permits. Flushing an assembled system can deposit and concentrate contaminants in stagnant areas.

9.11.3.1.2 Manufactured products (for example valves, regulators, and pumps) should preferably be cleaned by the manufacturer prior to final assembly and test. The purchaser should approve the cleaning procedure and packaging to ensure that they satisfy the system requirements.

9.11.3.1.3 Manufactured products that are cleaned by the purchaser must be disassembled for cleaning if the construction permits. The purchaser should follow the manufacturer's instructions for disassembly, inspection for damage, reassembly, and testing.

9.11.4 Practice G 93 contains additional information on cleaning methods, hindrances to effective cleaning, packaging, and inspection, including examples of specific applications.

9.12 *Passivation.*

9.12.1 When a new scrupulously cleaned fluorine system is pressed into service, it is still considered at serious risk, despite the compatibility of its materials of construction, unless a final passivation step is performed. In passivation, a dilute fluorine gas mixture with a nonreactive gas is purged into the system at low pressure and allowed to soak, after which subsequent mixtures at higher fluorine concentration and pressure are introduced until the system has been soaked at its maximum intended service concentration and pressure. Schedules for passivation are not published and are esoteric. Indeed, a common good practice with fluorine systems that have been depressurized and inactive for some times, is to 'bump" the pressure up in increments on first re-use, allowing the system to soak for some period (say fifteen minutes) between each bump, in order to reestablish the passivation and heal any areas that may have deteriorated at low pressure or on exposure to air.

9.12.2 Passivation is believed to accomplish two things, but its mechanism may be poorly understood. First, the aggressive fluorine reacts any trace remaining contamination in the system (hydrocarbon reacting largely to hydrofluoric acid and carbon tetrafluoride gas) and the surface then reacts to produce a very thin layer of metal fluorides that is inert and believed to be protective against fresh-metal exposure ignition. This is a time honored safety practice, however, its effects are extremely subtle, and anecdotal laboratory efforts to measure surface fluorides have found it difficult to actually measure significant differences between newly passivated and unpassivated surfaces, and anecdotal efforts to produce ignition of freshly broken metal specimens in commercial cylinder pressure, pure fluorine have not been successful. Nonetheless new systems that have *not* been passivated prior to use apparently do have a significantly greater risk of component fires.

9.12.3 Passivation should only be performed on scrupulously clean systems. Attempts to passivate systems that are no adequately clean will lead to corrosion from the additional acid that is produced and elevated production of particles that can be ignition aggravating hazards during gas or particle impact or resonant flows, and possibly during flow friction.

9.12.4 The passivation of systems should be preserved by maintaining the system in a dry sealed state. Moisture may dissolve some of the surface films produced and compromise their protection. Systems that are open to atmosphere for extended period or out of service may warrant re-passivation before return to service if there is any doubt as to the condition of the passivation, but as a minimum the slow bump-and-soak procedure described in Section 9.12.2 should be practiced on every restart. For this reason many fluorine systems that are shutdown or may be opened to atmosphere are often equipped to thoroughly purge with nitrogen and are often sealed with nitrogen pressure contained in them.

9.13 *Compatible Lubricants*

9.13.1 If cleanliness is the first special measure that is necessary, the next concern is with lubricants, for two reasons (*1*) the most common oils and greases are hydrocarbon, which are among the materials most necessary to remove from an oxidant system; and (*2*) they are fluids and pastes, which are more prone to migrate and collect than are solid materials.

9.13.2 Any lubricants reintroduced into a system cleaned for oxidant service should be selected to be fire resistant. In most instances, even with mild oxidant exposures at low pressures and at low oxidant concentrations (as low as 25% oxygen or 10% fluorine in nitrogen or argon), fire-resistant lubricants or other fluids are used.

9.13.2.1 Several halogenated oils and greases have been tested and used widely with success in oxygen service. Oxygen manufacturers can be consulted regarding appropriate lubricants for specific applications, Guide G 63 includes test data on many lubricants, thread compounds, seats and gaskets. Praxair L-5110N lists lubricants that manufacturer has used for low pressure systems. Specifications MIL-G-27617, MIL-G-47219 (MI), DOD-L-24575 (SH), and KSC 79K22280 may also be consulted for choosing analogous fluorine-compatible greases and lubricants.

Note 3: In oxygen service, material that includes halogens (specifically, fluorine and chlorine) in their chemical structure, tend to exhibit enhanced fire resistance. This is in part due to their lowered heats of formation and combustion, Table 1, but in the case of chlorine there is an acknowledged free radical scavenging action that yields a fire inhibiting effect greater than would be expected merely on the basis of reduced heat of formation. However, in fluorine systems the highly reactive fluorine can attack the bonds that chlorine forms and alter not only the compatibility but also the material properties of the underlying molecule. As a result, lubricants and polymers that contain chlorine may be altered in time and become undesirable for their intended purpose. In some cases materials based on CTFE may deteriorate like this and it is avoided by some in severe fluorine service.

9.13.3 Practice G 93, Section on Interferences, provides special guidance for lubrication of components.

9.13.3.1 *Lubricants*

9.13.3.1.1 Mechanical components are normally assembled with lubricants on seals, threads, and moving surfaces. The manufacturer should be consulted to determine the kind of lubricant originally used on the article to ensure that the cleaning solutions and methods selected are effective in removing the lubricant and will not damage the component. In some cases, fluorine systems omit the lubrication of certain components such as metal-to-metal valve seats. In these cases the tendency to gall and fret must be very carefully evaluated both to obtain a reasonable service life but also to avoid introducing ignition mechanisms..

9.13.3.1.2 When used, fluorine-compatible lubricants should be selected. In some cases lubricants can be evaluated as they would be for oxygen service using the methods of G 63 and treating pure high pressure fluorine with the same concern that would apply to pure high pressure oxygen, and treating the more dilute mixtures of fluorine as one would treat air. In time more specific guidance should be developed. The component manufacturer should also be consulted to ensure that the selected lubricant provides adequate lubrication for component performance. Oxidant compatible lubricants often have markedly different lubricating properties from conventional lubricants.

9.13.4 Scrupulous cleaning combined with the use of fire-resistant lubricants may be the only special precautions needed in moderate services. Until more precise recommendations are published, lubricants should be evaluated and selected following the guidance contained in Guide G 63. However, all lubricants should be used sparingly and with great caution.

9.14 *Compatible Polymers and Other Nonmetals*

9.14.1 As the severity of the hazards (such as higher pressure, temperature or oxidant concentration) increases to elevate system operating conditions above the level at which both cleaning and compatible lubricants are necessary, the next hazard threshold crossed is that of compatible polymers. Polymer use is avoided to a much greater degree in fluorine systems than in oxygen systems, however, in some effectively shielded systems latitude in material selection is sometimes taken as a economic risk only. In oxygen, at room temperature and low pressures—below about 350 kPa (50 psig)—and at oxygen concentrations between 30 and 100 %, most users switch to more fire-resistant polymers for gaskets, valve seats, packings, and other polymer parts. In fluorine, caution would often be extended down to the lowest commercial concentrations of 10 %, regardless of pressure. Such common systems of low oxidant severity may require compatible polymers and compatible lubricants in addition to scrupulous cleaning and passivation, but not need special consideration of the common metals components.

9.14.2 Most polymers burn in pure oxygen or pure fluorine, usually violently. They ignite more easily than metals and become the kindling chain that ignites the system. Also. most polymers produce toxic gases when they decompose, which can contaminate breathing gas systems even if there is no external fire, as noted in G 63. Fluorine is not used in breathing gas systems, but generates so much greater quantities of toxic and corrosive gases that its fires can present a general environmental toxicity concern. These materials include the many polymers and elastomers used in seats, stem tips, packing, gaskets, seals, and thread sealants in pumps, valves, regulators, filters, instruments, and most other piping components.

> Note 4: The general environmental concern of not only fluorine combustion products but of fluorine gas itself is so great that ventilation is usually a significant design consideration. Very often fluorine systems employ hoods and shields through which remote operation of valve and controls is effected. The hoods and shields are typically force-ventilated and the purge gas is fed to a fluorine burner or reactor (such as a charcoal-filled vessel) to capture and convert products and raw fluorine.

9.14.2.1 Polytetrafluorethylene (PTFE) and polychlorotrifluoroethylene (PCTFE) are listed by CGA G-4.4 as suitable for oxygen service and are used for many functions in piping components. Yet, even these materials begin to decompose at 200 to 300°C (400 to 600°F) and can ignite at higher temperatures. Both are used to a much smaller degree in comparable fluorine service, and are likely easier to ignite (also see Note 3).

9.14.2.2 As emphasized in Guide G 63, the successful use of even the best materials depends on the design of the component and where it is used. For example, PTFE-lined flexible hose has a large surface-area-to-mass ratio, and many instances involving the ignition of such hoses have been reported (Fig. 4 of G 128). The safe use of PTFE-lined hose in high-pressure oxygen may require special provision in the system design. In comparison, PTFE-lined hoses are avoided entirely in severe fluorine service, and used to a much smaller degree in less severe applications.

9.14.3 Operating conditions also must be considered in polymer selection. Continuous exposure to elevated temperatures or high oxidant concentrations can change a material into something quite different from what it was when new. With age, the material may become harder, softer, or brittle, or the surface may change. The molecular weight may decrease by scission or increase by cross-linkage. Such changes are accelerated by pressure and temperature and may decrease resistance to ignition and fire, as well as change performance properties. The tendency of fluorine to attack all surfaces even at ambient temperature can magnify this risk.

9.14.4 In oxygen at temperatures above the service limits of polymers, these materials sometimes are replaced by graphite, particularly in packings and gaskets. Being pure carbon, graphite will burn in an oxygen–enriched atmosphere. Although difficult to ignite in bulk form, graphite particles from packing wear may ignite more readily. Graphite introduces an additional concern because it is cathodic to most metals and causes corrosion in moist atmospheres. Although oxygen systems are generally dry, external moisture can initiate corrosion which can cause hidden damage. Fluorine is not used in piping systems at elevated temperatures, and exposed carbon would be a target for continuous surface reaction with the fluorine, and so carbon components would be an unlikely material to be used in *any* fluorine piping system.

9.14.5 All nonmetals should be tested and evaluated carefully before being used in a particular oxygen or fluorine system application. Guide G 63 presents a systematic approach to selecting nonmetallic materials, with numerous practical examples for oxygen, and it may be used by analogy with fluorine. It includes a compilation of test data for many nonmetallic materials frequently used in oxygen service. Chapter 5 of NFPA 53 also describes the ignition and combustion of materials commonly used in oxygen-enriched atmospheres. Materials that are acceptable for oxygen service are potential candidates for consideration for use in fluorine service, even though many may not prove acceptable and many may require additional care and control and reduced limits of approval.

9.15 *Compatible Metals*

9.15.1 Most common metals will burn in pure oxygen under at least some conditions of pressure and temperature. More likely, they will *all* burn under exposure to severe fluorine service, but depending upon the specific combustion mechanism, some metal/fluorine fires may be less intense than some metal/oxygen fires, and in some cases, diluents (and even some combustion products) may be more effective as a moderator or inhibitor of metal/fluorine fire than they are for metal/oxygen fire. The most familiar example is cutting steel with an oxygen torch (Fig 5 in G 128). A torch ignites the steel, and then a stream of oxygen keeps it burning. The heat of the burning steel continues the cutting action. The same process can happen accidentally in improperly designed oxygen or fluorine piping systems (Fig 6 in G 128).

9.15.2 Typically the last hazard threshold crossed as the severity of the hazards in an oxidant system increases is that for which compatible metals are required. For common systems at oxygen concentrations at up to 40 % and at pressures below 1 MPa (150 psig), few special materials are required. At higher concentrations and pressures, most users select more compatible metals. In fluorine systems, corrosion concerns often lead to the use of metals that also tend to exhibit better fire performance (corrosion employing many of the same chemical reactions as for combustion). Fluorine systems up to 10 % fluorine, at or below atmospheric pressure might require few special metals, but this would be in part dependent upon how they were located and the shielding and ventilation that is present. At high fluorine concentrations and pressures, the use of the most fire-resistant metals would typically be extreme with most metal selections being Alloy 400, or copper. In the case of fluorine systems, to a greater extent than with oxygen, one must rely on ignition prevention rather than nonflammability, and this is in part why shielding plays a much greater role in many fluorine systems—because so many more metals are flammable in fluorine.

9.15.3 NFPA 51 and CGA G-4.4/EIGA 13/02/E mention existing practices for the use of steel or stainless steel for oxygen systems. Historically CGA G-4.4 dealt only with 7 Mpa (1000psig) or less, but the new harmonized CGA G-4.4/EIGA 13/02/E is somewhat more expansive. Further, in regions of high velocity or impingement, such as valves, orifices, branch connections, and other critical areas, copper and nickel based alloys (brass and alloy

400) have been recommended—except for low pressures to 1.4 MPA (200 psig), where selected stainless steels have been used. For operating pressures above 7 MPa (1000 psig) CGA G-4.4 recommended asking the oxygen supplier to provide specific assistance. CGA G-4.4/EIGA 13/02/E has grand fathered these oxygen systems while providing additional guidance. Specific criteria for fluorine systems not been established but the practices for oxygen would be an upper bound.

9.15.4 Metals for fluorine service can be evaluated and selected following the guidance in CGA G-4.4/EIGA 13/02/E and Guide G 94, which provides extensive data on metals ignition in oxygen, guidance for metals selection, and several practical oxygen examples. Several papers, for example (**3**), offer similar, but still scant, data that apply specifically to fluorine. Any system that requires special metals to cope with the oxidant hazard also requires special consideration be given to cleaning, passivation, lubricants, and nonmetals.

9.16 *Isolation and Shielding*

9.16.1 When there is a concern that the hazards of a system can not be controlled to an acceptable level of risk with design, component selection, operating practices, and compatible materials—or when a system can not be modified to improve its compatibility—then isolation or shielding should be considered.

9.16.1.1 Isolation implies that a worst case fire event would be adequately remote from people or valuable materials so that the risk is acceptable. To apply this tactic, work stations may be moved, portions of systems or entire systems may be relocated, or other measures taken to increase the distance between the system and those items whose loss would be unacceptable. This tactic presumes that the loss of the isolated system is an acceptable unavoidable loss.

9.16.1.2 Shielding implies that a barrier can be provided around high-hazard or high-risk systems and that the barrier will contain or deflect a worst-case fire. This tactic also presumes that the loss of the shielded system is an acceptable, unavoidable loss, and in the case of fluorine, that the shielding can contain, ventilate or cleanup any released toxic fluorine or its combustion products.

9.16.1.2.1 At present the only systems that apply this technique routinely in oxygen service are compressors, pumps and some turbo-expanders. Rare high-risk valves are also sometimes shielded. This machinery often cannot employ the optimum materials, and usually there is so much kinetic energy involved that a mechanical failure produces at least a transient fire. Therefore, such machinery is designed using materials and practices that optimize its reliability and performance to minimize the number of mechanical failures and the fire hazard. In addition, such machinery is shielded to contain any fires that may occur and avoid secondary damages. In fluorine service, these tactics, in combination with positive ventilation, are more common than not and affect not only machinery but often whole systems.

9.16.1.2.2 Simple, inexpensive shields can also be effective. In small high-pressure systems, fires generally occur at components like valves and regulators that are manually actuated and therefore exposed to operating personnel. Mounting such components on a panel provides a simple, yet effective, local shield to protect nearby personnel.

9.16.2 There are no ASTM standards that provide help with the design of shields or adequate isolation distances. CGA, the Department of Defense, NFPA, BG Chemie, and EIGA publications describe some currently used shields.

10 Nitrogen Trifluoride (NF_3)

10.1 *Overview*—Nitrogen trifluoride (NF_3) is a strong oxidant. Table 1 lists the heats of combustion of several materials in the series of oxidants of interest here. However the presence of the three nitrogen bonds significantly reduce nitrogen trifluoride corrosiveness and reactivity in comparison to fluorine. In the distant past its hazard has been compared to that of air, but more recently it is generally treated as being more nearly between that of pure oxygen and fluorine being closer to one or the other depending upon specific conditions of use. Because it is a large molecule with a large specific heats (ratio of specific heats of 1.189), it is much less prone to compression heating and expansion cooling than oxygen (ratio of specific heats of 1.397), and also less than fluorine (ratio of specific heats of 1.364). However, it can decompose to release free fluorine and so adiabatic compression is still important and where decomposition occurs corrosion will obtain. Nitrogen trifluoride supports combustion and explosion of many chemicals. Pure nitrogen trifluoride gas is reported by the EIGA Code of Practice and one MSDS (**34**) as colorless and odorless. Both report nitrogen trifluoride has a melting point of –207°C (-341°F) and a boiling point at -129°C (-200°F).

10.1.1 *Commercial Uses of Nitrogen trifluoride:*

10.1.1.1 The overwhelming commercial use for nitrogen trifluoride is in the semiconductor industry where it is decomposed in assorted processes to produce fluorine that serves as a cleaning and etching agent.

10.1.2 *Chemical Processes:*

10.1.2.1

10.2 *Production and Distribution*—One published (**5**) process for the production of nitrogen trifluoride is similar to that for fluorine. Electrolysis of hydrogen fluoride acid mixed with ammonia and potassium fluoride produces nitrogen trifluoride and hydrogen from the combination of ammonia and hydrogen fluoride. The anode gas is chilled and passed through separation and adsorption stages to remove the hydrogen fluoride, then ultimately liquefied and distilled to remove any nitrogen and fluorine. Commercial nitrogen trifluoride is marketed in gas cylinders at pressures to ?? Mpa (?? Psig) and there is no current market for liquid.

10.3 *Hazards and Risks*

10.3.1 The hazards of nitrogen trifluoride are not as obvious as those of fluorine but not quite as subtle as those of oxygen. Because of its less aggressive nature, it is often used in a manner similar to that of oxygen but in many cases is used more nearly like fluorine in which there is much isolation, shielding and ventilation of the apparatus.

10.3.2 When a fire in nitrogen trifluoride occurs, it is resulting from the chemical reaction of liberated fluorine and bears strong similarity to fires in fluorine. A very wide spectrum of material is flammable.

10.3.3 Like oxygen and fluorine, nitrogen trifluoride is considered to be nonflammable (which means that when it reacts with "ordinary" fuels it gains rather than loses an electron). Otherwise, its contribution to the production of fire and heat is comparable to that of the fuel. If there is no fuel, there is no fire. If there is no nitrogen trifluoride, there is no fire (see Note 2). Nitrogen trifluoride is unlikely to lose electrons and be arbitrarily classed as "flammable" even in reactions with fluorine.

10.3.4 The ability of a nitrogen trifluoride-enriched atmosphere to support and enhance combustion after ignition occurs is its fire hazard. The risk to people and property that accompanies this hazard is variable. Sometimes the human risk is grave; sometimes the economic risk is severe. In these instances, the need to prevent combustion is strong. Occasionally, the risk is small enough that it can be accepted—and other tactics may be used to minimize the risk. The overall concept of hazard and risk have been lumped into the term "oxidant compatibility".

10.3.4.1 The ASTM Committee G-4 first codified its interpretation of the concept of "Oxygen Compatibility" in its Standards Technology Training (now Technical and Professional Training) course textbook *Fire Hazards In Oxygen Systems*. By analogy, the concept extends to oxidants, like nitrogen trifluoride, as follows:

> "The ability of a substance to coexist with both oxidant and a potential sources(s) of ignition within the acceptable risk parameter of the user [at an expected pressure and temperature]."

10.3.4.2 In this definition, a system is oxidant compatible if it cannot or is unlikely to burn, if the occurrence of fires is adequately infrequent, or even if potential fires can be isolated and their effects can be tolerated.

10.3.4. Other organizations have a similar respect for the hazards of oxidants in general and nitrogen trifluoride in particular. Oxygen is the most widely used oxidant and is thoroughly overviewed in ASTM G 128, and much of the material there is repeated here for comparison and contrast. Nitrogen trifluoride is much less extensively addressed, but there is material published by ASTM Committee G4 (**3**), the European Industrial Gases Association (EIGA) in its Code of Practice 92/03/E, the National Institute for Standard and Technology (NIST) (**4**), various vendor Material Safety Data Sheets (**34**) and in assorted technical papers (**5, 35-37**).

10.4 *Sources of Information*

10.4.1 Even though nitrogen trifluoride is more oxidizing than oxygen, and even though incidents are anecdotally known, the much smaller market for it results in a low number of incidents. For these same reasons the body of standards and publications that are available that deal with the fire hazard are all small in number. This section will overview what is available, but to a large extent the standards that come to be published to support this abstract standard may well prove to be the first public documents of their kind.

10.4.2 Designing equipment for use with nitrogen trifluoride enriched gases relies to a great extent on astute following of certain of the technology used for oxygen and fluorine. All of the hazard mechanisms that apply to oxygen also apply to nitrogen trifluoride and some of those that are most severe in fluorine are mirrored in nitrogen trifluoride. Correlating these practices is still a challenge. Still, whereas book-learning is highly worthwhile and practical in coping with the oxygen hazard, hands-on experience is still important in coping with the nitrogen trifluoride hazard. However current efforts to expand the knowledge and experimental data base for nitrogen trifluoride may shift it into the academic realm.

10.4.3 This standard is the first in the ASTM system to overview the nitrogen trifluoride hazard. But there are experimental data available in a limited number of technical papers, many of the older efforts of which were under government contracts and are listed along with the vastly larger body of oxygen papers in the ASTM Committee G-4 Reference Bibliography. The most recent and most pertinent to the ASTM G-4 approach are still underway and publication of them is just beginning and are eagerly awaited (**35**).

10.4.4 Commercial sources of nitrogen trifluoride have published MSDSs and one was consulted (**34**) in preparing this standard. EIGA has published a Code of Practice 92/03/E, and it was also reviewed.

10.5 *Causes of Fires in Nitrogen Trifluoride*

10.5.1 Although published documents and accident investigations for nitrogen trifluoride incidents are scant, with only one known of (**5)**, anecdotally such events are known to have happened. Virtually every fire mechanism known to exist for oxygen applies also to nitrogen trifluoride in theory, and there are some additional mechanisms that are known to apply for nitrogen trifluoride that do not affect oxygen. The mechanisms cited for oxygen in the current G 128 and G 88 are also cited here along with others and elaborated upon. The order cited is slightly different than those used in G 88-05 and G 128-95.

10.5.2 Kindling Chain. Ignition often starts with a small generation of heat, that grows and amplifies itself and shifts from one behavior to another and another, involving other materials and mechanisms, until it is in a runaway condition—a self-sustaining fire. The material that is most flammable that initially responds to the first heating in this sequence of events or “chain” is the “tinder” or “kindling’. Numerous mechanisms, specifically ignition mechanisms, can provide for the first small (and some times not so small) generation of heat.

10.5.3 Ignition Mechanisms. Fires in nitrogen trifluoride require an initial source of energy (which may sometimes be self produced) as is also the case with fires in oxygen. Incident histories are not adequately documented or numerous to reliably rank ignition causes for the many potential ignition mechanisms.

10.5.3.1 Autogenous Ignition (Autoignition). Ignition temperatures have been measured for several metals in nitrogen trifluoride (**35**). A greater range of metals is flammable in nitrogen triifluoride than is flammable in oxygen. However, the most extensive data for ignition temperatures of polymers in nitrogen trifluoride are recent (**35**). Some papers refer to this type of ignition that occurs when a material is heated in oxidant to be “thermal ignition”, but that is not common usage of the term. Since nitrogen trifluoride breaks down to release fluorine at elevated temperatures, one might expect ignition in nitrogen trifluoride to perhaps relate to ignition temperatures of polymers in fluorine for those materials that ignite in nitrogen trifluoride above the breakdown temperature of nitrogen trifluoride and to be near the breakdown temperature for some of the others (assuming some materials would ignite as soon as the fluorine became available). Present testing (**35**) reports ignition temperatures are often higher than those that occur for the same polymers in oxygen..

10.5.3.2 Thermal (Spontaneous) Ignition. Thermal ignition is commonly taken to be when a material reacting at a low rate is capable of heating itself to the autogenous ignition point of 10.5.3.1. In oxygen the most commonly cited cases of thermal ignition are the spontaneous fires that occur (1) when linseed oil soaked rags are piled up, and (2) when machinery such as compressors are run in on nitrogen or other nonreactive gas producing wear-dust debris and then converted to oxygen service. In each case, there is a high surface-area-to-volume insulating situation that allows low level reactions to self-heat and produce a kindling chain. Similar effect should also obtain in much more reactive nitrogen trifluoride, however, even in this case laboratory data are few and anecdotal data indicate that even with the more reactive fluorine gas, that whereas metal-fines piles may react and heat to the melting or sintering point, outright fires and explosions are not always a certainty. Comparable data, even anecdotal data, for nitrogen trifluoride are not available. Nor are there data to indicate how nitrogen trifluoride would react in the presence of carbon-fines. These fines can yield sudden violent explosions with fluorine. And because the reaction products in the pile should include gases like carbon tetrafluoride of high vapor pressure, the volatility of the reaction products in nitrogen trifluoride should be a key factor in the hazard of nitrogen trifluoride in comparison to other oxidants.

10.5.3.3 Particle Impact. Particles present or generated in nitrogen trifluoride systems carry the same risk of ignition as in oxygen systems. Upon impact (and perhaps due to spontaneous self-reaction) these particles can ignite and serve as tinder in a kindling chain.

10.5.3.3.1 Nitrogen trifluoride systems should not commonly generate particles/powder during service (as is the case for fluorine), unless there is a mechanism decomposing the gas.

10.5.3.4 Pneumatic Impact or Compression Heating. Because nitrogen trifluoride has much greater heat capacities than oxygen, it does not heat as much in rapid (near-adiabatic) compression for comparable starting and finishing pressures (**4**), but because pure nitrogen trifluoride is shipped and used commercially at much higher pressures than fluorine (??? Versus 400 psig), peak temperatures during abrupt compression are much less than for oxygen but more than for lower pressure fluorine. The maximum heat transfer that occurs to polymers (**32**) is apparently less also. Since nitrogen trifluoride can decompose to release more reactive fluorine at elevated temperatures, rapid compression may lead to the production of fluorine and subsequent corrosion, particulate production and perhaps facilitate ignition and fire to a degree greater than its temperatures and heat transfer might initially suggest.

10.5.3.4.1 Adiabatic compression processes for nitrogen trifluoride in relation to other gases are reviewed in a recent tutorial (**32**), and NIST software allows for estimation of peak adiabatic (isentropic) compression temperatures and heat transfers of numerous real (as opposed to ideal) gases including nitrogen trifluoride (**4**).

10.5.3.5 Mechanical Impact. There are few experimental data nor is there anecdotal experience to assess mechanical impact in either pure or dilute nitrogen trifluoride service. Because impact heats, abrades, scrapes, and otherwise upsets metals, all processes are more likely to initiate reactions than for oxygen, mechanical impact should be a more serious risk in nitrogen trifluoride than in oxygen, less serious than in fluorine.

10.5.3.6 Friction and Galling. Friction and galling should both be important mechanisms in a theoretical regard. Both should yield particles of metal and expose fresh surface area that would begin to react with nitrogen trifluoride. The known rate of incidents in nitrogen trifluoride is too low to speculate on whether there is a greater tendency for the fire to affect the valve being operated more so than for oxygen which more often affects the system farther downstream.

10.5.3.6 To the extent that scrupulously clean nickel alloy and stainless steel alloy are used with nitrogen trifluoride, it would not uncommon for galling to occur. Valves have often locked up on their first operation. This may be a cause of fire in nitrogen trifluoride, because it is very likely to have caused some fires in fluorine service. However, lab testing that has ruptured and rubbed these metals in high pressure fluorine does not confirm this possibility to date.

10.5.3.7 Resonance. Resonance tends to produce the most intense heating at high flows, something that is more likely to present in nitrogen trifluoride systems than in fluorine systems (due to higher pressures). However, resonance temperatures have been magnified by the presence of particles which are a common occurrence in older fluorine systems but less likely in nitrogen trifluoride, though more likely than in oxygen. The effect of the large molecular weight of nitrogen trifluoride on acoustic resonance has not been tested and could be significant in either direction.

10.5.3.8 Static Electric Discharge. There are no static electricity measurements reported in the literature for nitrogen trifluoride flows. However, in some oxygen systems static electricity has been greatest in insulating systems (such as polymer-lined hoses) rather than in conductive systems. In most of the severe fluorine service systems, polymers are nearly totally avoided. However, polymer–lined hose may be attractive for nitrogen trifluoride service and, here again, particles can magnify the formation of charge separation, and nitrogen trifluoride systems should have fewer systemic particles than fluorine but may have greater numbers than would oxygen systems.

10.5.3.9 Electric Arc. Electric arcing is a highly effective method of igniting materials in oxygen and has when welding is attempted on pressurized oxygen systems. It should be similarly hazardous on nitrogen trifluoride systems.

10.5.3.10 Flow Friction. Flow friction is a speculative mechanism used to explain incidents that resist all other forms of explanation. It is analyzed as waves of motion that occur during gas flow over polymers that produce internal friction processes that might heat polymers to the ignition point (**33**). Lab experiments to date to demonstrate it in oxygen systems have not been successful. They have produced heating but not ignition. However, any tendency for polymers to heat under cyclic stress and strain would tend to be more significant in nitrogen trifluoride systems where decomposition to produce fluorine and reaction rates are much more affected by temperature.

10.5.3.10.1 “Flow friction” should be more aggressive in nitrogen trifluoride than in oxygen, and nitrogen trifluoride systems are more likely to employ polymers than lower pressure fluorine systems. Therefore it is difficult to say whether flow friction is a more valid or greater concern. than for oxygen or fluorine systems.

10.5.3.11 Fresh Metal Exposure. Many believe that every surface that is exposed to an oxidant will experience some degree of initial reaction that is likely to be much greater in fluorine than in oxygen. In oxygen bulk specimens of fresh titanium surface exposed to oxygen have ignited, but otherwise, ignitions have only been observed in piles of fines. In fluorine, evidence of surface reactions is a common and an often speculated but not certain cause of ignition, because anecdotal lab tests have exposed even piles of fines to fluorine that have heated but not ignited. Nitrogen trifluoride should be more prone than oxygen to this mechanism due to its greater heat of combustion and the possibility that it may have decomposed to produce a fluorine constituent. The small number of known nitrogen trifluoride incidents do not allow for a conclusion as to the relative importance of fresh metal exposure in nitrogen trifluoride systems. However passivation (see 10.12) is a commonly practiced precaution especially in severe nitrogen trifluoride services.

10.5.3.12 Decomposition. Nitrogen trifluoride is an exothermic molecule that can be decomposed to release fluorine under the influence of heating. Neither literature nor the anecdotal record cite any common endothermic molecules for nitrogen trifluoride and its trace compounds formed in systems. There are no citations of molecules with other elements that correspond to the endothermic molecule nitrous oxide (reviewed elsewhere in this standard) and none that would correspond to the endothermic molecule ozone, (also reviewed elsewhere in this standard).

10.5.3.13 Other Ignition Mechanisms. Other mechanisms can not be ruled out, but none are speculated upon in the available literature.

10.6 **Hazards**

10.6.1 *Recognized hazards.* Nitrogen trifluoride is extremely dangerous more so because of the potential toxicity of its combustion products than because of it own toxicity and they will not be covered here except as they affect the fire hazard. Because of the great reactivity of nitrogen trifluoride in comparison to oxygen, every fire hazard known to oxygen use (with only rare exception) is a similar or greater hazard to fluorine use, although individual features of these hazards may not always be more severe than for oxygen. Further, even potential hazards of oxygen use that have not been observed may be realized in corresponding nitrogen trifluoride systems. These include (1) nitrogen trifluoride concentration and associated diluents, (2) pressure, (3) temperature, (4) phase, (5) velocity. (6) time and age, (7) mechanical failure.

10.6.1.1 *Nitrogen Trifluoride Concentration and Associated Diluents.* Higher nitrogen trifluoride concentrations increase the hazards of ignition and fire intensity because more nitrogen trifluoride is present to mix with the fuel. Diluents are as important as they are for oxygen systems. Nonreactive diluents that have large molecular size are more effective at attenuating flammability (however keep in mind that nitrogen trifluoride is a large molecule itself and therefore many diluent gases that would lower the risk in mixture with oxygen are in comparison smaller than nitrogen trifluoride and might act to increase the hazard in mixture with it). In oxygen systems even tenths of a percent of diluents can be important, but whether a similar less extreme effect for trace diluents is operative in nitrogen trifluoride is not certain but is likely. There are a number of volatile metal fluorides that may form and inhibit the rate of relative combustion in nitrogen trifluoride (and indeed the decomposing nitrogen trifluoride molecule, itself, may release relatively low reactivity nitrogen diluent gas). These diluents may lower the reaction rate but being volatile might therefore magnify the potential pressures produced.

10.6.1.2 *Pressure.* Higher pressures increase the hazards of ignition and fire intensity. Pressure increases the density of the gas, with the same effect as increasing the concentration: more nitrogen trifluoride is available to the fuel, so materials ignite easier and burn faster. Pressure also increases the gas velocity at restrictions such as valves, regulators, and intersections—which increases friction, particle impact, and compression heating.

10.6.1.3 *Temperature.* Unlike oxygen, practical use temperatures have a significant affect on the reactivity of nitrogen trifluoride (by affecting its decompositin), and therefore its ignition tendencies and potentially even the intensity of combustion and resulting damage. Elevated temperatures are even more risky than for oxygen and more likely to induce autogenous or thermal (self-induced temperature) ignition—and they may enable combustion to occur in a system that is not otherwise flammable, even if it is made of some of the most normally fire-resistant metals and polymers. As for oxygen, any high temperature can accelerate aging of polymers and thereby reduce their compatibility with nitrogen trifluoride.

10.6.1.4 *Phase.* Nitrogen trifluoride liquid may be used in distillation processes to purify the products, but nitrogen trifluoride is not stored, used nor sold as a liquid. The base of liquid phase experience is small (however one of the few known documented nitrogen trifluoride incidents (**5**) involved liquid. Its behavior and risks as a liquid should mirror or exceed the same behaviors of liquid oxygen.

10.6.1.5 *Velocity*. Increased nitrogen trifluoride velocities in flowing systems lead to higher particle velocities, which increase the likelihood of ignition by particle impact. Particles in nitrogen trifluoride systems should tend to be somewhat more numerous than in oxygen systems, but less numerous than in fluorine systems, but they tend to be overwhelmingly of lower-risk metal fluorides and very seldom of higher risk reactive materials and contaminants. “Flow friction” which is speculated but unproven as an ignition mechanism in oxygen, is an uncertain risk in nitrogen trifluoride systems. Some testing indicates (**35**) that ignition temperature may be higher in nitrogen trifluoride than in oxygen but the greater molecular mass and momentum of the gas stream may yield more heating. The consequences on flow friction of the heavy nitrogen trifluoride molecule in shifting resonant frequencies is not known and there is no known anecdotal incident experience to suggests nitrogen trifluoride systems experience any different or greater ratio of fires in operated valves than downstream relative to oxygen experience.

10.6.1.6 *Time.* Time and age are important hazards. However the base of experience is too small and undocumented to assess the role of time on nitrogen trifluoride system fire risks.

10.6.1.7 *Mechanical Failure.* The same mechanical failures that jeopardize oxygen systems also threaten fluorine and nitrogen trifluoride systems. These include impact of broken parts, rubbing, particle generation, failed seals, etc. Friction and galling are a particular risk in fluorine, both in tendency to occur and consequence when they do occur, therefore they are a risk in severe nitrogen trifluoride systems that may mimic the material selections for fluorine systems. Many of these mechanisms also violate the “passivation” (see 10.12) of the system and are therefore suspected to be of even greater risk in fluorine or decomposed nitrogen trifluoride than they are in oxygen. Indeed, in oxygen service, the components (namely oxygen compressors and pumps) most at risk of failure and therefore most likely to experience fires are often placed behind barriers, because their reliability can not be made sufficiently high to address the risk to life and injury otherwise. In many (especially pure) fluorine systems, and perhaps the more severe nitrogen trifluoride systems these same items and much of the more mundane hardware also can not be made sufficiently reliable to cope with the risk of fire, and so many valves and other components are also placed behind barriers and are remotely operated.

10.7 *Fire Prevention*

10.7.1 G 128 patterns the approaches to preventing fires in oxygen to those used for preventing fires in air. The following sections will pattern the approach for nitrogen trifluoride fire to both those for oxygen and fluorine fires. In each there is a gradation of steps taken with greater numbers and more extensive use depending on the severity of the situation.

10.7.2 In oxygen and fluorine systems there is always an oxidant (oxygen, fluorine, respectively) present, often there is fuel present (in the materials of the system itself), and sometimes there are ignition mechanisms present (heat of compression, particle impact, etc). So in oxygen and fluorine systems there is effort to pick the best materials possible and to minimize the number and intensity of ignition sources. In fluorine, there is a smaller number of materials that will resist fire, and more sources of ignition present. In nitrogen trifluoride there is a wider spectrum of materials that will burn than in oxygen, approaching the number that will burn in fluorine.

10.7.3 As for oxygen and fluorine, depending on the nitrogen trifluoride or nitrogen trifluoride mixture system, there are progressively stringent measures applied in the order cleaning/passivation, compatible lubricants, compatible polymers and other nonmetals, and compatible metals. However, unlike oxygen systems in which some of these steps may be unnecessary, in nitrogen trifluoride and nitrogen-trifluoride-mixture systems all of these steps are often, if not always, required.

10.7.4 In some nitrogen trifluoride systems, not only will all four of the previous tactics be applied but there will be additional protective measures taken in terms of barriers, ventilation, and the like.

10.7.5 Recognizing, identifying and controlling potential sources of ignition and possible causes of fires in nitrogen trifluoride is not simple. Present knowledge does not enable us to identify all possible ignition sources. Hence few nitrogen trifluoride systems can enjoy a certainty that fires are not possible. There is a strong empirical influence in the approach to oxygen safety that is even greater for fluorine safety, and this is also the case in nitrogen trifluoride safety. To a large extent, one does what has been successful in the past, provided it has been successful often for long periods of time, and is based on sound principle. For this reason ASTM G-4 standards take a multi-pronged approach that attempts to align as many factors as possible toward reducing the likelihood of ignition and fire.

10.7.6 This approach is based on using the extensive body of information available on the ignition and flammability of materials and methods with demonstrated ability to reduce the number and severity of fires in oxygen with adjustments to it based on the known properties and behavior of nitrogen trifluoride. Guides G 63, G 88 and G 94 as well as Practice G 93, describe the many factors affecting oxygen and oxygen-enriched systems and describe how to reduce the hazards associated with these systems. These same guides are often taken as a starting point for nitrogen trifluoride and nitrogen-trifluoride-enriched systems and are then expanded upon. Only rarely would any less stringent practices be followed.

10.7.7 ASTM G-4 and other resources correlate control of oxidant system hazards with special attention to (1) system design; (2) component selection; (3) operating procedures; (4) cleaning; (5) passivation; (6) compatible lubricants; (7) compatible polymers and other nonmetals; (8) compatible metals; and (9) isolation and shielding. Each of these approaches is discussed in more detail below.

10.8 *System Design*

10.8.1 Oxygen and even more so nitrogen trifluoride system design should not be undertaken casually—these systems require careful and specialized design considerations. The first and most important rule is: Consult an expert! Guides G 63, G 88, Practice G 93 and Guides G 94 and G 128 define “Qualified technical personnel” and provide vital information for use by these experts. Indeed, in many companies, individuals are designated as specialists to acquire the expertise and assist others in oxidant system design.

10.8.2 System design for any oxidant should begin with the same mechanical principles as conventional air or gas system design and follow the same nationally recognized codes and standards—there are no special codes that mandate how to design oxidant systems. Keep in mind that when portions of systems are barricaded, as is done often with nitrogen trifluoride components, in such a way that they do not travel in commence and are not used as ordinarily specified in codes, they may not fall under the legal mandates of the codes, and this may allow latitude and flexibility in coping with the nitrogen trifluoride hazard. The added hazards inherent in the use of oxidants should then be evaluated to modify conventional practices while still conforming to appropriate requirements. In general that leads to a more—not less—conservative design. Nitrogen trifluoride system designs can usually be approached as more careful modifications of similar oxygen system designs that (unless barricaded or isolated) also meet or exceed the compatibility measures that would be taken with oxygen.

10.8.3 The severity of system operating conditions is defined similarly to those for oxygen. Concentration, pressure, temperature, phase, and time are all crucial (however, except at the manufacturing and purification stage, the liquid phase is not typically encountered in today's commercial nitrogen trifluoride practices). As these factors increase, the risk increases, and the system design must be modified to a greater extent. Nitrogen trifluoride concentration and phase are established by the system function. But the others can be influenced by the system design. For example pressure can be reduced with a regulator as close to the gas source as possible to minimize the hazard (and most nitrogen trifluoride systems have a regulator right on the source cylinders, often shielded for the most severe services). Temperatures can be limited, for example by including protection from runaway heaters. The effects of time and age can be mitigated by designing for effective preventive maintenance.

> 10.8.3.1 Velocity is a hazard that is controlled primarily by overall system design. Line sizes should be selected to limit nitrogen trifluoride gas velocity. There are no adopted velocity criteria for nitrogen trifluoride systems but existing guides for oxygen systems may suggest an upper limit and may be adjusted downward when needed and when possible. Rules applied to oxygen systems as to abrupt line size changes, locations of intersections and risk of particle impingement and compression heating in certain geometries are all applicable to nitrogen trifluoride systems near polymers and perhaps elsewhere, as well. As for oxygen, one reduces velocity and upgrades the fire resistance of nitrogen trifluoride system materials wherever needed to cope with velocity and particle hazards. However, with nitrogen trifluoride as with fluorine, it is not always possible to upgrade to a nonflammable metal.

10.8.4 Additional considerations are reviewed in the remaining sections are integrated into the design of a nitrogen trifluoride system. Again in many cases, care beyond that normally accorded oxygen systems can be required. For example, the initial cleanliness of an oxygen system is established as the components are built and the system fabricated, and it is crucial to prevent contamination during the systems life. However, the reactivity of nitrogen trifluoride and the fact that it may partially decompose to fluorine would call for an even greater cleanliness.

10.8.5 The only specific guidance on nitrogen trifluoride system design itself is found in the various vendor's Material Safety Data Sheets and an EIGA document on nitrogen trifluoride. However, oxygen design materials such as Guide G 63, CGA G-4.4, EIGA 13/02/E, NFPA 50 and 51, and many others provide excellent guidelines for system design that can be considered by analogy in the design of nitrogen trifluoride systems, although these references are not handbooks. This includes material in the ASTM G-4 Committee Technical and Professional Training Course *Controlling Fire Hazards in Oxygen Systems* which teaches the fundamentals of oxygen safety for oxygen process designers and equipment specifiers and includes a textbook.

10.8.5.1 Many references on oxygen hazards are cautious and explicit about the use of their data, and this caution is worthwhile to apply to other data and other oxidants such as nitrogen trifluoride. For example, Praxair Publication L-5110N warns:

> "This publication is not a design handbook and does not relieve the user from exercising competent engineering judgment or using qualified professional personnel who can tailor your design to your specific situation.
>
> "In situations where qualified people are not available locally to design the system, obtain professional assistance from a competent source. If the oxygen supplier can not offer assistance, he should be able to direct you to a consultant who can provide the necessary service. Remember that design of oxygen systems requires specialized knowledge. Liability problems associated with improperly designed systems can far outweigh the cost of professional services."

10.9 *Component Selection*

9.9.1 ASTM Committee G-4 standards do not recommend specific products. Indeed, they are disclaimed as specifications. Further, their nature is not such that products can be marketed under a blanket claim of meeting any of the four applicable oxygen standards (G 63, G 88, G 93, or G 94) and this applies even more so to nitrogen trifluoride systems as well. Clearly the thrust of these standards is to enable evaluation of system needs in the context of a particular application. As the application changes, such as exposure to higher pressure, a host of conditions change—or hazard thresholds are crossed—that may render previously accepted products unacceptable for further use. Therefore, although there may be a few products that are acceptable in any and all oxygen applications, one can not consider products to be "approved for oxygen or any other service" under the procedures of these standards without also specifying the conditions for which the approvals are intended.

10.9.2 Some products are marketed for nitrogen trifluoride service, but not every experienced designer agrees that every one of these products has adequate nitrogen trifluoride compatibility or even that a blanket approval is reasonable. Some companies do list materials that are approved across the board, but many others tie approval to specific applications and level of application hazard. It behooves the user to determine whether the properties of the particular products (whether or not they are marketed for nitrogen trifluoride service) actually meet the needs of the users application.

10.9.2.1 Performance tests conducted by hardware manufacturers generally do not simulate any specific application. Laboratory tests can not duplicate the endless variety of actual operating conditions; such tests only indicate a predicted result in a controlled laboratory setting and cannot assure the same result in a particular application or service.

10.9.2.2 Material qualification tests are also method specific and rarely afford blanket approval. The user should evaluate the material test results along with the test method to determine if they correspond to the way the material will be used in a specific design.

10.9.3 It is also important to note that most common industrial components—such as valves, fittings, filters, regulators, gages, and other instruments—are not designed for specific applications. Rather, they are versatile, general purpose products that can be used properly in many types of applications and systems. Hardware manufacturers in general have neither the experience nor expertise to select the most appropriate components for a specific use, such as a nitrogen trifluoride system. Only the nitrogen trifluoride system designer or user can have full knowledge of the entire system and each component's function, which must be considered when selecting the system components. nitrogen trifluoride system designers and users both must be sensitive to product function, material compatibility, adequate ratings, and proper installation, operation, and maintenance.

10.9.4 Valve selection requires special attention by the system designer, because valves are one of the few mechanical items that are actuated routinely while the system is in use. The designer must determine the type of valve, its location, how it will be operated, and—often neglected— how it might be operated incorrectly.

10.9.4.1 Particular attention should be directed to valve pressure and temperature ratings, internal materials of construction, and how readily the valve can be cleaned and kept clean. Valves often are selected with higher ratings, greater wall thicknesses, and more fire resistant materials than the rest of the system because they are exposed to more severe service conditions. In some cases, oxygen valves of certain metals can be considered nonpropagating if they are sufficiently thick, but some test data suggest this approach may not be applicable to fluorine and nitrogen fluoride service (**3,35**).

10.9.5 As valves are opened and closed they almost always generate localized high velocities near the valve seat or immediately downstream. This creates a local increase in the hazard level at the valve location and often requires that special consideration be given to the selection of seat materials and potential impingement areas nearby.

10.9.5.1 Nitrogen trifluoride system valves also pose a more serious risk of personal injury, because many are opened and closed manually—so that at the very moment they are most susceptible to the conditions that can cause a fire, someone's hand is on them. Indeed, the risk is so much greater with nitrogen trifluoride than with oxygen, that valve handles and sometime whole systems are commonly shielded and extended or remote operators used on severe service valves.

10.9.5.2 Oxygen Guides G 88, CGA G-4.4, EIGA 13/02/E and NFPA 51 unanimously emphasize that valves must be opened slowly. Opening speed is controlled by valve design, as well as by operating procedures. Ball, plug and butterfly valves are used in some low-pressure systems such as pipelines, because their straight-through design provides a lower pressure drop than a globe valve. However, ball and plug valves are quick-opening and create high velocity when opened, whereas needle valves are designed to open slowly (Fig. 3 of G 128). If a full-flow valve is used in a high pressure service, the piping system must be designed carefully to equalize the pressure across the valve before it is opened.

10.9.5.3 Even while closed, valves require extra consideration. Valves used in gas service often have seats or stem tips made of polymers that are exposed to the system fluid when the valve is closed. They can be subject to impingement from high velocity generated by another component upstream, and thus become a potential ignition point. For this reason, in some of the more severe nitrogen trifluoride gas services one might choose to use metal-to-metal seated valves, although this practice is not as extensive as is the case for fluorine-system valves.

10.10. *System Operation*

10.10.1 Nitrogen trifluoride appears to ignite at an infrequent rate more like oxygen than fluorine but to produce damage when it does ignite more like fires in fluorine. Due to the greater consequence nitrogen trifluoride is usually accorded more care than oxygen in both the system design and the cautions employed by system operators. Perhaps the most neglected aspect of controlling oxygen systems hazards involve system operation. Oxygen fires frequently are caused by systems whose safe operation depend so greatly on the operator's strict adherence to certain procedures that they can not tolerate simple human error. In these poorly designed systems, a single mistake—such as actuating one of a series of valves in the wrong sequence—can lead to a catastrophe. G 128 cites (in its sections 15.1.1 through 15.4) and reviews example events documented in the ASTM video adjunct entitled, *Oxygen Safety*, that illustrate several design errors that invited and then compounded operator errors, causing serious accidents.

10.10.1.1 In both examples rapid compression led to ignition. In one an operator was supposed to open a ball valve, then slowly pressurize a downstream system with the valve on an adjacent cylinder, but instead left the ball valve closed until the cylinder valve was open, then shocked the downstream system. Other episodes with ball valves were similar. All of the events could have been prevented with more cautious system operation.

10.10.1.2 In nitrogen trifluoride systems the high pressures would have produced high temperature approaching those produced by oxygen (attenuated somewhat by the higher specific heats of nitrogen trifluoride). The maximum potential heat transfers during rapid pressurization would have likely been less (**32**). Since the high transient temperatures may liberate fluorine that is very active, ignition might be a very possible result. In addition other factors such as flow friction may demand specific operating practices.

10.10.2 Therefore, as noted in the *Oxygen Safety* video adjunct, thorough planning and careful monitoring of operating procedures and maintenance practices are important in oxidant fire prevention. However, safe operation should be engineered into the design of an oxygen system—by the selection and placement of components—and not rely solely on operator compliance with procedures to prevent oxygen fires. As noted in G 88 Section 7.19.4 "Avoid Overly Complicated Procedures", one must remember that complex and repetitive procedures are more prone to discrepancy than simple straightforward procedures. Since human error is difficult to prevent, in crucial systems, automation may be required to achieve reliable system operation.

10.11 *Cleaning.*

10.11.1 A nitrogen trifluoride system requires cleaning comparable to or greater than that of an oxygen system. Cleaning is the first measure required, even though it may be the last step accomplished in preparing a system for oxidant service. Any such system typically must be evaluated carefully for cleanliness, and most will be cleaned scrupulously. In fact, the extent of cleanliness used on a system exposed to dilute nitrogen trifluoride may be very similar to that applied to pure oxygen or pure-fluorine, high pressure systems.

10.11.2 Organic particles and fine particles burn violently in concentrated oxidant and are often the beginning of the kindling chain that starts a fire. Hydrocarbon oil or grease contamination is particularly undesirable. In mild applications, inert particles may be removed less scrupulously. A mild nitrogen trifluoride exposure may not be subject to any other requirements, but its cleanliness should always be a concern.

10.11.2.1 The basis for determining the oxidant concentration and pressure at which more scrupulous cleaning is needed should be related to the flammability of the contaminants, lubricants, polymers, and metals. If the contaminants are unidentified, one must assume they may be flammable and therefore must be eliminated at even a small increase in oxidant concentration or pressure.

10.11.3 Cleaning methods used with oxygen systems are often applied to other oxidant systems including nitrogen trifluoride systems and should be evaluated and selected by analogy following the guidance contained in Practice G 93, CGA G-4.1, EIGA 33/86/E, and Praxair GS-39. Practice G 93 provides special guidance for cleaning components in its Section on Interferences.

10.11.3.1 *Disassembly:*

10.11.3.1.1 It is imperative that oxidant systems be cleaned as individual articles, preferably prior to assembly. Assembled systems must be disassembled for cleaning if construction permits. Flushing an assembled system can deposit and concentrate contaminants in stagnant areas.

10.11.3.1.2 Manufactured products (for example valves, regulators, and pumps) should preferably be cleaned by the manufacturer prior to final assembly and test. The purchaser should approve the cleaning procedure and packaging to ensure that they satisfy the system requirements.

10.11.3.1.3 Manufactured products that are cleaned by the purchaser must be disassembled for cleaning if the construction permits. The purchaser should follow the manufacturer's instructions for disassembly, inspection for damage, reassembly, and testing.

10.11.4 Practice G 93 contains additional information on cleaning methods, hindrances to effective cleaning, packaging, and inspection, including examples of specific applications.

10.12 *Passivation.*

10.12.1 When a new scrupulously cleaned nitrogen trifluoride system is pressed into service, like a new fluorine system, it is still considered at serious risk, despite the compatibility of its materials of construction, unless a final passivation step is performed. In passivation of a fluorine system, a dilute fluorine gas mixture with a nonreactive gas is purged into the system at low pressure and allowed to soak, after which subsequent mixtures at higher fluorine concentration and pressure are introduced until the system has been soaked at its maximum intended service concentration and pressure. Because of the lower reactivity of nitrogen trifluoride gas, it is ineffective for passivation and so fluorine mixtures are used instead. EIGA 92/03 presents one suggested schedule for passivation of nitrogen trifluoride systems with fluorine mixtures. Indeed, a common good practice with fluorine systems that have been depressurized and inactive for some times, is to ‘bump” the pressure up in increments on first re-use, allowing the system to soak for some period (say fifteen minutes) between each bump, in order to reestablish the passivation and heal any areas that may have deteriorated at low pressure or on exposure to air. Nitrogen trifluoride is not comparably reactive and so even though slow pressurization is still a worthwhile precaution, this procedure would not reinforce the systems passivation, and would not be used. However, if there were reason to suspect the passivation may have been seriously compromised, a re-passivation with fluorine might be performed.

10.12.2 Passivation is believed to accomplish two things, but its mechanism may be poorly understood. First, the aggressive fluorine reacts any trace remaining contamination in the system (hydrocarbon reacting largely to hydrofluoric acid and carbon tetrafluoride gas) and the surface then reacts to produce a very thin layer of metal fluorides that is inert and believed to be protective against fresh-metal exposure ignition. This is a time honored safety practice, however, its effects are extremely subtle, and anecdotal laboratory efforts to measure surface fluorides have found it difficult to actually measure differences between newly passivated and unpassivated surfaces, and anecdotal efforts to produce ignition of freshly broken metal specimens in cylinder pressure, pure fluorine have not been successful. Nonetheless new systems that have *not* been passivated prior to use apparently do have a significantly greater risk of component fires.

10.12.3 Passivation should only be performed on scrupulously clean systems. Attempts to passivate systems that are not adequately clean will lead to corrosion from the additional acid that is produced and elevated production of particles that can be ignition aggravating hazards during gas or particle impact or resonant flows, and possibly during flow friction. When passsivation of nitrogen trifluoride systems is complete, a thorough purging of the system may be needed to remove the fluorine, diluent and any reaction-product gases.

10.12.4 The passivation of systems should be preserved by maintaining the system in a dry sealed state. Moisture may dissolve some of the surface films produced and compromise their protection. Systems that are open to atmosphere for extended periods or out of service may warrant re-passivation before return to service if there is any doubt as to the condition of the passivation. For this reason many nitrogen trifluoride systems that are shutdown or may be opened to atmosphere are often equipped to thoroughly purge with nitrogen and are often sealed with nitrogen pressure contained in them.

10.13 *Compatible Lubricants*

10.13.1 If cleanliness is the first special measure that is necessary, the next concern is with lubricants, for two reasons (*1*) the most common oils and greases are hydrocarbon, which are among the materials most necessary to remove from an oxidant system; and (*2*) they are fluids and pastes, which are more prone to migrate and collect than are solid materials.

10.13.2 Any lubricants reintroduced into a system cleaned for oxidant service should be selected to be fire resistant. In most instances, even with mild oxidant exposures at low pressures and at low oxidant concentrations (as low as 25% oxygen or 10% fluorine in nitrogen or argon or equivalent), fire-resistant lubricants or other fluids are used.

10.13.2.1 Several halogenated oils and greases have been tested and used widely with success in oxygen service. Oxygen manufacturers can be consulted regarding appropriate lubricants for specific applications, Guide G 63 includes test data on many lubricants, thread compounds, seats and gaskets. Praxair L-5110N lists lubricants that manufacturer has used for low pressure systems. Specifications MIL-G-27617, MIL-G-47219 (MI), DOD-L-24575 (SH), and KSC 79K22280 may also be consulted for choosing analogous nitrogen trifluoride-compatible greases and lubricants.

Note 5: In oxygen service, material that includes halogens (specifically, fluorine, chlorine) in their chemical structure, tend to exhibit enhanced fire resistance. This is in part due to their lowered heats of formation and combustion Table 1, but in the case of chlorine there is an acknowledged free radical scavenging action that yields a fire inhibiting effect greater than would be expected merely on the basis of reduced heat of formation. However, in fluorine systems the highly reactive fluorine can attack the bonds that chlorine forms and alter not only the compatibility but also the material properties of the underlying molecule. As a result, lubricants and polymers that contain chlorine may be altered in time and become undesirable for their intended purpose. In some cases materials based on CTFE may deteriorate like this and it is avoided by some in severe fluorine service. In nitrogen trifluoride, the only fluorine present would be any that resulted from decomposition, and the same effect does not appear to be present for nitrogen trifluoride, itself. PCTFE polymers and CTFE lubricants appear to be in wide common use with good success.

10.13.3 Practice G 93, Section on Interferences, provides special guidance for lubrication of components.

10.13.3.1 *Lubricants*

10.13.3.1.1 Mechanical components are normally assembled with lubricants on seals, threads, and moving surfaces. The manufacturer should be consulted to determine the kind of lubricant originally used on the article to ensure that the cleaning solutions and methods selected are effective in removing the lubricant and will not damage the component. In some cases, nitrogen trifluoride systems omit the lubrication of certain components such as metal-to-metal valve seats. In these cases the tendency to gall and fret must be very carefully evaluated both to obtain a reasonable service life but also to avoid introducing ignition mechanisms..

10.13.3.1.2 When used, nitrogen-trifluoride compatible lubricants should be selected. In some cases lubricants can be evaluated as they would be for oxygen service using the methods of G 63 and treating pure high pressure nitrogen trifluoride with the same concern that would apply to pure high pressure oxygen, and treating the more dilute mixtures of nitrogen trifluoride as one would treat air. In time more specific guidance should be developed. The component manufacturer should also be consulted to ensure that the selected lubricant provides adequate lubrication for component performance. Oxidant compatible lubricants often have markedly different lubricating properties from conventional lubricants.

10.13.4 Scrupulous cleaning combined with the use of fire-resistant lubricants may be the only special precautions needed in moderate services. Until more precise recommendations are published, lubricants should be evaluated and selected following the guidance contained in Guide G 63. However, all lubricants should be used sparingly and with great caution.

10.14 *Compatible Polymers and Other Nonmetals*

10.14.1 As the severity of the hazards (such as higher pressure, temperature or oxidant concentration) increases to elevate system operating conditions above the level at which both cleaning and compatible lubricants are necessary, the next hazard threshold crossed is that of compatible polymers. Polymer use is common but not vast in nitrogen trifluoride, however, in some effectively shielded systems latitude in material selection is sometimes taken as a economic risk only. In oxygen, at room temperature and low pressures—below about 350 kPa (50 psig)—and at oxygen concentrations between 30 and 100 %, most users switch to more fire-resistant polymers for gaskets, valve seats, packings, and other polymer parts. In fluorine, caution would be extended down to the lowest commercial concentrations of 10 %, regardless of pressure. In nitrogen trifluoride, polymer selections would be intermediate, perhaps often being the same as would be used in oxygen. Such common systems of low oxidant severity may require compatible polymers and compatible lubricants in addition to scrupulous cleaning, but not need special consideration of the common metals components.

10.14.2 Most polymers burn in pure oxygen, pure fluorine, and pure nitrogen trifluoride usually violently. They ignite more easily than metals and become the kindling chain that ignites the system. Also. most polymers produce toxic gases when they decompose, which can contaminate breathing gas systems even if there is no external fire, as noted in G 63. Nitrogen trifluoride is not used in breathing gas systems, but generates so much greater quantities of toxic and corrosive gases than oxygen that its fires can present a general environmental toxicity concern. These materials include the many polymers and elastomers used in seats, stem tips, packing, gaskets, seals, and thread sealants in pumps, valves, regulators, filters, instruments, and most other piping components.

> Note 6: The general environmental concern of not only nitrogen trifluoride combustion products which include fluorine gas that may evolve in nitrogen trifluoride combustion is so great that ventilation is usually a significant design consideration. In many cases, but not all, nitrogen trifluoride systems employ hoods and shields through which remote operation of valve and controls is effected. In many cases, commercial “gas cabinets” provide this function. The hoods and shields are typically force-ventilated and the purge gas is fed to an

abatement vessel (See EIGA 92/03) to capture and convert products and raw fluorine.

10.14.2.1 Polytetrafluorethylene (PTFE) and polychlorotrifluoroethylene (PCTFE) are listed by CGA G-4.4 as suitable for oxygen service and are used for many functions in piping components. Yet, even these materials begin to decompose at 200 to 300°C (400 to 600°F) and can ignite at higher temperatures. Both are used to a high degree in comparable nitrogen trifluoride service, and recent test data (**35**) indicate their ignition temperatures are higher in nitrogen trifluoride than in oxygen (also see Note 3).

10.14.2.2 As emphasized in Guide G 63, the successful use of even the best materials depends on the design of the component and where it is used. For example, PTFE-lined flexible hose has a large surface-area-to-mass ratio, and many instances involving the ignition of such hoses with oxygen have been reported (Fig. 4 in G 128). The safe use of PTFE-lined hose in high-pressure oxygen may require special provision in the system design. PTFE-lined hoses are generally avoided (is this true???) in severe nitrogen trifluoride service.

10.14.3 Operating conditions also must be considered in polymer selection. Continuous exposure to elevated temperatures or high oxidant concentrations can change a material into something quite different from what it was when new. With age, the material may become harder, softer, or brittle, or the surface may change. The molecular weight may decrease by scission or increase by cross-linkage. Such changes are accelerated by pressure and temperature and may decrease resistance to ignition and fire, as well as change performance properties. The possibility of nitrogen trifluoride decomposing to yield even low levels of fluorine which can attack all surfaces even at ambient temperature can magnify this risk.

10.14.4 In oxygen at temperatures above the service limits of polymers, these materials sometimes are replaced by graphite, particularly in packings and gaskets. Being pure carbon, graphite will burn in an oxygen–enriched atmosphere. Although difficult to ignite in bulk form, graphite particles from packing wear may ignite more readily. Graphite introduces an additional concern because it is cathodic to most metals and causes corrosion in moist atmospheres. Although oxygen systems are generally dry, external moisture can initiate corrosion which can cause hidden damage. Nitrogen trifluoride is not used in piping systems at elevated temperatures, and exposed carbon would be a target for continuous surface reaction with trace fluorine, and so carbon components would be an unlikely material to be used in nitrogen trifluoride piping systems.

10.14.5 All nonmetals should be tested and evaluated carefully before being used in a particular oxygen or nitrogen trifluoride system application. Guide G 63 presents a systematic approach to selecting nonmetallic materials, with numerous practical examples for oxygen, and it may be used by analogy with nitrogen trifluoride. It includes a compilation of test data for many nonmetallic materials frequently used in oxygen service and there are recent data for nitrogen trifluoride itself available (**35**). Chapter 5 of NFPA 53 also describes the ignition and combustion of materials commonly used in oxygen-enriched atmospheres. Materials that are acceptable for oxygen service are potential candidates for consideration for use in nitrogen trifluoride service, even though many may not prove acceptable and many may require additional care and control and reduced limits of approval.

10.15 *Compatible Metals*

10.15.1 Most common metals will burn in pure oxygen under at least some conditions of pressure and temperature. More likely, they will *all* burn under exposure to severe nitrogen trifluoride service, but depending upon the specific combustion mechanism, some metal/nitrogen trifluoride fires may be less intense than some metal/oxygen fires, and in some cases, diluents (and even some combustion products) may be more effective as a moderator or inhibitor of metal/nitrogen-trifluoride fire than they are for metal/oxygen fire. The most familiar example is cutting steel with an oxygen torch (Fig 5 in G 128). A torch ignites the steel, and then a stream of oxygen keeps it burning. The heat of the burning steel continues the cutting action. The same process can happen accidentally in improperly designed oxygen or nitrogen trifluoride piping systems (Fig 6 in G 128).

10.15.2 Typically the last hazard threshold crossed as the severity of the hazards in an oxidant system increases is that for which compatible metals are required. For common systems at oxygen concentrations at up to 40 % and at pressures below 1 MPa (150 psig), few special materials are required. At higher concentrations and pressures, most users select more compatible metals. In nitrogen trifluoride systems, corrosion concerns often lead to the use of metals that also tend to exhibit better fire performance (corrosion employing many of the same chemical reactions as for combustion). Dilute nitrogen trifluoride systems, at or below atmospheric pressure might require few special metals, but this would be in part dependent upon how they were located and the shielding and ventilation that is present. At high nitrogen trifluoride concentrations and pressures, the use of the most fire-resistant metals similar to those used with fluorine might be employed with many metal selections for the most severe service being Alloy 400, or copper. In the case of nitrogen trifluoride systems, to a greater extent then with oxygen, one must rely on ignition prevention rather than nonflammability, and this is why shielding plays a much greater role in many nitrogen trifluoride systems—because more metals are flammable in nitrogen trifluoride than in oxygen.

10.15.3 NFPA 51 and CGA G-4.4/EIGA 13/02/E mention existing practices for the use of steel or stainless steel for oxygen systems. Historically CGA G-4.4 dealt only with 7 Mpa (1000psig) or less, but the new harmonized CGA G-4.4/EIGA 13/02/E is somewhat more expansive. Further, in regions of high velocity or impingement, such as valves, orifices, branch connections, and other critical areas, copper and nickel based alloys (brass and alloy 400) have been recommended—except for low pressures to 1.4 MPA (200 psig), where selected stainless steels have been used. For operating pressures above 7 MPa (1000 psig) CGA G-4.4 recommended asking the oxygen supplier to provide specific assistance. CGA G-4.4/EIGA 13/02/E has grand fathered these oxygen systems while providing additional guidance. Specific criteria for nitrogen trifluoride systems have not been established but the same practice as for oxygen are often observed.

10.15.4 Metals for nitrogen trifluoride service can be evaluated and selected following the guidance in CGA G-4.4/EIGA 13/02/E and Guide G 94, which provides extensive data on metals ignition in oxygen, guidance for metals selection, and several practical oxygen examples. A recent paper (**35**) offer recent similar, but scant, data that apply to nitrogen trifluoride. Any system that requires special metals to cope with the oxidant hazard also requires special consideration be given to cleaning, lubricants and nonmetals.

10.16 *Isolation and Shielding*

10.16.1 When there is a concern that the hazards of a system can not be controlled to an acceptable level of risk with design, component selection, operating practices, and compatible materials—or when a system can not be modified to improve its compatibility—then isolation or shielding should be considered.

10.16.1.1 Isolation implies that a worst case fire event would be adequately remote from people or valuable materials so that the risk is acceptable. To apply this tactic, work stations may be moved, portions of systems or entire systems may be relocated, or other measures taken to increase the distance between the system and those items whose loss would be unacceptable. This tactic presumes that the loss of the isolated system is an acceptable unavoidable loss.

10.16.1.2 Shielding implies that a barrier can be provided around high-hazard or high-risk systems and that the barrier will contain or deflect a worst-case fire. This tactic also presumes that the loss of the shielded system is an acceptable, unavoidable loss, and in the case of nitrogen trifluoride, that the shielding can contain, ventilate or cleanup any released nitrogen trifluoride as well as toxic fluorine or its combustion products that form.

10.16.1.2.1 At present the only systems that apply this technique routinely in oxygen service are compressors, pumps and some turbo-expanders. Rare high risk valves are also sometime shielded. This machinery often cannot employ the optimum materials, and usually there is so much kinetic energy involved that a mechanical failure produces at least a transient fire. Therefore, such machinery is designed using materials and practices that optimize its reliability and performance to minimize the number of mechanical failures and the fire hazard. In addition, such machinery is shielded to contain any fires that may occur and avoid secondary damages. In nitrogen trifluoride service, these tactics, in combination with positive ventilation, are more common than not and affect not only machinery but often whole systems.

10.16.1.2.2 Simple, inexpensive shields can also be effective. In small high-pressure systems, fires generally occur at components like valves and regulators that are manually actuated and therefore exposed to operating personnel. Mounting such components on a panel provides a simple, yet effective, local shield to protect nearby personnel.

10.16.2 There are no ASTM standards that provide help with the design of shields or adequate isolation distances. CGA, the Department of Defense, NFPA, BG Chemie, and EIGA publications describe some currently used shields.

11. Nitrous Oxide (N_2O)

11.1 *Overview*—Nitrous oxide is less oxidizing than is oxygen but presents a categorically different hazard that oxygen does not. When completely decomposed to oxygen and nitrogen (however, it does not necessarily always completely decompose nor always produce only oxygen and nitrogen) it would produce up to a 33% oxygen-in-nitrogen mixture, a useful first lower-bound approximation of its hazard. However, being an endothermic molecule it also releases a significant amount of energy during the decomposition. It can decompose explosively under some conditions of temperature and pressure even in the absence of any fuel materials. When decomposing as a liquid into gases, the pressures it produces can be extreme. Table 1 lists the heats of combustion of several materials in the series of oxidants of interest here. Because it is a larger molecule with a larger specific heat than is oxygen, it is much less prone to produce high temperatures during compression heating and low temperatures during expansion cooling (ratio of specific heats of 1.28) than is oxygen (ratio of specific heats of 1.397), and also less than fluorine (ratio of specific heats of 1.364). Nitrous oxide supports combustion and explosion of many chemicals. Pure nitrous oxide gas is reported in the EIGA Code of Practice and one MSDS as colorless (**38**) and having a sweet odor and being 1.5 times as dense as air. Liquid nitrous oxide boils at –88.5° C (-127°F), and has a density 1.2 times that of water. Nitrous oxide has a melting point of –90.81°C (-131°F).

11.1.1 *Commercial Uses of Nitrous oxide:*

11.1.1.1 Nitrous oxide is used extensively as an anesthetic, in the electronics industry, as a food additive specifically a propellant, and as a performance enhancer in internal combustion engines.

11.1.2 *Chemical Processes:*

11.1.2.1

11.2 *Production and Distribution*—One published process in the EIGA Code of Practice (among several) has been the principal method for nitrous oxide production in the past and involves a simple thermal decomposition. The common explosive and fertilizer, ammonium nitrate (AN), molten salt with or without enhancers such as mono– or diammonium phosphate at about 130°C cause the ammonium nitrate to break down upon vaporization into nitrous oxide, water and several other chemicals from which the nitrous oxide is purified. Other production methods include reacting zinc with dilute nitric acid or by reacting hydroxylamine with sodium nitrate (**2**). Commercial nitrous oxide is marketed as a liquefied compressed gas or as a refrigerated liquid. It is sold in standard cylinders and tanks at its saturation pressure of about 50 MPa (737 psia) and in low temperature insulated vessels at temperatures as low as roughly –20°C at 18 bar pressure.

11.3 *Hazards and Risks*

11.3.1 The hazards of nitrous oxide are even more subtle than those of oxygen. Although the market for nitrous oxide is much smaller than for oxygen, nitrous oxide has been involved in several serious explosions of cylinders, storage vessels, and tankers, some of which have been deadly. And because of its potential explosive property, shielding and barricading is seldom a realistic safeguard. Notwithstanding, these hazards, the number of these events has not been as large as one might anticipate, because these hazards are effectively controlled by present safety practices.

11.3.2 When an ignition in nitrous oxide occurs (which does not always produce an explosion even at elevated pressures), it behaves much like combustion in oxygen, and the heat release can be directly related to that from combustion in oxygen supplemented with the heat release due to any heat of decomposition that results. The EIGA Code of Practice indicates decomposition to nitrogen and oxygen releases 82 kJ/mol of heat. However, not every material is flammable in nitrous oxide below it explosive decomposition limits but a significant number are and in comparing nitrous oxide to oxygen one series of tests found it to behave as from 44 to 68 percent oxygen in nitrogen depending on the properties of the material (**39**).

11.3.3 Like oxygen and fluorine, nitrous oxide will not tend to react with air or common environmental materials to lose an electron and so is sometimes referred to as a “nonflammable”. But it will react similarly to gain an electron and so it is classed as an “oxidant”. It is referred as “liquefied compressed gas”, “refrigerated liquid”, “liquefied oxidizing gas” and even “refrigerated liquefied oxidizing gas”, but it is capable of reactions that are as hazardous as combustion but in which there is no net gain or loss of electrons. Nitrous oxide is difficult to categorize to the system designer. Nitrous oxide (like acetylene and ozone) is clearly capable of “readily changing (as by decomposing) in chemical composition or biological activity” which is one dictionary’s (**40**) definition of “unstable” but this appellation is usually reserved for high explosive materials that are far more temperamental and unpredictable. As a result, hazard classification groups stress the oxidizing nature of nitrous oxide (the hazard most typically encountered in environmental releases) and does not stress the less often encountered, but nonetheless real, explosive possibility.

11.3.4 The ability of a nitrous oxide-enriched atmosphere to support and enhance combustion after ignition occurs is its most common fire hazard. The risk to people and property that accompanies this hazard is variable. Sometimes the human risk is grave; sometimes the economic risk is severe. In these instances, the need to prevent combustion is strong. Occasionally, the risk is small enough that it can be accepted—and other tactics may be used to minimize the risk. The overall concept of hazard and risk have been lumped into the term “oxidant compatibility”.

11.3.4.1 The ASTM Committee G-4 first codified its interpretation of the concept of “Oxygen Compatibility” in its Standards Technology Training (now Technical and Professional Training) course textbook *Fire Hazards In Oxygen Systems*. By analogy, the concept extends to oxidants, like nitrous oxide, as follows:

> “The ability of a substance to coexist with both oxidant and a potential sources(s) of ignition within the acceptable risk parameter of the user [at an expected pressure and temperature].”

11.3.4.2 In this definition, a system is oxidant compatible if it cannot or is unlikely to burn, if the occurrence of fires is adequately infrequent, or even if potential fires can be isolated and their effects can be tolerated.

11.3.4. Other organizations have a similar respect for the hazards of oxidants in general and nitrous oxide in particular. Oxygen is the most widely used oxidant and is thoroughly overviewed in ASTM G 128, and much of the material there is repeated here for comparison and contrast. Nitrous oxide is much less extensively addressed, but there is material published by ASTM Committee G4, the European Industrial Gases Association (EIGA), the National Institute for Standard and Technology (NIST) (**4**), various vendor Material Safety Data Sheets (MSDS) (**38**) and in assorted technical papers (**41-49**).

11.4 *Sources of Information*

11.4.1 Even though nitrous oxide is less oxidizing than oxygen, and even though incidents are known, the much smaller market for it results in a low total number of incidents. For these same reasons the body of standards and publications that are available that deal with the fire hazard are all small in number. This section will overview what is available, but to a large extent the standards that come to be published to support this abstract standard may well prove to be the first public documents of their kind.

11.4.2 Designing equipment for use with nitrous-oxide-enriched gases relies to a great extent on astute following of certain of the technology used for oxygen. All of the hazard mechanisms that apply to oxygen also apply to nitrous oxide and most of the information and test data available for oxygen have at least indirect pertinence for nitrous oxide systems. Correlating these practices is still a challenge. Book-learning is highly worthwhile and practical in coping with both the oxygen and nitrous oxide hazards, and hands-on experience is worthwhile but not critical.

11.4.3 This standard is the first in the ASTM system to overview the nitrous oxide hazard. But there are experimental data available in a limited number of technical papers and are listed along with the vastly larger body of oxygen papers in the ASTM Committee G-4 Reference Bibliography.

11.4.4 Commercial sources of nitrous oxide have published MSDSs and one was consulted in preparing this standard. EIGA has published a Code of Practice, and it was also reviewed.

11.5 *Causes of Fires in Nitrous Oxide*

11.5.1 Although accident investigations for nitrous oxide incidents are largely anecdotal, such events are known to have happened. Of the several events known to have occurred, they have apparently been due to such things as mechanical failure that produced mechanical impact and initiated decomposition and explosion of liquid nitrous oxide, welding on a vessel containing liquid nitrous oxide leading to decomposition and explosion, overheating of associated machinery, and environmental fires when nitrous oxide leaked in enclosed spaces (closets) and area materials became ignited in the enriched atmosphere. There are few other types of incidents known of but that may be due more to the small size of the market than due to a low hazard. However, virtually every fire mechanism known to exist for diluted oxygen applies also to nitrous oxide in theory. The mechanisms cited for oxygen in the current G 128 and G 88 are also cited here along with others and elaborated upon. The order cited is slightly different than those used in G 88-05 and G 128-95.

11.5.2 Kindling Chain. Ignition often starts with a small generation of heat, that grows and amplifies itself and shifts from one behavior to another and another, involving other materials and mechanisms, until it is in a runaway condition— a self sustaining fire. The material that is most flammable that initially responds to the first heating in this sequence of events or “chain” is the “tinder” or “kindling’. Numerous mechanisms, specifically ignition mechanisms, can provide for the first small (and some times not so small) generation of heat.

11.5.3 Ignition Mechanisms. Fires in nitrous oxide require an initial source of energy as is also the case with fires in oxygen, but to a significant extent these sources do not seem to be self-produced to nearly the same degree. Nitrous oxide is much less reactive then oxygen even in the presence of moisture. It is much less corrosive than oxygen and appears less likely to experience low level reactions that bootstrap themselves upward in temperature. Incident histories are not adequately documented or numerous to reliably rank ignition causes for the many potential ignition mechanisms.

11.5.3.1 Autogenous Ignition (Autoignition). Ignition temperatures are not published for materials in nitrous oxide, and an important temperature is likely to be the decomposition temperature, which may be on the order of the normal ignition temperature for materials in dilute oxygen. And when decomposition begins, intense gas heating and heat transfer to materials is likely to result, very possibly igniting nonmetals in the resulting decomposed nitrogen/oxygen mixture. In spite of the heat of decomposition that may be released to facilitate combustion, there are no data to suggest and it is unlikely any common metals would burn in nitrous oxide. Some papers refer to this type of ignition that occurs when a material is heated in oxidant to be “thermal ignition”, but that is not common usage of the term. Since nitrous oxide breaks down to release oxygen and nitrogen at elevated temperatures, one might expect ignition in nitrous oxide to perhaps relate to ignition temperatures of polymers in oxygen for those materials that ignite in oxygen.

11.5.3.2 Thermal (Spontaneous) Ignition. Thermal ignition is commonly taken to be when a material reacting at a low rate is capable of heating itself to the autogenous ignition point of 11.5.3.1. In oxygen the most commonly cited cases of thermal ignition are the spontaneous fires that occur (1) when linseed oil soaked rags are piled up, and (2) when machinery such as compressors are run in on nitrogen or other nonreactive gas producing wear-dust debris and then converted to oxygen service. In each case, there is a high surface-area-to-volume insulating-pile situation that allows low level reactions to self-heat and produce a kindling chain. Nitrous oxide should be much less reactive under these conditions than oxygen, and there are no known incidents involving a self-heating reaction like this. However, nitrous oxide in the presence of metal fines, carbon fines and also normally flammable materials may still react intensely if an ignition source is applied.

11.5.3.3 Particle Impact. Particles present or generated in nitrous oxide systems carry the same risk of ignition as in oxygen systems. Upon impact (and perhaps due to spontaneous self-reaction) these particles may ignite and serve as tinder in a kindling chain.

11.5.3.3.1 Nitrous oxide systems should not commonly generate reaction particles/powder during service (as is the case for fluorine).

11.5.3.4 Pneumatic Impact or Compression Heating. Because nitrous oxide has greater heat capacities than oxygen, it does not heat as much in rapid (near-adiabatic) compression for comparable starting and finishing pressures (**4**), and because nitrous oxide is shipped as a saturated liquid, at a pressure of only about 50 MPa (737 psia) the maximum pressure – ratio increase it can produce is much smaller than for oxygen from a full cylinder. The result is a much smaller peak final temperature and lower heat transfer. Indeed, few if any incidents in oxygen attributed to rapid pressurization have occurred at final pressures near these levels. However, because nitrous oxide can decompose with a release of heat and pressure, this effect can still be an important design consideration. Explosive or slow decomposition can be a serious incident whether or not it leads to the ignition of other system materials.

11.5.3.4.1 Adiabatic compression processes for nitrous oxide in relation to other gases are reviewed in a recent tutorial (**32**), and NIST software allows for estimation of peak adiabatic (isentropic) compression temperatures and heat transfers of numerous real (as opposed to ideal) gases including nitrous oxide (**4**).

11.5.3.5 Mechanical Impact. There is anecdotal experience to suggest at least one serious incident in nitrous oxide resulted from mechanical impact under liquid, leading to explosive decomposition. However, there does not appear to be any significant amount of data using mechanical impact test procedures.

11.5.3.6 Friction and Galling. Gross friction, as can occur in machinery rubs and the like is such a compelling source of heat and particles that it must always be taken as a viable ignition source. However, low-level friction and galling in nitrous oxide is not likely to produce bulk material ignition, but here again, there are few data that allow one to rule out the initiation of a nitrous oxide decomposition reaction. The anecdotal record includes at least one machinery-induced incident, but there are numerous compatible lubricants that would tend to minimize low-level friction and galling effects.

11.5.3.7 Resonance. Resonance tends to produce its most intense heating at high flows, something that is more likely to present in high pressure systems than in nitrous oxide systems (due its much lower saturation pressures). However, resonance ignition can not be completely ruled out and there do not appear to be experimental data to help clarify this issue.

11.5.3.8 Static Electric Discharge. There are no static electricity measurements reported in the literature for nitrous oxide flows. However, in some oxygen systems static electricity has been greatest in insulating systems (polymer-lined hoses) rather than in conductive systems. Polymer–lined hoses are very attractive for nitrous oxide service and, compatible polymers are available. Here again, particles can magnify the formation of charge separation, but nitrous oxide systems should have few systemic particles. Whether static discharge is capable of initiating explosive decomposition is unknown, but there do not appear to be any incidents attributed to this mechanism nor for reaction of polymer-lined hose.

11.5.3.9 Electric Arc. Electric arcing is a highly effective method of igniting materials in most oxidants and has when welding is attempted on pressurized oxidant systems. It should be similarly hazardous on nitrous oxide systems, and has been involved in one particularly serious vessel event in the anecdotal record. However, this scenario is one which can only be prevented by good operating practices that prevent such welding operations.

11.5.3.10 Flow Friction. Flow friction is a speculative mechanism used to explain incidents that resist all other forms of explanation. It is analyzed as waves of motion that occur during gas flow over polymers that produce internal friction processes that might heat polymers to the ignition point (**33**). Lab experiments to date to demonstrate it in oxygen systems have not been successful. They have produced heating but not ignition. Flow friction should be no more of a hazard in nitrogen/oxygen than mixtures that result from decomposed nitrous oxide, but may be important as a means to initiate the decomposition.

11.5.3.10.1 "Flow friction" should be less aggressive as a heating mechanism in nitrous oxide than in oxygen due to the lower pressures present. It is difficult to say whether flow friction is an important concern. However there do not appear to have been any anecdotal incidents that might be attributed to this mechanism in the past.

11.5.3.11 Fresh Metal Exposure. Many believe that every surface that is exposed to an oxidant will experience some degree of initial surface reaction that is likely to be much less in nitrous oxide than in more reactive oxygen. In oxygen bulk specimens of fresh titanium surface exposed to oxygen have ignited, but otherwise, ignitions have only been observed in piles of fines. This mechanism is not likely to be effective in nitrous oxide and there are no known documented or anecdotal incidents in nitrous oxide that are attributed to this mechanism.

11.5.3.12 Decomposition. Nitrous oxide is an endothermic molecule that can be exothermically decomposed to release oxygen under the influence of heating. There is an extensive discussion of the mechanism and its risky circumstances in other references (**41,43,47**). However, neither literature nor the anecdotal record cite any higher endothermic molecules incorporating nitrous oxide (ala ozone which incorporates oxygen).

11.5.3.13 Other Ignition Mechanisms. Other mechanisms can not be ruled out, but none are speculated upon in the available literature.

11.6 **Hazards**

11.6.1 *Recognized hazards.* Nitrous oxide is extremely dangerous because of the potential consequence of it ability to explosively decompose, but although such explosions have occurred, they appear to have been the result of rare failures or grossly dangerous practices, and the prevention of such events appears to be relatively straightforward to achieve. Nitrous oxide has not shown any temperamental tendencies. Nonetheless, in comparison to oxygen, every fire hazard known to use of dilute oxygen/nitrogen mixture (with only rare exception) is a similar or greater hazard to nitrous-oxide use. Potential hazards of oxygen use may be observed in corresponding nitrous-oxide systems. These include (1) nitrous oxide concentration and associated diluents, (2) pressure, (3) temperature, (4) phase, (5) velocity. (6) time and age, (7) mechanical failure.

11.6.1.1 *Nitrous Oxide Concentration and Associated Diluents.* Higher nitrous oxide concentrations increase the hazards of ignition and fire intensity because more nitrous oxide is present to mix with the fuel. Diluents are as important as they are for oxygen systems. Nonreactive diluents that have large molecular size (larger than nitrous oxide) are more effective at attenuating flammability (however keep in mind that nitrous oxide is a large molecule itself and therefore many diluent gases that would lower the risk in mixture with oxygen are in comparison smaller than nitrous oxide and might act to increase the hazard in mixture with it). In oxygen systems even tenths of a percent of diluents can be important, but whether a similar extreme effect for trace diluents is operative in nitrous oxide is unlikely, and this may be reflected by the apparent lack of flammability of many common metals in nitrous oxide.

11.6.1.2 *Pressure.* Higher pressures also increase the hazards of ignition and fire intensity. Pressure increases the density of the gas, with the same effect as increasing the concentration: more nitrous oxide is available to the fuel, so materials ignite easier and burn faster. Pressure also increases the gas velocity at restrictions such as valves, regulators, and intersections—which increases friction, particle impact, and compression heating. Nitrous oxide which is shipped as a saturated liquid is also easy to condense downstream in gas systems due to its strong refrigeration effect during expansion, and liquid may commonly occur downstream of pressure drop points, such liquid of which may become trapped and upon warming produce unanticipated elevated pressures in the gas service there or conceivably could even become trapped as a warming hydraulic liquid and produce relatively enormous pressures.

11.6.1.3 *Temperature.* Like oxygen, practical use temperatures have little affect on the reactivity of nitrous oxide, unless temperatures approach those for decomposition. As for oxygen, any high temperature can accelerate aging of polymers and thereby reduce their compatibility with nitrous oxide.

11.6.1.4 *Phase.* Nitrous oxide liquid is present in most supply systems and can easily condense for some distance downstream of the supply system. Therefore, the base of liquid-phase experience is nearly as large as for the gas. Its behavior and risks as a liquid include the risk of explosive decomposition that is not present with liquid oxygen.

11.6.1.5 *Velocity.* Increased nitrous oxide velocities in flowing systems lead to higher particle velocities, which increase the likelihood of ignition by particle impact. Particles in nitrous-oxide systems should be no more and presumably much less numerous than in oxygen systems “Flow friction” which is speculated but unproven as an ignition mechanism in oxygen, is an uncertain risk in nitrous oxide systems, and to the extent that it poses risk, the risk may be more likely due to the prospect of explosive decomposition than polymer ignition.

11.6.1.6 *Time.* Time and age are important hazards. However the base of experience suggests the role of time on nitrous oxide system fire risks is relatively low.

However, nitrous oxide is among a number of chemicals (like carbon dioxide) that can enter pores or dissolve into polymers over time and produce excessive "swelling" or "inflation" of the polymers when pressure is reduced, leading to a series of undesirable mechanical failures.

11.6.1.7 *Mechanical Failure.* The same mechanical and other failures (11.6.1.6) that jeopardize oxygen systems also threaten nitrous-oxide systems. These include impact of broken parts, rubbing, particle generation, failed seals, etc (indeed one serious explosive decomposition incident in the anecdotal record is attributed to this mechanism). There are no present data on the risk of friction or galling as initiators of explosive decomposition. Indeed, in oxygen service, the components (namely oxygen compressors and pumps and occasional high-risk valves) most at risk of failure and therefore most likely to experience fires are often placed behind barriers, because their reliability can not be made sufficiently high to address the risk to life and injury otherwise. (Are barriers commonly used it nitrous oxide machinery?) Barriers for nitrous oxide safeguards must be designed for any additional energy that can result from explosive decomposition. To date, it does not appear the use of barriers has been necessary in most common piping systems.

11.7 *Fire Prevention*

11.7.1 G 128 patterns the approaches to preventing fires in oxygen to those used for preventing fires in air. The following sections will pattern the approach for nitrous oxide fire to those for oxygen fires. In each there is a gradation of steps taken with greater numbers and more extensive use depending on the severity of the situation.

11.7.2 In oxygen systems there is always an oxidant (oxygen) present, often there is fuel present (in the materials of the system itself), and sometimes there are ignition mechanisms present (heat of compression, particle impact, etc). So in oxygen systems there is effort to pick the best materials possible and to minimize the number and intensity of ignition sources.

11.7.3 As for oxygen, depending on the nitrous oxide mixture present in a system, there are progressively stringent measures applied in the order cleaning, compatible lubricants, compatible polymers and other nonmetals, and compatible metals.

11.7.4 In many, perhaps most, nitrous oxide systems, only three of the previous tactics will be applied and there will usually be no additional protective measures taken in terms of barriers, but there may be extra care taken in venting and ventilation, and the like.

11.7.5 Recognizing, identifying and controlling potential sources of ignition and possible causes of fires in nitrous oxide is not simple. Present knowledge does not enable us to identify all possible ignition sources. Hence few nitrous oxide systems can enjoy a certainty that fires are not possible. There is a strong empirical influence in the approach to oxygen safety that is present also in nitrous oxide safety. To a large extent, one does what has been successful in the past, provided it has been successful often for long periods of time, and is based on sound principle. For this reason ASTM G-4 standards take a multi-pronged approach that attempts to align as many factors as possible toward reducing the likelihood of ignition and fire.

11.7.6 This approach is based on using the extensive body of information available on the ignition and flammability of materials and methods with demonstrated ability to reduce the number and severity of fires in oxygen with adjustments to it based on the known properties and behavior of nitrous oxide. Guides G 63, G 88 and G 94 as well as Practice G 93, describe the many factors affecting oxygen and oxygen-enriched systems and describe how to reduce the hazards associated with these systems. These same guides are often taken as a starting point for nitrous oxide systems and are then expanded upon. With nitrous oxide in some cases much less stringent practices may be followed, but in others more stringent practices may be needed.

11.7.7 ASTM G-4 and other resources correlate control of oxidant system hazards with special attention to (1) system design; (2) component selection; (3) operating procedures; (4) cleaning; (5) passivation; (6) compatible lubricants; (7) compatible polymers and other nonmetals; (8) compatible metals; and (9) isolation and shielding. Each of these approaches is discussed in more detail below.

11.8 *System Design*

11.8.1 Oxygen and nitrous oxide system design should not be undertaken casually—these systems require careful and specialized design considerations. The first and most important rule is: Consult an expert! Guides G 63, G 88, Practice G 93 and Guides G 94 and G 128 define “Qualified technical personnel” and provide vital information for use by these experts. Indeed, in many companies, individuals are designated as specialists to acquire the expertise and assist others in oxidant system design.

11.8.2 System design for any oxidant should begin with the same mechanical principles as conventional air or gas system design and follow the same nationally recognized codes and standards—there are no special codes that mandate how to design oxidant systems. The added hazards inherent in the use of oxidants should then be evaluated to modify conventional practices while still conforming to appropriate requirements. In general that leads to a more—not less—conservative design. Nitrous oxide system designs can usually be approached as variants of similar oxygen system designs that (unless barricaded or isolated) also meet or exceed the compatibility measures that would be taken with oxygen mixtures.

11.8.3 The severity of system operating conditions is defined similarly to those for oxygen. Concentration, pressure, temperature, phase, and time are all crucial. As these factors increase, the risk increases, and the system design must be modified to a greater extent. Nitrous oxide concentration and phase are established by the system function. But the others can be influenced by the system design. For example pressure can be reduced with a regulator as close to the gas source as possible to minimize the hazard (and most nitrous oxide systems have a regulator right on the source cylinders). Temperatures can be limited, for example by including protection from runaway heaters (this can be important since nitrous oxide regulators may contain electrical heaters to help offset the refrigeration and condensation that can occur downstream upon throttling of many saturated gases). The effects of time and age can be mitigated by designing for effective preventive maintenance.

11.8.3.1 Velocity is a hazard that is controlled primarily by overall system design. Line sizes should be selected to limit nitrous oxide gas velocity. There are no adopted velocity criteria for nitrous oxide systems but existing guides for oxygen systems may suggest an upper limit and may be adjusted downward when needed and when possible. Rules applied to oxygen systems as to abrupt line size changes, locations of intersections and risk of particle impingement and compression heating in certain geometries are all applicable to nitrous oxide systems near polymers and perhaps elsewhere, as well. As for oxygen, one reduces velocity and upgrades the fire resistance of nitrous oxide system materials wherever needed to cope with velocity and particle hazards. However, with nitrous oxide many metals are considered nonflammable and the control of velocity is as much to prevent explosive decomposition as to prevent material fires.

11.8.4 Additional considerations as reviewed in the remaining sections are integrated into the design of a nitrous oxide system. Care beyond that normally accorded oxygen systems is seldom required, but can be. The initial cleanliness of an oxygen system is established as the components are built and the system fabricated, and it is crucial to prevent contamination during the system's life.

11.8.5 Specific guidance on nitrous oxide system design itself is found in the various vendor's Material Safety Data Sheets and an EIGA Code of Practice on nitrous oxide. However, oxygen design materials such as Guide G 63, CGA G-4.4, EIGA 13/02/E, NFPA 50 and 51, and many others provide excellent guidelines for system design that can be considered by analogy in the design of nitrous oxide systems, although these references are not handbooks. This includes material in the ASTM G-4 Committee Technical and Professional Training Course Controlling Fire Hazards in Oxygen Systems which teaches the fundamentals of oxygen safety for oxygen process designers and equipment specifiers and includes a textbook.

11.8.5.1 Many references on oxygen hazards are cautious and explicit about the use of their data, and this caution is worthwhile to apply to other data and other oxidants such as nitrous oxide. For example, Praxair Publication L-5110N warns:

> "This publication is not a design handbook and does not relieve the user from exercising competent engineering judgment or using qualified professional personnel who can tailor your design to your specific situation.
>
> "In situations where qualified people are not available locally to design the system, obtain professional assistance from a competent source. If the oxygen supplier can not offer assistance, he should be able to direct you to a consultant who can provide the necessary service. Remember that design of oxygen systems requires specialized knowledge. Liability problems associated with improperly designed systems can far outweigh the cost of professional services."

11.9 *Component Selection*

11.9.1 ASTM Committee G-4 standards do not recommend specific products. Indeed, they are disclaimed as specifications. Further, their nature is not such that products can be marketed under a blanket claim of meeting any of the four applicable oxygen standards (G 63, G 88, G 93, or G 94) and this applies equally to nitrous oxide systems as well. Clearly the thrust of these standards is to enable evaluation of system needs in the context of a particular application. As the application changes, such as exposure to higher pressure, a host of conditions change—or hazard thresholds are crossed—that may render previously accepted products unacceptable for further use. Therefore, although there may be a few products that are acceptable in any and all oxygen applications, one can not consider products to be "approved for oxygen or any other service" under the procedures of these standards without also specifying the conditions for which the approvals are intended.

11.9.2 Some products are marketed for nitrous oxide service, but not every experienced designer agrees that every one of these products has adequate nitrous oxide compatibility or even that a blanket approval is reasonable. Some companies do list materials that are approved across the board, but many others tie approval to specific applications and level of application hazard. It behooves the user to determine whether the properties of the particular products (whether or not they are marketed for nitrous oxide service) actually meet the needs of the user's application.

11.9.2.1 Performance tests conducted by hardware manufacturers generally do not simulate any specific application. Laboratory tests can not duplicate the endless variety of actual operating conditions; such tests only indicate a predicted result in a controlled laboratory setting and cannot assure the same result in a particular application or service.

11.9.2.2 Material qualification tests are also method specific and rarely afford blanket approval. The user should evaluate the material test results along with the test method to determine if they correspond to the way the material will be used in a specific design.

11.9.3 It is also important to note that most common industrial components—such as valves, fittings, filters, regulators, gages, and other instruments—are not designed for specific applications. Rather, they are versatile, general purpose products that can be used properly in many types of applications and systems. Hardware manufacturers in general have neither the experience nor expertise to select the most appropriate components for a specific use, such as a nitrous-oxide system. Only the nitrous-oxide system designer or user can have full knowledge of the entire system and each component's function, which must be considered when selecting the system components. Nitrous-oxide system designers and users both must be sensitive to product function, material compatibility, adequate ratings, and proper installation, operation, and maintenance.

11.9.4 Valve selection requires special attention by the system designer, because valves are one of the few mechanical items that are actuated routinely while the system is in use. The designer must determine the type of valve, its location, how it will be operated, and—often neglected— how it might be operated incorrectly.

11.9.4.1 Particular attention should be directed to valve pressure and temperature ratings, internal materials of construction, and how readily the valve can be cleaned and kept clean. Valves often are selected with higher ratings, greater wall thicknesses, and more fire resistant materials than the rest of the system because they are exposed to more severe service conditions.

11.9.5 As valves are opened and closed they almost always generate localized high velocities near the valve seat or immediately downstream. This creates a local increase in the hazard level at the valve location and often requires that special consideration be given to the selection of seat materials and potential impingement areas nearby.

11.9.5.1 Nitrous oxide system valves also pose a more serious risk of personal injury, because many are opened and closed manually—so that at the very moment they are most susceptible to the conditions that can cause a fire, someone's hand is on them. The risk of fire and of the fire breeching metal components is much smaller with nitrous oxide than with oxygen, but there is the potential for explosive decomposition, and even fragmentation, in some systems. The former do not require shielding or remote operators, and the latter would be difficult to protect against so that valve handles are seldom shielded.

11.9.5.2 Oxygen Guides G 88, CGA G-4.4/EIGA 13/02/E, and NFPA 51 unanimously emphasize that valves must be opened slowly. Opening speed is controlled by valve design, as well as by operating procedures. Ball, plug and butterfly valves are used in some low-pressure systems such as pipelines, because their straight-through design provides a lower pressure drop than a globe valve. However, ball and plug valves are quick-opening and create high velocity when opened, whereas needle valves are designed to open slowly (Fig. 3 of G 128). If a full-flow valve is used in a high pressure service, the piping system must be designed carefully to equalize the pressure across the valve before it is opened.

11.9.5.3 Even while closed, valves require extra consideration. Valves used in gas service often have seats or stem tips made of polymers that are exposed to the system fluid when the valve is closed. They can be subject to impingement from high velocity generated by another component upstream, and thus become a potential ignition point. In the case of nitrous oxide valves, intense refrigeration at valve seats can distort them and make sealing a problem. In some cases heaters are used when upstream conditions are saturated, in some cases metal-to-metal seats are used and in many cases polymers that have good low temperature properties are used. Polymers may also be exposed to liquid nitrous oxide which may diffuse into porous polymers or cracks or crevices and become a source of hydraulic pressure and swelling upon warming or depressurization.

11.10. *System Operation*

11.10.1 Nitrous oxide appears to experience ignition at a less frequent rate than oxygen but can produce extreme damage if explosive decomposition occurs. In these cases of greater consequence, nitrous oxide warrants more care than oxygen in both the system design and the cautions employed by system operators. However, in most other cases, care comparable to that used with oxygen is appropriate. Perhaps the most neglected aspect of controlling oxygen systems hazards involves system operation. Oxygen fires frequently are caused by systems whose safe operation depend so greatly on the operator's strict adherence to certain procedures that they can not tolerate simple human error. In these poorly designed systems, a single mistake—such as actuating one of a series of valves in the wrong sequence—can lead to a catastrophe. G 128 cites (in its sections 15.1.1 through 15.4) and reviews example events documented in the ASTM video adjunct entitled, *Oxygen Safety*, that illustrate several design errors that invited and then compounded operator errors, causing serious accidents.

11.10.1.1 In both examples rapid compression led to ignition. In one an operator was supposed to open a ball valve, then slowly pressurize a downstream system with the valve on an adjacent cylinder, but instead left the ball valve closed until the cylinder valve was open, then shocked the downstream system. Other episodes with ball valves were similar. All of the events could have been prevented with more cautious system operation.

10.10.1.2 In current commercial nitrous oxide systems the highest source pressures would not produce high temperature remotely approaching those produced by oxygen (attenuated by the higher specific heats of nitrous oxide). The maximum potential heat transfers during rapid pressurization would typically be smaller (**32**).

11.10.2 Therefore, as noted in the *Oxygen Safety* video adjunct, thorough planning and careful monitoring of operating procedures and maintenance practices are important in oxidant fire prevention. However, safe operation should be engineered into the design of an oxygen system—by the selection and placement of components—and not rely solely on operator compliance with procedures to prevent oxygen fires. As noted in G 88 Section 7.19.4 "Avoid Overly Complicated Procedures" one must remember that complex and repetitive procedures are more prone to discrepancy than simple straightforward procedures. Since human error is difficult to prevent, in crucial systems, automation may be required to achieve reliable system operation.

11.11 *Cleaning.*

11.11.1 A nitrous oxide system requires cleaning comparable to that of an oxygen system. Cleaning is the first measure required, even though it may be the last step accomplished in preparing a system for oxidant service. Any such system typically must be evaluated carefully for cleanliness, and most will be cleaned scrupulously. In fact, the extent of cleanliness used on a system exposed to dilute nitrous oxide may be very similar to that applied to pure oxygen high pressure systems.

11.11.2 Organic particles and fine particles burn violently in concentrated oxidant and are often the beginning of the kindling chain that starts a fire. Hydrocarbon oil or grease contamination is particularly undesirable. In mild applications, inert particles may be removed less scrupulously. A mild nitrous oxide exposure may not be subject to any other requirements, but its cleanliness should always be a concern.

11.11.2.1 The basis for determining the oxidant concentration and pressure at which more scrupulous cleaning is needed should be related to the flammability of the contaminants, lubricants, polymers, and metals. If the contaminants are unidentified, one must assume they may be flammable and therefore must be eliminated at even a small increase in oxidant concentration or pressure.

11.11.3 Cleaning methods used with oxygen systems are often applied to other oxidant systems including nitrous oxide systems and should be evaluated and selected by analogy following the guidance contained in Practice G 93, CGA G-4.1, EIGA 33/86/E, and Praxair GS-39. Practice G 93 provides special guidance for cleaning components in its Section on Interferences.

11.11.3.1 *Disassembly:*

11.11.3.1.1 It is imperative that oxidant systems be cleaned as individual articles, preferably prior to assembly. Assembled systems must be disassembled for cleaning if construction permits. Flushing an assembled system can deposit and concentrate contaminants in stagnant areas.

11.11.3.1.2 Manufactured products (for example valves, regulators, and pumps) should preferably be cleaned by the manufacturer prior to final assembly and test. The purchaser should approve the cleaning procedure and packaging to ensure that they satisfy the system requirements.

11.11.3.1.3 Manufactured products that are cleaned by the purchaser must be disassembled for cleaning if the construction permits. The purchaser should follow the manufacturer's instructions for disassembly, inspection for damage, reassembly, and testing.

11.11.4 Practice G 93 contains additional information on cleaning methods, hindrances to effective cleaning, packaging, and inspection, including examples of specific applications.

11.12 *Passivation.*

11.12.1 Since the room temperature reactivity of nitrous oxide is even less than that of oxygen, and because corrosion is so low in nitrous oxide, passivation is generally not practiced on these systems. Perhaps only in the case of machinery that is run in on inert gases, might passivation be performed. In this case, if it were to be performed, one would probably not use nitrous oxide as the passivating gas. Instead, for the same reasons that fluorine is used to passivate nitrogen trifluoride systems, one would probably elect to use oxygen to passivate fines in a nitrous oxide system.

11.13 *Compatible Lubricants*

11.13.1 If cleanliness is the first special measure that is necessary, the next concern is with lubricants, for two reasons (*1*) the most common oils and greases are hydrocarbon, which are among the materials most necessary to remove from an oxidant system; and (*2*) they are fluids and pastes, which are more prone to migrate and collect than are solid materials.

11.13.2 Any lubricants reintroduced into a system cleaned for oxidant service should be selected to be fire resistant. In most instances, even with mild oxidant exposures at low pressures and at low oxidant concentrations (as low as 25% oxygen in nitrogen or argon), fire-resistant lubricants or other fluids are used, and the same practice would apply to nitrous oxide and its mixtures.

11.13.2.1 Several halogenated oils and greases have been tested and used widely with success in oxygen service. Oxygen manufacturers can be consulted regarding appropriate lubricants for specific applications, Guide G 63 includes test data on many lubricants, thread compounds, seats and gaskets. Praxair L-5110N lists lubricants that manufacturer has used for low pressure systems. Specifications MIL-G-27617, MIL-G-47219 (MI), DOD-L-24575 (SH), and KSC 79K22280 may also be consulted for choosing analogous nitrous oxide-compatible greases and lubricants.

11.13.3 Practice G 93, Section on Interferences, provides special guidance for lubrication of components.

11.13.3.1 *Lubricants*

11.13.3.1.1 Mechanical components are normally assembled with lubricants on seals, threads, and moving surfaces. The manufacturer should be consulted to determine the kind of lubricant originally used on the article to ensure that the cleaning solutions and methods selected are effective in removing the lubricant and will not damage the component.

11.13.3.1.2 When used, nitrous oxide compatible lubricants should be selected. In some cases, lubricants can be evaluated as they would be for oxygen service using the methods of G 63 and treating pure high-pressure nitrous oxide with the same concern that would apply to pure high-pressure oxygen, and treating the more dilute mixtures of nitrous oxide as one would treat air. In time more specific guidance should be developed. The component manufacturer should also be consulted to ensure that the selected lubricant provides adequate lubrication for component performance. Oxidant compatible lubricants often have markedly different lubricating properties from conventional lubricants.

11.13.4 Scrupulous cleaning combined with the use of fire-resistant lubricants may be the only special precautions needed in moderate services. Until more precise recommendations are published, lubricants should be evaluated and selected following the guidance contained in Guide G 63. However, all lubricants should be used sparingly and with great caution.

11.14 *Compatible Polymers and Other Nonmetals*

11.14.1 As the severity of the hazards (such as higher pressure, temperature or oxidant concentration) increases to elevate system operating conditions above the level at which both cleaning and compatible lubricants are necessary, the next hazard threshold crossed is that of compatible polymers. Polymer use is common in nitrous oxide, however, extra mechanical consideration is need in cases where there is refrigeration occurring. In oxygen, at room temperature and low pressures—below about 350 kPa (50 psig)—and at oxygen concentrations between 30 and 100 %, most users switch to more fire-resistant polymers for gaskets, valve seats, packings, and other polymer parts. In nitrous oxide, polymer selections would be virtually the same as would be used in oxygen, but additional latitude would be acceptable in some cases. Such common systems of low oxidant severity may require compatible polymers and compatible lubricants in addition to scrupulous cleaning, but not need special consideration of the common metals components (but keeping in mind that where refrigeration downstream of pressure drops occurs, embrittlement of some metal and polymer materials may be a problem).

11.14.2 Most polymers burn in pure oxygen, usually violently, but fewer of them burn in nitrous oxide. They ignite more easily than metals and become the kindling chain that ignites the system. Also, most polymers produce toxic gases when they decompose, which can contaminate breathing gas systems even if there is no external fire, as noted in G 63. Nitrous oxide is used extensively in breathing gas systems (anesthesia machines), and toxic combustion products are a concern, but the frequency of fires that has been observed is so much less than for oxygen systems that combustion product formation is a real possibility but a low probability risk. These materials include the many polymers and elastomers used in seats, stem tips, packing, gaskets, seals, and thread sealants in pumps, valves, regulators, filters, instruments, and most other piping components.

Note 7: Venting and ventilation of nitrous oxide can be necessary to avoid the health effects of nitrous oxide itself as much or more than to cope with combustion products.

11.14.2.1 Polytetrafluorethylene (PTFE) and polychlorotrifluoroethylene are listed by CGA G-4.4 as suitable for oxygen service and are used for many functions in piping components. Yet, even these materials begin to decompose at 200 to 300°C (400 to 600°F) and can ignite at higher temperatures. Both are often used in nitrous oxide service.

11.14.2.2 As emphasized in Guide G 63, the successful use of even the best materials depends on the design of the component and where it is used. For example, PTFE-lined flexible hose has a large surface-area-to-mass ratio, and many instances involving the ignition of such hoses in oxygen have been reported (Fig. 4 of G 128). The safe use of PTFE-lined hose in high-pressure oxygen may require special provision in the system design. PTFE-lined hoses are often used in nitrous oxide service up to the normal room temperature saturation condition present in cylinders.

11.14.3 Operating conditions also must be considered in polymer selection. Continuous exposure to elevated temperatures or high oxidant concentrations can change a material into something quite different from what it was when new. With age, the material may become harder, softer, or brittle, or the surface may change. The molecular weight may decrease by scission or increase by cross-linkage. Such changes are accelerated by pressure and temperature and may decrease resistance to ignition and fire, as well as change performance properties. The effects of nitrous oxide to cause aging are believed to be slight in this aspect. However, the tendency of liquid nitrous oxide to form downstream of certain pressure drops can lead to components being saturated with liquid which can yield a more explosive form of combustion or can lead to swelling and other mechanical failure mechanisms.

11.14.4 In oxygen at temperatures above the service limits of polymers, these materials sometimes are replaced by graphite, particularly in packings and gaskets. Being pure carbon, graphite will burn in an oxygen–enriched atmosphere. Although difficult to ignite in bulk form, graphite particles from packing wear may ignite more readily. Graphite introduces an additional concern because it is cathodic to most metals and causes corrosion in moist atmospheres. Although oxygen systems are generally dry, external moisture can initiate corrosion which can cause hidden damage. Nitrous oxide is not used in piping systems at elevated temperatures to specifically avoid dangerous explosive decomposition and so carbon for high temperatures would be an unlikely need.

11.14.5 All nonmetals should be tested and evaluated carefully before being used in a particular oxygen system application. Guide G 63 presents a systematic approach to selecting nonmetallic materials, with numerous practical examples for oxygen, and it may be used by analogy with nitrous oxide. It includes a compilation of test data for many nonmetallic materials frequently used in oxygen service. Chapter 5 of NFPA 53 also describes the ignition and combustion of materials commonly used in oxygen-enriched atmospheres.

11.15 *Compatible Metals*

11.15.1 Most common metals will burn in pure oxygen under at least some conditions of pressure and temperature. Few if any common metals are considered flammable in nitrous oxide. Assorted carbon steels, stainless steels, brass, copper, copper alloys and aluminum are all in current use. The most familiar example is cutting steel with an oxygen torch (Fig 5 of G 128). A torch ignites the steel, and then a stream of oxygen keeps it burning. The heat of the burning steel continues the cutting action. The same process can happen accidentally in improperly designed oxygen piping systems (Fig 6 of G 128). This process should not be possible with nitrous oxide for all common engineering metals.

11.15.2 Typically the last hazard threshold crossed as the severity of the hazards in an oxidant system increases is that for which compatible metals are required. For common systems at oxygen concentrations at up to 40 % and at pressures below 1 MPa (150 psig), few special materials are required. At higher concentrations and pressures, most users select more compatible metals. Much more latitude than this is acceptable with metal components in nitrous oxide.

11.15.3 NFPA 51 and CGA G-4.4/EIGA 13/02/E mention existing practices for the use of steel or stainless steel for oxygen systems. Historically CGA G-4.4 dealt only with 7 Mpa (1000psig) or less, but the new harmonized CGA G-4.4/EIGA 13/02/E is somewhat more expansive. Further, in regions of high velocity or impingement, such as valves, orifices, branch connections, and other critical areas, copper and nickel based alloys (brass and alloy 400) have been recommended—except for low pressures to 1.4 MPA (200 psig), where selected stainless steels have been used. For operating pressures above 7 MPa (1000 psig) CGA G-4.4 recommended asking the oxygen supplier to provide specific assistance. CGA G-4.4/EIGA 13/02/E has grand fathered these oxygen systems, and these velocity limits are useful with nitrous oxide even though most common metals are not believed flammable in nitrous oxide, because particle impact can be a potential igniter for polymers, lubricants and may even initiate explosive decomposition.

11.15.4 Metals for nitrous oxide service can be evaluated and selected following the guidance in CGA G-4.4 and Guide G 94, which provides extensive data on metals ignition in oxygen, guidance for metals selection, and several practical oxygen examples. However, several metals should be avoided despite a lack of specific data for them. The catalytic metals (palladium, platinum, etc) may serve to promote the decomposition reaction. Palladium has proven to be a risk in oxygen systems both with regard to exothermic alloying reactions with aluminum and other spontaneous processes. And powdered palladium oxide is a common getter in vacuum jacketed insulation that has resulted in incidents (see G 88-05 Section 7.15.4). Any system that requires special metals to cope with the oxidant hazard also requires special consideration be given to cleaning, lubricants and nonmetals.

11.16 *Isolation and Shielding*

11.16.1 When there is a concern that the hazards of a system can not be controlled to an acceptable level of risk with design, component selection, operating practices, and compatible materials—or when a system can not be modified to improve its compatibility—then isolation or shielding should be considered.

11.16.1.1 Isolation implies that a worst case fire event would be adequately remote from people or valuable materials so that the risk is acceptable. To apply this tactic, work stations may be moved, portions of systems or entire systems may be relocated, or other measures taken to increase the distance between the system and those items whose loss would be unacceptable. This tactic presumes that the loss of the isolated system is an acceptable unavoidable loss.

11.16.1.2 Shielding implies that a barrier can be provided around high-hazard or high-risk systems and that the barrier will contain or deflect a worst-case fire. This tactic also presumes that the loss of the shielded system is an acceptable, unavoidable loss, and in the case of nitrous oxide, the explosive effect can be significant (with a TNT equivalency perhaps as high as 0.4 (**50**)). Shielding to contain a nitrous-oxide blast wave, and to ventilate or cleanup any released nitrous oxide, as well as toxic combustion products would have to be robust and costly.

11.16.1.2.1 At present the only systems that apply this technique routinely in oxygen service are compressors, pumps and some turbo-expanders. Rare high risk valves are also sometimes shielded. This machinery often cannot employ the optimum materials, and usually there is so much kinetic energy involved that a mechanical failure produces at least a transient fire. Therefore, such machinery is designed using materials and practices that optimize its reliability and performance to minimize the number of mechanical failures and the fire hazard. In addition, such machinery is shielded to contain any fires that may occur and avoid secondary damages. In most if not all common nitrous oxide services, these tactics are seldom used and present technology enables an adequate safety to be achieved .

11.16.1.2.2 Simple, inexpensive shields for mild service can also be effective. In small or dilute systems, fires generally occur at components like valves and regulators that are manually actuated and therefore exposed to operating personnel. Mounting such components on a panel provides a simple, yet effective, local shield to protect nearby personnel.

11.16.2 There are no ASTM standards that provide help with the design of shields or adequate isolation distances. CGA, the Department of Defense, NFPA, BG Chemie, and EIGA publications describe some currently used shields.

12. Ozone (O_3)

12.1 *Overview*—Ozone exhibits all the compatibility hazards of previously reviewed oxidants. It is a powerful oxidizer approaching fluorine in scale and is similarly corrosive. Being an endothermic molecule it also releases a significant amount of energy during decomposition into oxygen. It is among the more unstable (temperamental) molecules prone to explode when concentrated into liquid. Table 1 lists the heats of decomposition and combustion of several materials in the series of oxidants of interest here. Because it is a larger, triatomic, molecule with a larger specific heat than is oxygen, it would be much less prone to compression heating and expansion cooling than oxygen (ratio of specific heats of 1.397) or fluorine (ratio of specific heats of 1.364) and more nearly similar to nitrous oxide (ratio of specific heats of 1.28). Ozone is so aggressive that it reacts with many materials even at room temperature and can produce chemicals called ozonides which unlike fluorides are endothermic molecules and very reactive and like similar endothermic acetylides can be potential ignition sources. Room-temperature reaction in ozone may be far too fast to call corrosion, yet too slow to call combustion. Thermal (spontaneous) ignition is a serious risk. Ozone supports combustion, causes metals and many other materials to corrode (slow oxidation including rusting), and reacts with many chemicals. Pure ozone gas or ozone mixed with air is reported in one MSDS as colorless-to-blue gas with a very pungent odor (**51**) and as colorless with an unpleasant sulfur-like odor in another (**52**). It is 1.66 times as dense as air, boils at –112°C (-170°F), has a melting point of –251.4°C (-420°F), and decomposes rapidly at temperatures above 100°C (212°F)(**2**).

12.1.1 *Commercial Uses of Ozone:*

11.1.1.1 Ozone is used to convert olefins into aldehydes or ketones. It is a potent germicide and is used to sterilize drinking water as an alternative to chlorine.

12.1.2 *Chemical Processes:*

12.1.2.1

12.2 *Production and Distribution*—Owing to its tendency to decompose into oxygen, ozone is more often produced at the point of use than produced, stored and shipped as a commercial product. Production at the site where it is needed and immediate use minimizes inventories and its assorted hazards. Ozone is typically produced by exposing oxygen to either an electrical discharge (for higher concentrations) or ultraviolet light (for lower concentrations). If an oxygen-ozone mixture is liquefied, it separates into a two liquids with the denser one being about 76% ozone (**2**). The liquefied state is so unstable, that its preparation is more likely to be in the realm of research rather than commercial use and experience appears to be so limited that it will not be addressed here.

12.3 *Hazards and Risks*

12.3.1 The hazards of ozone are not subtle and are signaled by its strong aggressive odor. Ozone combines the aggressive corrosion (even at room temperature) and attack of materials similar to that of fluorine with an energetic explosive decomposition prospect similar to that of nitrous oxide. As with fluorine, much of this risk is often dealt with by producing ozone only at rather low pressures (much lower than the maximum pressure at which fluorine is shipped in cylinders) and in relatively small invenories. As a result, the market is not so much for ozone as it is for ozone production equipment, but that market is small in comparison to the market for oxygen. Therefore most experience to date is for low–pressure ozone/oxygen mixtures, Fires in ozone are clearly theoretical prospects but there were no documented or anecdotally supported incidents known as of this writing, even though ozone is commonly used in mixture with pure oxygen. This is likely because dilute ozone is generally produced in low pressure oxygen systems where the scale of its fire hazard and the fire hazard of the associated oxygen are both much reduced. Indeed, because of the intense corrosion and attack by ozone of most system materials, and because corrosion typically involves similar chemical reactions to those of combustion, only relatively oxygen compatible materials would be practical. Further, as with fluorine, the aggressive attack of ozone on organic materials even at room temperature would tend to produce, preserve and even improve the cleanliness of systems.

12.3.2 When a fire in ozone/oxygen occurs, the high temperatures of combustion are far above temperatures at which ozone decomposes. As an ozone molecule approaches a flame front the temperature and radiation from the flame should decompose the molecule converting it into ambient–pressure oxygen and releasing its heat of decomposition. As a result, ozone/oxygen mixtures after igniting should to a first approximation combust much like a somewhat higher-temperature oxygen gas. As for nitrous oxide, the heat release can be directly related to that from combustion in oxygen supplemented with the heat release due to any heat of decomposition that results. Heat of formation data in the *Handbook of Chemistry and Physics* (**53**) indicates that upon decomposition to oxygen, ozone should release about 34.4 Kg cal.mol. Every material that is flammable in oxygen should be even more flammable in every ozone/oxygen mixture. And since ozone is unstable as a liquid, there should be various gaseous ozone and ozone/oxygen mixtures capable of explosive decomposition, however there do not appear to be any data indicating where any fire limits (thresholds of concentration, pressure and temperature) are located. However, there are no documented nor anecdotal instances of this happening at present operating practices of dilute low pressure gaseous ozone.

12.3.3 Like oxygen, fluorine, and nitrous oxide, ozone will not tend lose an electron when it reacts with common environmental materials and it will not tend to react with air, so it is sometimes referred to as a “nonflammable”. But it will react similarly to gain electrons and so it is classed as an “oxidant”. If it could be safely marketed as a liquid or if dilute mixtures with oxygen were marketed, they would probably be classified as “liquefied compressed gas”, “refrigerated liquid”, “liquefied oxidizing gas” and even “refrigerated liquefied oxidizing gas”. However, like nitrous oxide, ozone is capable of decomposition reactions that are as hazardous as combustion in which there is no gain or loss of electrons. Therefore ozone is difficult to fully categorize to the system designer. Ozone (like nitrous oxide and acetylene) is clearly capable of “readily changing (as by decomposing) in chemical composition or biological activity” which is one dictionary’s (**40**) definition of “unstable” and liquid ozone is clearly described as being unstable in some resource material (**2**). This rating is usually reserved for high explosive materials that are temperamental and unpredictable and liquid ozone and some of its mixture with oxygen might qualify. However, hazard classification groups in MSDSs reviewed stress the oxidizing nature of gaseous ozone and dilute mixtures (the hazard most typically encountered in environmental releases) and does not stress the less often encountered, but nonetheless real, explosive possibility.

12.3.4 The ability of an ozone-enriched atmosphere to support and enhance combustion after ignition occurs is its most common fire hazard. The risk to people and property that accompanies this hazard is variable. Sometimes the human risk is grave (apart from the additional toxicity concern); sometimes the economic risk is severe. In these instances, the need to prevent combustion is strong. Occasionally, the risk is small enough that it can be accepted—and other tactics may be used to minimize the risk. The overall concept of hazard and risk have been lumped into the term “oxidant compatibility”.

12.3.4.1 The ASTM Committee G-4 first codified its interpretation of the concept of “Oxygen Compatibility” in its Standards Technology Training (now Technical and Professional Training) course textbook *Fire Hazards In Oxygen Systems*. By analogy, the concept extends to oxidants, like ozone, as follows:

> “The ability of a substance to coexist with both oxidant and a po-

tential source(s) of ignition within the acceptable risk parameter of the user [at an expected pressure and temperature]."

12.3.4.2 In this definition, a system is oxidant compatible if it cannot or is unlikely to burn, if the occurrence of fires is adequately infrequent, or even if potential fires can be isolated and their effects can be tolerated.

12.3.4. Other organizations have a similar respect for the hazards of oxidants in general and ozone in particular. Oxygen is the most widely used oxidant and is thoroughly overviewed in ASTM G 128, and much of the material there is repeated here for comparison and contrast. Ozone is much less extensively addressed, but there is material published by ASTM Committee G4, various vendor Material Safety Data Sheets (MSDS) (**51,52**) and in a few technical papers (**54,55**).

12.4 *Sources of Information*

12.4.1 Even though ozone is more oxidizing than oxygen, the much smaller market for it and perhaps the great caution given to it, there are no incidents that can be cited here either explicitly or anecdotally. For these same reasons the body of standards and publications that are available that deal with the fire hazard are all small in number. This section will overview what is available, but to a large extent the standards that come to be published to support this abstract standard may well prove to be the first public documents of their kind.

12.4.2 Designing equipment for use with ozone-enriched gases can rely to a great extent on astute following of certain of the technology used for oxygen. All of the hazard mechanisms that apply to oxygen also apply to ozone and most of the information and test data available for oxygen have at least indirect pertinence for ozone systems. Correlating these practices is still a challenge. Book-learning is highly worthwhile and practical in coping with both the oxygen and ozone hazards, and hands-on experience is worthwhile but not critical (unless one is dealing with high pressure and purity or liquid ozone).

12.4.3 This standard is the first in the ASTM system to overview the ozone hazard. There are only a few papers known to date among with the vastly larger body of oxygen papers in the ASTM Committee G-4 Reference Bibliography.

12.4.4 Commercial sources of ozone have published MSDSs and several were consulted in preparing this standard.

12.5 *Causes of Fires in Ozone*

12.5.1 Although accident reports for ozone-enriched atmospheres are not known, such events are likely to have happened. Even at the low pressures and dilute conditions in which ozone is used, its aggressive tendency to react would tend to magnify the ordinary hazards of oxygen. Virtually every fire mechanism known to exist for diluted oxygen applies also in even greater degree to ozone in theory. The mechanisms cited for oxygen in the current G 128 and G 88 are also cited here along with others and elaborated upon. The order cited is slightly different than those used in G 88-05 and G 128-95.

12.5.2 Kindling Chain. Ignition often starts with a small generation of heat, that grows and amplifies itself and shifts from one behavior to another and another, involving other materials and mechanisms, until it is in a runaway condition— a self sustaining fire. The material that is most flammable that initially responds to the first heating in this sequence of events or "chain" is the "tinder" or "kindling'. Numerous mechanisms, specifically ignition mechanisms, can provide for the first small (and some times not so small) generation of heat. Tinder would be much more responsive to even low concentrations of ozone than to oxygen.

12.5.3 Ignition Mechanisms. Fires in ozone require an initial source of energy as is also the case with fires in oxygen, and some of these sources can be self-produced. Ozone is much more reactive then oxygen even in the presence of moisture. It is much more corrosive than oxygen and is therefore more likely to experience low level reactions that bootstrap themselves upward in temperature. Incident histories are too scant to reliably rank ignition causes for the many potential ignition mechanisms.

12.5.3.1 Autogenous Ignition (Autoignition). Ignition temperatures are not published for materials in ozone. However, all materials should be more easily ignited in ozone/oxygen than in oxygen owing to the great reactivity and decomposition tendencies. And when decomposition begins, intense gas heating and heat transfer to materials is likely to result, very possibly igniting nonmetals in the resulting decomposed nitrogen/oxygen mixture. Some papers refer to this type of ignition that occurs when a material is heated in oxidant to be “thermal ignition”, but that is not common usage of the term. Since ozone breaks down to release oxygen at elevated temperatures, one might expect ignition in ozone to perhaps relate to, but to be lower than, ignition temperatures of polymers in oxygen for those materials that ignite in oxygen.

12.5.3.2 Thermal (Spontaneous) Ignition. Thermal ignition is commonly taken to be when a material reacting at a low rate is capable of heating itself to the autogenous ignition point of 12.5.3.1. In oxygen the most commonly cited cases of thermal ignition are the spontaneous fires that occur (1) when linseed-oil-soaked rags are piled up, and (2) when machinery such as compressors are run in on nitrogen or other nonreactive gas producing wear-dust debris and then converted to oxygen service. In each case, there is a high surface-area-to-volume insulating-pile situation that allows low level reactions to self-heat and produce a kindling chain. Ozone should be much more reactive under these conditions than oxygen, but there are no known incidents that can be cited involving a self heating reaction like this. However, ozone in the presence of metal fines, carbon fines and also normally flammable materials should also react intensely if an ignition source is applied.

12.5.3.3 Particle Impact. Particles present or generated in ozone systems carry the same risk of ignition as in oxygen systems. Upon impact (and perhaps due to spontaneous self-reaction) these particles may ignite and serve as tinder in a kindling chain.

12.5.3.3.1 Ozone systems should generate corrosion reaction particles/powder during service (as is the case for fluorine).

12.5.3.4 Pneumatic Impact or Compression Heating. Because ozone has greater heat capacities than oxygen, it would not heat as much in rapid (near-adiabatic) compression for comparable starting and finishing pressures, but because ozone can decompose following compression it may supplement the mechanical heat of compression to produce high temepratures. The result mould be a much greater final temperature and higher heat transfer. However, few if any incidents in oxygen have been attributed to rapid pressurization at the low final pressures currently used with ozone or its mixtures. .

12.5.3.4.1 There are no analyses of adiabatic compression of ozone or it mixtures and it is not covered by the NIST software (**4**) that has been cited with regard to several other oxidants reviewed in this standard. However to a first approximation its gaseous state should be roughly similar to other triatomic molecules (like nitrogen trifluoride)

12.5.3.5 Mechanical Impact. There do not appear to be any data using mechanical impact procedures with ozone or its mixtures.

12.5.3.6 Friction and Galling. Gross friction, as can occur in machinery rubs and the like is such a compelling source of heat and particles that it must always be taken as a viable ignition source. However, low level friction and galling in ozone may well be able to produce ignition, but here again, there are few data, and none that allow one to assess the thresholds for decomposition reaction. However, the anecdotal record does not appear to include either type of incident in the systems of most common usage today, but one must note that there is little machinery presently used with common ozone applications.

12.5.3.7 Resonance. Resonance tends to produce its most intense heating at high flows, something that is more likely to present in high pressure systems than in ozone systems (due the low present-use pressures). However, resonance ignition can not be completely ruled out and there do not appear to be experimental data to help clarify this issue.

12.5.3.8 Static Electric Discharge. There are no static electricity measurements reported in the literature for ozone flows. However, in some oxygen systems static electricity has been greatest in insulating systems (polymer-lined hoses) rather than in conductive systems. Polymer–lined hose may be attractive for ozone service and, compatible polymers are available. Indeed in many systems of interest, bulk use of polymers with ozone can be desirable for dealing with corrosion and other issues. Here again, particles (perhaps corrosion particles) can magnify the formation of charge separation, and because of the aggressive reactivity of ozone, corrosion particles may be common in some ozone systems. Whether static discharge is capable of initiating explosive decomposition is unknown, but there do not appear to be any incidents attributed to this mechanism nor for reaction of polymer-lined hoses or other polymer components.

Note 8: Static discharge in oxygen systems is known to have occurred. Any such discharge will tend to produce some ozone that might flow or collect throughout an oxygen system. For that reason and perhaps others, there may be an erratic presence of low-level ozone in some oxygen systems. Because of its tendency and potential to decompose and to form ozonides, and to react in general, ozone may be a significant factor in some hard-to-explain oxygen incidents. It has been considered as a possible factor in some incidents but has not been indicted to date (however, acetylides which are very similar in their tendency to decompose and form unstable molecules, especially with copper, have been a frequently indicted cause of numerous incidents especially in LOX sumps that may have experienced "dry boiling"). For this reason, static electricity cannot be ruled out as a source of concern in at least some circumstances in oxygen, and also presumably ozone, systems.

12.5.3.9 Electric Arc. Electric arcing is a highly effective method of igniting materials in most oxidants and has when welding is attempted on pressurized oxidant systems. It should be similarly hazardous on ozone systems. However, this scenario is one which can only be prevented by good operating practices that prevent such welding operations.

12.5.3.10 Flow Friction. Flow friction is a speculative mechanism used to explain incidents that resist all other forms of explanation. It is analyzed as waves of motion that occur during gas flow over polymers that produce internal friction processes that might heat polymers to the ignition point (**33**). Lab experiments to date to demonstrate it in oxygen systems have not been successful. They have produced heating but not ignition. Flow friction should be an equal or greater hazard in ozone and ozone mixtures than in oxygen and such heating may also lead to decomposition. However, in present-day ozone systems flow friction should be at least as serious as in pure oxygen systems.

12.5.3.10.1 "Flow friction" should be less aggressive as a heating mechanism in ozone than in oxygen due to the lower pressures present. It is difficult to say whether flow friction is an important concern. However there do not appear to have been any anecdotal incidents that might be attributed to this mechanism in the past.

12.5.3.11 Fresh Metal Exposure. Many believe that every surface that is exposed to an oxidant will experience some degree of initial surface reaction that is likely to be much more aggressive when ozone is present than in less reactive oxygen. Bulk specimens of fresh titanium surface exposed to oxygen have ignited, but otherwise, ignitions have only been observed in piles of fines. This mechanism may be more effective with ozone present and especially so where piles of fines are involved, however, there are no known anecdotal incidents in present-day ozone systems that are attributed to this mechanism.

12.5.3.12 Decomposition. Ozone is an endothermic molecule that can be exothermically decomposed to release oxygen under the influence of heating. In addition, ozonides can form with other materials (analogous to the way acetylene can form unstable copper acetylides). However, neither literature nor the anecdotal record cite any incidents attributed to such molecules.

12.5.3.13 Other Ignition Mechanisms. Other mechanisms can not be ruled out, but none are speculated upon in the available literature.

12.6 **Hazards**

12.6.1 *Recognized hazards.* Ozone is potentially extremely dangerous because of the potential consequence of it ability to explosively decompose and its aggressive reactivity (as well as for toxicity), but although such explosions have occurred, they appear to have been the result of laboratory study that does not reflect current systems which are used with ozone mixtures. Only very concentrated or liquefied ozone has shown these temperamental tendencies. Nonetheless, in comparison to oxygen, every fire hazard known to oxygen use (with only rare exception) is a similar or greater hazard when ozone is added in any degree. Potential hazards of oxygen use may be observed in corresponding ozone mixtures systems. These include (1) ozone concentration and associated diluents, (2) pressure, (3) temperature, (4) phase, (5) velocity. (6) time and age, (7) mechanical failure.

12.6.1.1 *Ozone Concentration and Associated Diluents.* Higher ozone concentrations increase the hazards of ignition and fire intensity because more ozone is present to mix with the fuel. Diluents are as important as they are for oxygen systems. Nonreactive diluents that have large molecular size (larger than ozone) are more effective at attenuating flammability (however keep in mind that ozone is a large molecule itself and therefore many diluent gases that would lower the risk in mixture with oxygen are in comparison smaller than ozone and might act to increase the hazard in mixture with it). In oxygen systems even tenths of a percent of diluents can be important, but whether a similar extreme effect for trace diluents is operative in ozone is unknown.

12.6.1.2 *Pressure.* Higher pressures also increase the hazards of ignition and fire intensity. Pressure increases the density of the gas, with the same effect as increasing the concentration: more ozone is available to the fuel, so materials ignite easier and burn faster. Pressure also increases the gas velocity at restrictions such as valves, regulators, and intersections—which increases friction, particle impact, and compression heating.

12.6.1.3 *Temperature.* Unlike oxygen, practical use temperatures should have a significant affect on the reactivity of ozone, increasing its reactivity at all temperatures and especially bad as temperatures approach those for decomposition. As for oxygen, any high temperature can accelerate aging of polymers and thereby reduce their compatibility with ozone. Indeed, environmental ozone itself, even at the fairly low levels present in air, plays an important role in the aging of many polymers (rubber products, tires, etc. This aging effect is magnified in higher ozone concentrations.

12.6.1.4 *Phase.* Ozone is rarely liquefied outside of laboratory study. However, some low-level ozone may appear in LOX systems. There is little or no practical experience with it. Its behavior and risks as a liquid include the risk of explosive decomposition that is not present with liquid oxygen, and if liquid applications come to be desirable, then study and great care will be needed to deal with liquids containing ozone.

12.6.1.5 *Velocity.* Increased ozone velocities in flowing systems lead to higher particle velocities, which increase the likelihood of ignition by particle impact. Particles in ozone systems should be more common than in oxygen systems (and particles can affect static charge separation). “Flow friction” which is speculated but unproven as an ignition mechanism in oxygen, is an uncertain risk in ozone systems, and to the extent that it poses risk, the risk may be more likely due to the prospect of decomposition (whether explosive or merely heating) than polymer ignition.

12.6.1.6 *Time.* Time and age are important hazards. However the base of experience suggests the role of time on current ozone system fire risks is relatively low.

12.6.1.7 *Mechanical Failure.* The same mechanical failures that jeopardize oxygen systems also threaten ozone systems. These include impact of broken parts, rubbing, particle generation, failed seals, etc. There are no present data on the risk of friction or galling as initiators of explosive decomposition. Indeed, in oxygen service, the components (namely oxygen compressors and pumps and occasional high-risk valves) most at risk of failure and therefore most likely to experience fires are often placed behind barriers, because their reliability can not be made sufficiently high to address the risk to life and injury otherwise. Barriers for ozone safeguards must be designed for the additional energy that can result from explosive decomposition. To date, it does not appear the use of barriers has been necessary in most common piping systems and due to processes (water treatment) in which the ozone is sparged into water which has a heat capacity sufficient to swamp any reaction heat) and due to the largely unattended nature of some ozone applications (again water treatment), inherent isolation from personnel is itself a safeguard.

12.7 *Fire Prevention*

12.7.1 G 128 patterns the approaches to preventing fires in oxygen to those used for preventing fires in air. The following sections will pattern the approach for ozone fire to those for oxygen fires. In each there is a gradation of steps taken with greater numbers and more extensive use depending on the severity of the situation.

12.7.2 In oxygen systems there is always an oxidant (oxygen) present, often there is fuel present (in the materials of the system itself), and sometimes there are ignition mechanisms present (heat of compression, particle impact, etc). So in oxygen systems there is effort to pick the best materials possible and to minimize the number and intensity of ignition sources.

12.7.3 As for oxygen, depending on the ozone mixture present in a system, there are progressively stringent measures applied in the order cleaning, compatible lubricants, compatible polymers and other nonmetals, and compatible metals.

12.7.4 In pure or concentrated ozone systems all of the above measures would likely be crucial. However, in any, perhaps most, current low pressure ozone-mixture systems, these tactics may be abbreviated, and there may be no additional protective measures taken in terms of barriers or isolation beyond that inherent in the existing equipment, but there may be extra care taken in venting and ventilation, and the like.

12.7.5 Recognizing, identifying and controlling potential sources of ignition and possible causes of fires in ozone is not simple. Present knowledge does not enable us to identify all possible ignition sources. Hence few ozone systems can enjoy a certainty that fires are not possible. There is a strong empirical influence in the approach to oxygen safety that is present also in ozone safety. To a large extent, one does what has been successful in the past, provided it has been successful often for long periods of time, and is based on sound principle. For this reason ASTM G-4 standards take a multi-pronged approach that attempts to align as many factors as possible toward reducing the likelihood of ignition and fire.

12.7.6 This approach is based on using the extensive body of information available on the ignition and flammability of materials and methods with demonstrated ability to reduce the number and severity of fires in oxygen with adjustments to it based on the known properties and behavior of ozone. Guides G 63, G 88 and G 94 as well as Practice G 93, describe the many factors affecting oxygen and oxygen-enriched systems and describe how to reduce the hazards associated with these systems. These same guides are often taken as a starting point for ozone systems and are then expanded upon. With ozone more stringent practices would be followed than for any oxygen system of comparable pressure, temperature, and phase.

12.7.7 ASTM G-4 and other resources correlate control of oxidant system hazards with special attention to (1) system design; (2) component selection; (3) operating procedures; (4) cleaning; (5) passivation; (6) compatible lubricants; (7) compatible polymers and other nonmetals; (8) compatible metals; and (9) isolation and shielding. Each of these approaches is discussed in more detail below.

12.8 *System Design*

12.8.1 Oxygen and ozone system design should not be undertaken casually—these systems require careful and specialized design considerations. The first and most important rule is: Consult an expert! Guides G 63, G 88, Practice G 93 and Guides G 94 and G 128 define "Qualified technical personnel" and provide vital information for use by these experts. Indeed, in many companies, individuals are designated as specialists to acquire the expertise and assist others in oxidant system design.

12.8.2 System design for any oxidant should begin with the same mechanical principles as conventional air or gas system design and follow the same nationally recognized codes and standards—there are no special codes that mandate how to design oxidant systems. The added hazards inherent in the use of oxidants should then be evaluated to modify conventional practices while still conforming to appropriate requirements. In general that leads to a more—not less—conservative design. Ozone system designs can usually be approached as variants of similar oxygen system designs that (unless barricaded or isolated) also meet or exceed the compatibility measures that would be taken with oxygen mixtures.

12.8.3 The severity of system operating conditions is defined similarly to those for oxygen. Concentration, pressure, temperature, phase, and time are all crucial. As these factors increase, the risk increases, and the system design must be modified to a greater extent. Ozone concentration and phase are established by the system function. But the others can be influenced by the system design. For example pressure can be reduced with a regulator as close to the gas source as possible to minimize the hazard (and most current ozone systems operate at such low pressure that pressure reduction is unnecessary). Temperatures can be limited, for example by including protection from runaway heaters. The effects of time and age can be mitigated by designing for effective preventive maintenance.

12.8.3.1 Velocity is a hazard that is controlled primarily by overall system design. Line sizes should be selected to limit ozone gas velocity. There are no adopted velocity criteria for ozone systems but existing guides for oxygen systems may suggest an upper limit and may be adjusted downward when needed and when possible. Rules applied to oxygen systems as to abrupt line size changes, locations of intersections and risk of particle impingement and compression heating in certain geometries are all applicable to ozone systems near polymers and perhaps elsewhere, as well. As for oxygen, one reduces velocity and upgrades the fire resistance of ozone system materials wherever needed to cope with velocity and particle hazards.

12.8.4 Additional considerations as reviewed in the remaining sections are integrated into the design of a ozone system. Care equal to or beyond that normally accorded oxygen systems is always required. The initial cleanliness of an oxygen system is established as the components are built and the system fabricated, and it is crucial to prevent contamination during the system's life. In systems that contain ozone, it reactivity with many of the most hazardous contaminants would tend to help preserve cleanliness through a continuous reaction process of low-level contaminants that might be introduced.

12.8.5 Specific guidance on ozone system design itself is found in the various vendor's Material Safety Data Sheets. However, oxygen design materials such as Guide G 63, CGA G-4.4, EIGA 13/02/E, NFPA 50 and 51, and many others provide excellent guidelines for system design that can be considered by analogy in the design of ozone systems, although these references are not handbooks. This includes material in the ASTM G-4 Committee Technical and Professional Training Course Controlling Fire Hazards in Oxygen Systems which teaches the fundamentals of oxygen safety for oxygen process designers and equipment specifiers and includes a textbook.

12.8.5.1 Many references on oxygen hazards are cautious and explicit about the use of their data, and this caution is worthwhile to apply to other data and other oxidants such as ozone. For example, Praxair Publication L-5110N warns:

> "This publication is not a design handbook and does not relieve the user from exercising competent engineering judgment or using qualified professional personnel who can tailor your design to your specific situation.
>
> "In situations where qualified people are not available locally to design the system, obtain professional assistance from a competent source. If the oxygen supplier can not offer assistance, he should be able to direct you to a consultant who can provide the necessary service. Remember that design of oxygen systems requires specialized knowledge. Liability problems associated with improperly designed systems can far outweigh the cost of professional services."

12.9 *Component Selection*

12.9.1 ASTM Committee G-4 standards do not recommend specific products. Indeed, they are disclaimed as specifications. Further, their nature is not such that products can be marketed under a blanket claim of meeting any of the four applicable oxygen standards (G 63, G 88, G 93, or G 94) and this applies equally to ozone systems as well. Clearly the thrust of these standards is to enable evaluation of system needs in the context of a particular application. As the application changes, such as exposure to higher pressure, a host of conditions change—or hazard thresholds are crossed—that may render previously accepted products unacceptable for further use. Therefore, although there may be a few products that are acceptable in any and all oxygen applications, one can not consider products to be "approved for oxygen or any other service" under the procedures of these standards without also specifying the conditions for which the approvals are intended.

12.9.2 Some products are marketed for ozone service, but not every experienced designer agrees that every one of these products has adequate ozone compatibility or even that a blanket approval is reasonable. Some companies do list materials that are approved across the board, but many others tie approval to specific applications and level of application hazard. It behooves the user to determine whether the properties of the particular products (whether or not they are marketed for ozone service) actually meet the needs of the user's application.

12.9.2.1 Performance tests conducted by hardware manufacturers generally do not simulate any specific application. Laboratory tests can not duplicate the endless variety of actual operating conditions; such tests only indicate a predicted result in a controlled laboratory setting and cannot assure the same result in a particular application or service.

12.9.2.2 Material qualification tests are also method specific and rarely afford blanket approval. The user should evaluate the material test results along with the test method to determine if they correspond to the way the material will be used in a specific design.

12.9.3 It is also important to note that most common industrial components—such as valves, fittings, filters, regulators, gages, and other instruments—are not designed for specific applications. Rather, they are versatile, general purpose products that can be used properly in many types of applications and systems. Hardware manufacturers in general have neither the experience nor expertise to select the most appropriate components for a specific use, such as an ozone system. Only the ozone system designer or user can have full knowledge of the entire system and each component's function, which must be considered when selecting the system components. Ozone system designers and users both must be sensitive to product function, material compatibility, adequate ratings, and proper installation, operation, and maintenance.

12.9.4 Valve selection requires special attention by the system designer, because valves are one of the few mechanical items that are actuated routinely while the system is in use. The designer must determine the type of valve, its location, how it will be operated, and—often neglected— how it might be operated incorrectly.

12.9.4.1 Particular attention should be directed to valve pressure and temperature ratings, internal materials of construction, and how readily the valve can be cleaned and kept clean. Valves often are selected with higher ratings, greater wall thicknesses, and more fire resistant materials than the rest of the system because they are exposed to more severe service conditions.

12.9.5 As valves are opened and closed they almost always generate localized high velocities near the valve seat or immediately downstream. This creates a local increase in the hazard level at the valve location and often requires that special consideration be given to the selection of seat materials and potential impingement areas nearby.

12.9.5.1 Ozone system valves also pose a more serious risk of personal injury, because many are opened and closed manually—so that at the very moment they are most susceptible to the conditions that can cause a fire, someone's hand is on them. The risk of fire and of the fire breeching metal components is larger with ozone than with oxygen, and there is also the potential for decomposition (providing additional heating and in concentrated-ozone systems, the possibility of explosion), and even fragmentation, in some systems. Since the hazard may range from small for low pressure or sparged-water systems to enormous for pure liquid ozone, the need for shielding or remote operators, can only be individually evaluated.

12.9.5.2 Oxygen Guides G 88, CGA G-4.4/EIGA 13/02/E and NFPA 51 unanimously emphasize that valves must be opened slowly. Opening speed is controlled by valve design, as well as by operating procedures. Ball, plug and butterfly valves are used in some low-pressure systems such as pipelines, because their straight-through design provides a lower pressure drop than a globe valve. However, ball and plug valves are quick-opening and create high velocity when opened, whereas needle valves are designed to open slowly (Fig. 3 of G 128). If a full-flow valve is used in a high pressure service, the piping system must be designed carefully to equalize the pressure across the valve before it is opened.

12.9.5.3 Even while closed, valves require extra consideration. Valves used in gas service often have seats or stem tips made of polymers that are exposed to the system fluid when the valve is closed. They can be subject to impingement from high velocity generated by another component upstream, and thus become a potential ignition point.

12.10. *System Operation*

12.10.1 Current low pressure ozone systems appear to experience ignition at a low rate comparable to low-pressure oxygen systems, but if high-pressure or liquid systems came into use, they could likely produce extreme damage, especially if explosive decomposition occurs. In these cases of greater consequence, ozone warrants more care than oxygen in both the system design and the cautions employed by system operators. However, in most current cases, care comparable to that used with oxygen (but sensitive to the greater corrosion concern) is appropriate. Perhaps the most neglected aspect of controlling oxygen systems hazards involves system operation. Oxygen fires frequently are caused by systems whose safe operation depend so greatly on the operator's strict adherence to certain procedures that they can not tolerate simple human error. In these poorly designed systems, a single mistake—such as actuating one of a series of valves in the wrong sequence—can lead to a catastrophe. G 128 cites (in its sections 15.1.1 through 15.4) and reviews example events documented in the ASTM video adjunct entitled, *Oxygen Safety*, that illustrate several design errors that invited and then compounded operator errors, causing serious accidents.

12.10.1.1 In both examples rapid compression led to ignition. In one an operator was supposed to open a ball valve, then slowly pressurize a downstream system with the valve on an adjacent cylinder, but instead left the ball valve closed until the cylinder valve was open, then shocked the downstream system. Other episodes with ball valves were similar. All of the events could have been prevented with more cautious system operation.

12.10.1.2 In current commercial ozone systems, the highest source pressures would not produce high temperature remotely approaching those produced by oxygen (attenuated by the higher specific heats of ozone). The maximum potential heat transfers during rapid pressurization would probably have been smaller (**32**).

12.10.2 Therefore, as noted in the *Oxygen Safety* video adjunct, thorough planning and careful monitoring of operating procedures and maintenance practices are important in oxidant fire prevention. However, safe operation should be engineered into the design of an oxygen system—by the selection and placement of components—and not rely solely on operator compliance with procedures to prevent oxygen fires. As noted in G 88 Section 7.19.4 "Avoid Overly Complicated Procedures" one must remember that complex and repetitive procedures are more prone to discrepancy than simple straightforward procedures. Since human error is difficult to prevent, in crucial systems, automation may be required to achieve reliable system operation.

12.11 *Cleaning.*

12.11.1 An ozone system requires cleaning comparable to that of an oxygen system. Cleaning is the first measure required, even though it may be the last step accomplished in preparing a system for oxidant service. Any such system typically must be evaluated carefully for cleanliness, and most will be cleaned scrupulously. In fact, the extent of cleanliness used on a system exposed to dilute ozone may be very similar to that applied to pure oxygen high pressure systems.

12.11.2 Organic particles and fine particles burn violently in concentrated oxidant and are often the beginning of the kindling chain that starts a fire. Hydrocarbon oil or grease contamination is particularly undesirable. In mild applications, inert particles may be removed less scrupulously. A mild ozone exposure may not be subject to any other requirements, but its cleanliness should always be a concern.

12.11.2.1 The basis for determining the oxidant concentration and pressure at which more scrupulous cleaning is needed should be related to the flammability of the contaminants, lubricants, polymers, and metals. If the contaminants are unidentified, one must assume they may be flammable and therefore must be eliminated at even a small increase in oxidant concentration or pressure.

12.11.3 Cleaning methods used with oxygen systems are often applied to other oxidant systems including ozone systems and should be evaluated and selected by analogy following the guidance contained in Practice G 93, CGA G-4.1, EIGA 33/86/E, and Praxair GS-39. Practice G 93 provides special guidance for cleaning components in its Section on Interferences.

12.11.3.1 *Disassembly:*

12.11.3.1.1 It is imperative that oxidant systems be cleaned as individual articles, preferably prior to assembly. Assembled systems must be disassembled for cleaning if construction permits. Flushing an assembled system can deposit and concentrate contaminants in stagnant areas.

12.11.3.1.2 Manufactured products (for example valves, regulators, and pumps) should preferably be cleaned by the manufacturer prior to final assembly and test. The purchaser should approve the cleaning procedure and packaging to ensure that they satisfy the system requirements.

12.11.3.1.3 Manufactured products that are cleaned by the purchaser must be disassembled for cleaning if the construction permits. The purchaser should follow the manufacturer's instructions for disassembly, inspection for damage, reassembly, and testing.

12.11.4 Practice G 93 contains additional information on cleaning methods, hindrances to effective cleaning, packaging, and inspection, including examples of specific applications.

12.12 *Passivation.*

12.12.1 Because the reactivity of ozone is high like that of fluorine, even at room temperature, passivation of ozone systems prior to service warrants discussion. In passivation, a dilute gas mixture of the reactive gas with a nonreactive gas is purged into the system at low pressure and allowed to soak, after which subsequent mixtures at higher reactive-gas concentration and pressure are introduced until the system has been soaked at its maximum intended service concentration and pressure.

12.12.2 Passivation is believed to accomplish two things, but its mechanism may be poorly understood. First, the aggressive gas reacts slowly because of its dilution with any trace of remaining contamination in the system (for ozone passivation, any hydrocarbon would react largely to carbon dioxide and water) and the surface then "reacts" (corrodes in the case of ozone) to produce a very thin layer of metal oxides that is inert and believed to be protective against fresh-metal exposure ignition. This is a time honored safety practice for fluorine, however, its effects are extremely subtle. Passivation has not been practiced with present-day ozone systems in part because the majority are used only with dilute ozone gas mixtures (albeit with oxygen diluent instead of non reactive diluent, but at conditions where low pressure oxygen is not highly reactive). Hence normal use of the mixture serves to some degree as a passivation step. Furthermore, most hardware for ozone service is stored in an air environment where surface oxidation is possible, such oxidation of which would yield the same surface result that ozone would produce (especially in cases of fresh metal surfaces which are themselves prone to oxidize). If pure ozone or ozone mixtures of high concentration came into common use, formal passivation might be a worthwhile and even necessary precaution.

12.13 *Compatible Lubricants*

12.13.1 If cleanliness is the first special measure that is necessary, the next concern is with lubricants, for two reasons (*1*) the most common oils and greases are hydrocarbon, which are among the materials most necessary to remove from an oxidant system; and (*2*) they are fluids and pastes, which are more prone to migrate and collect than are solid materials.

12.13.2 Any lubricants reintroduced into a system cleaned for oxidant service should be selected to be fire resistant. In most instances, even with mild oxidant exposures at low pressures and at low oxidant concentrations (as low as 25% oxygen in nitrogen or argon), fire-resistant lubricants or other fluids are used, and the same practice would apply to ozone and its mixtures.

12.13.2.1 Several halogenated oils and greases have been tested and used widely with success in oxygen service. Oxygen manufacturers can be consulted regarding appropriate lubricants for specific applications, Guide G 63 includes test data on many lubricants, thread compounds, seats and gaskets. Praxair L-5110N lists lubricants that manufacturer has used for low pressure systems. Specifications

MIL-G-27617, MIL-G-47219 (MI), DOD-L-24575 (SH), and KSC 79K22280 may also be consulted for choosing analogous ozone-compatible greases and lubricants.

12.13.3 Practice G 93, Section on Interferences, provides special guidance for lubrication of components.

12.13.3.1 *Lubricants*

12.13.3.1.1 Mechanical components are normally assembled with lubricants on seals, threads, and moving surfaces. The manufacturer should be consulted to determine the kind of lubricant originally used on the article to ensure that the cleaning solutions and methods selected are effective in removing the lubricant and will not damage the component.

12.13.3.1.2 When used, ozone-compatible lubricants should be selected. In some cases, lubricants can be evaluated as they would be for oxygen service using the methods of G 63 and treating ozone/oxygen mixtures with at least the same or greater concern that would apply to pure oxygen. In time more specific guidance should be developed. The component manufacturer should also be consulted to ensure that the selected lubricant provides adequate lubrication for component performance. Oxidant compatible lubricants often have markedly different lubricating properties from conventional lubricants.

12.13.4 Scrupulous cleaning combined with the use of fire-resistant lubricants may be the only special precautions needed in moderate services. Until more precise recommendations are published, lubricants should be evaluated and selected following the guidance contained in Guide G 63. However, all lubricants should be used sparingly and with great caution.

12.14 *Compatible Polymers and Other Nonmetals*

12.14.1 As the severity of the hazards (such as higher pressure, temperature or oxidant concentration) increases to elevate system operating conditions above the level at which both cleaning and compatible lubricants are necessary, the next hazard threshold crossed is that of compatible polymers. Polymer use is common in ozone/oxygen mixtures. In oxygen, at room temperature and low pressures—below about 350 kPa (50 psig)—and at oxygen concentrations between 30 and 100 %, most users switch to more fire-resistant polymers for gaskets, valve seats, packings, and other polymer parts. In ozone/oxygen mixtures, polymer selections would be at least as compatible as would any to be used in oxygen, but additional latitude would be acceptable in some cases. Such common systems of low oxidant severity may require compatible polymers and compatible lubricants in addition to scrupulous cleaning, but not need special consideration of the common metals components.

12.14.2 Most polymers burn in pure oxygen, usually violently, and each should burn more aggressively in ozone and its mixtures. They ignite more easily than metals and become the kindling chain that ignites the system. These materials include the many polymers and elastomers used in seats, stem tips, packing, gaskets, seals, and thread sealants in pumps, valves, regulators, filters, instruments, and most other piping components.

Note 9: Venting and ventilation of ozone can be necessary to avoid the health effects of ozone itself as much or more than to cope with combustion products. Ozone in vent streams is often passed through destructors to convert it to oxygen.

12.14.2.1 Polytetrafluorethylene (PTFE) and polychlorotrifluoroethylene are listed by CGA G-4.4 as suitable for oxygen service and are used for many functions in piping components. Yet, even these materials begin to decompose at 200 to 300°C (400 to 600°F) and can ignite at higher temperatures. Both are often used in ozone/oxygen service.

12.14.2.2 As emphasized in Guide G 63, the successful use of even the best materials depends on the design of the component and where it is used. For example, PTFE-lined flexible hose has a large surface-area-to-mass ratio, and many instances involving the ignition of such hoses in oxygen have been reported (Fig. 4 of G 128). The safe use of PTFE-lined hose in high-pressure oxygen may require special provision in the system design. PTFE-lined hoses used in ozone/oxygen service at present-day low pressure systems should face little risk of the adiabatic compression hazard.

12.14.3 Operating conditions also must be considered in polymer selection. Continuous exposure to elevated temperatures or high oxidant concentrations can change a material into something quite different from what it was when new. With age, the material may become harder, softer, or brittle, or the surface may change. The molecular weight may decrease by scission or increase by cross-linkage. Such changes are accelerated by pressure and temperature and may decrease resistance to ignition and fire, as well as change performance properties. The effects of ozone to cause aging are extreme in this aspect even at low pressures and concentrations.

12.14.4 In oxygen at temperatures above the service limits of polymers, these materials sometimes are replaced by graphite, particularly in packings and gaskets. Being pure carbon, graphite will burn in an oxygen–enriched atmosphere. Although difficult to ignite in bulk form, graphite particles from packing wear may ignite more readily. Graphite introduces an additional concern because it is cathodic to most metals and causes corrosion in moist atmospheres. Although oxygen systems are generally dry, external moisture can initiate corrosion which can cause hidden damage. Ozone is not used in piping systems at elevated temperatures to specifically avoid it decomposition (even where slow decomposition rather than explosive decomposition would result) and so carbon for high temperatures would be an unlikely present-day need.

12.14.5 All nonmetals should be tested and evaluated carefully before being used in a particular oxygen system application. Guide G 63 presents a systematic approach to selecting nonmetallic materials, with numerous practical examples for oxygen, and it may be used by analogy with ozone. It includes a compilation of test data for many nonmetallic materials frequently used in oxygen service. Chapter 5 of NFPA 53 also describes the ignition and combustion of materials commonly used in oxygen-enriched atmospheres.

12.15 *Compatible Metals*

12.15.1 Most common metals will burn in pure oxygen under at least some conditions of pressure and temperature. Their flammability would increase in ozone mixtures with oxygen. Assorted carbons steels, stainless steels, brass, copper, copper alloys and aluminum are all in current use where corrosion is acceptable but in many cases polymer piping is used in wet applications to deal with ozone aging. The most familiar example is cutting steel with an oxygen torch (Fig 5 of G 128). A torch ignites the steel, and then a stream of oxygen keeps it burning. The heat of the burning steel continues the cutting action. The same process can happen accidentally in improperly designed oxygen piping systems (Fig 6 of G 128).

12.15.2 Typically the last hazard threshold crossed as the severity of the hazards in an oxidant system increase is that for which compatible metals are required. For common systems at oxygen concentrations at up to 40 % and at pressures below 1 MPa (150 psig), few special materials are required. At higher concentrations and pressures, most users select more compatible metals.

12.15.3 NFPA 51 and CGA G-4.4/EIGA 13/02/E mention existing practices for the use of steel or stainless steel for oxygen systems. Historically CGA G-4.4 dealt only with 7 Mpa (1000psig) or less, but the new harmonized CGA G-4.4/EIGA 13/02/E is somewhat more expansive. Further, in regions of high velocity or impingement, such as valves, orifices, branch connections, and other critical areas, copper and nickel based alloys (brass and alloy 400) have been recommended—except for low pressures to 1.4 MPA (200 psig), where selected stainless steels have been used. For operating pressures above 7 MPa (1000 psig) CGA G-4.4 recommended asking the oxygen supplier to provide specific assistance. These velocity limits are useful with ozone even though most common metals are not believed flammable in low pressure oxygen and may be similarly fire resistant in some dilute ozone/oxygen mixtures.

12.15.4 Metals for ozone/oxygen mixture service can be evaluated and selected following the guidance in CGA G-4.4/EIGA 13/02/E and Guide G 94, which provides extensive data on metals ignition in oxygen, guidance for metals selection, and several practical oxygen examples. However, several metals should be avoided despite a lack of specific data for them. The catalytic metals (palladium, platinum, etc) may serve to promote the decomposition reaction. Palladium has proven to be a risk in oxygen systems both with regard to exothermic alloying reactions with aluminum and other spontaneous processes. And powdered palladium oxide is a common getter in vacuum jacketed insulation that has resulted in incidents (see G 88-05 Section 7.15.4). Any system that requires special metals to cope with the oxidant hazard also requires special consideration be given to cleaning/passivation, lubricants and nonmetals.

12.16 *Isolation and Shielding*

12.16.1 When there is a concern that the hazards of a system can not be controlled to an acceptable level of risk with design, component selection, operating practices, and compatible materials—or when a system can not be modified to improve its compatibility—then isolation or shielding should be considered.

12.16.1.1 Isolation implies that a worst case fire event would be adequately remote from people or valuable materials so that the risk is acceptable. To apply this tactic, work stations may be moved, portions of systems or entire systems may be relocated, or other measures taken to increase the distance between the system and those items whose loss would be unacceptable. This tactic presumes that the loss of the isolated system is an acceptable unavoidable loss.

12.16.1.2 Shielding implies that a barrier can be provided around high-hazard or high-risk systems and that the barrier will contain or deflect a worst-case fire. This tactic also presumes that the loss of the shielded system is an acceptable, unavoidable loss, and in the case of ozone, the explosive effect could be significant if pure ozone or liquid ozone were to come into common use, with a TNT equivalency perhaps close to TNT itself—based on complete conversion of it heat of decomposition into blast wave (**50,53**). However, most current dilute ozone/ozygen mixtures should not require these tactics.

12.16.1.2.1 At present the only systems that apply this technique routinely in oxygen service are compressors, pumps and some turbo-expanders. Rare high- risk valves are also sometimes shielded. Machinery often cannot employ the optimum materials, and usually there is so much kinetic energy involved that a mechanical failure produces at least a transient fire. Therefore, such machinery is designed using materials and practices that optimize its reliability and performance to minimize the number of mechanical failures and the fire hazard. In addition, such machinery is shielded to contain any fires that may occur and avoid secondary damages. In most if not all present-day ozone/oxygen service, these tactics are seldom used and present technology enables an adequate safety to be achieved .

12.16.1.2.2 Simple, inexpensive shields for mild service can also be effective. In small or dilute systems, fires generally occur at components like valves and regulators that are manually actuated and therefore exposed to operating personnel. Mounting such components on a panel provides a simple, yet effective, local shield to protect nearby personnel.

12.16.2 There are no ASTM standards that provide help with the design of shields or adequate isolation distances. CGA, the Department of Defense, NFPA, BG Chemie, and EIGA publications describe some currently used shields.

Closure/Reconciliation

This paper has attempted to exhibit what one rough form of a composite abstract standard on oxidants other than oxygen might look like. It has sought to maintain a close parallel between four other oxidants and oxygen through adoption of text closely related to the ASTM G4 abstract standard G 128. If any feature of oxidant performance was important enough to mention in G 128, then it was important enough to mention for each other oxidant. Even where concerns were not important, it was considered important to be explicit about the non-importance. Anyone looking up a feature in G 128 can go to the corresponding section for any of the other oxidants and find the corresponding aspect.

G 128 has been in use for more than a decade and has proven to be a superb document. It has not been materially revised in this period, and yet the writer considered it an obvious guide. However, that is not to say that G 128 is perfect or completely current. Since its completion there have been a few developments that while not earthshaking in importance would be appropriate for coverage in the standard at some point. A few have been included in these other oxidant sections and should sometime be added to G 128. A few others have not been added but are listed in this Closure/Reconciliation for potential addition to all abstract materials. When these topics are added to G 128, they should similarly be folded into each of the other oxidant sections provided here, or whatever alternative materials might come to be adopted.

A summary of a few of these classes of items is presented here.

Items for Addition to G 128 Suggested by This Other Oxidants Draft

Passivation is not employed with oxygen systems but is crucial to some other oxidants, and G 128 should for consistency indicate that deliberate passivation is not usually practiced (except in special cases) and defend the basis. Explosive decomposition is not an issue with oxygen systems but is crucial with some other oxidants, and G 128 should again for consistency indicate that explosive decomposition is not observed in oxygen systems. Flow friction is a new "speculative" ignition mechanism that enjoys more potential credibility with other oxidants than it does with oxygen, but because of the speculation related to oxygen, it should be reviewed in G 128. The new harmonized CGA/EIGA piping document has been incorporated into the other oxidant text but needs to be included in G 128.

Items for Addition to Both G 128 and This Other Oxidants Draft

Since publication of G 128, several new standards have been published. Several are routine additions to the existing body of thought on oxygen (such as cleaning and analysis techniques in G 131, G 136, G 144). However, G 145 addressing incident study is an important new area that warrants mention in G 128, and then similarly in any "other oxidants" material. Finally, G 175 is a component test standard for a subject that is treated only generically in G 128, and when included in that standard, discussion should be reflected in any other oxidant works also.

Items for Addition to This Other Oxidants Draft

Publication of an EIGA Code of Practice for fluorine is imminent but was not available for review herein. Nor were many other obvious documents available, including the *Matheson Gas Handbook*, *The BOC Gas Handbook*, and the *Air Liquide Gas Handbook*. All of these and perhaps other time-honored references need to be considered for material for potential inclusion or elaboration within. If this rough draft is ever pursued or used to influence other oxidant materials, the panel of experts will need to keep all of these references and still other reference materials in mind.

Summary

ASTM Committee G4 has always recognized a need and expressed a desire and has taken fledgling steps towards development of safety standards for oxidants other than oxygen. One potential first step to any standards effort (but a first step that G4 was not able to use and did contemplate in its original oxygen efforts) is with a document that introduces and overviews the entire field—called an abstract standard by ASTM. G 128 was developed ex-post-facto and serves this purpose today for the body of work G4 has developed for oxygen safety and may be a worthy model.

However, it is unlikely that G4 could undertake to replicate the extensive body of work (experiment and experience) that has obtained for oxygen for every other oxidant of interest—nor should it be necessary. The background to do that does not exist, nor is there interest, nor is there economic incentive or resource. Other oxidants will need to analogize or otherwise piggyback on oxygen technology and the oxygen model.

One potential first-step abstract standard has been roughed out here without great attention to detail nor scrupulous devotion to accuracy and little or no peer comment. This will allow G4 to become acquainted and familiar with this approach, from whence it may decide to condense this material (after expanding, correcting, validating and completing it), to split it into a series of abstract standards, to meld it all into G 128, or even to forego an abstract function entirely. But in time, it may also come to accept this approach and to use it as the starting point for an official consensus product.

Hopefully this crude preliminary effort will help advance and expedite any of these efforts.

Acknowledgements

This effort clones four copies of the standard G 128. G 128 was prepared and its adoption led by Ulrich Koch (based on a paper of his) more than a decade ago. It has served well and persisted with little change, and the writer foresees only modest changes at most in the near future. Without it, this approach and this paper would not have been possible.

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