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Technical and Human Factors Affecting Special Cleaning of Oxidant-Rich Systems[2]

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ABSTRACT: Data pertinent to contamination fire hazards thresholds for ignition, propagation, and consequence are considered as a function of oxygen concentration. Most current criteria for threshold concentrations of special cleaning appear to be based on jurisdiction and caution more than on precise hazard thresholds. Research into the effects of moisture and liquid phase flammability is encouraged and might yield better understanding and increased latitude in the cleaning of oxygen systems. Improved fire-limit interpretation techniques are also needed.

KEY WORDS: Special cleaning, oxygen rich, oxygen enriched, oxygen compatibility

Special cleaning has long been associated with oxidant-rich hardware. For many years and for many systems, special cleaning was the only specified safety precaution. And indeed, even in today's much more advanced technology, whenever any precautions are taken at all, scrupulous cleaning is *always* one of them, and is always one of the most important.

As a result, virtually any group that has confronted the issue of oxidant safety has of necessity confronted the issue of when cleaning becomes a requirement. At what oxidant concentration? At what pressure? To what degree? Fortunately, as would be expected and hoped, almost every group that asserts an opinion, has adopted similar (but not identical) criteria.

However, in the 1990s, an emergent group, the recreational diving industry, adopted considerably different and novel practices for oxygen-enriched breathing-gas systems than were commonly observed. These differing practices were doubtless driven in part by the economy achieved by less scrupulous cleaning, such economy of which can be substantial. This led many in industry, government and others to re-examine there own opinions about special-cleaning thresholds and to defend their practices. Various correspondence contemplated the differing practices, and the Compressed Gas Association launched a Docket 96-86 to explore it. The Docket, in turn, launched a Task Force to study the basis for establishing

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such criteria and make a recommendation to the CGA.

The 96-86 Task Force was initially chaired by the writer until his retirement in 1999 and contained members from a spectrum of companies. Its charter was to consider the experiential, theoretical, and experimental bases for adopting threshold criteria. The majority opinion among old-guard practitioners of oxidant safety was that the emergent practices were too liberal. However, if the emergent practices could somehow be validated, that perhaps then the economies could be exploited in other systems as well.

The Task Force surveyed and interviewed numerous old-guard practitioners (in industry, government, military and academia) as to what their internal criteria were and why. It also conducted a literature search for incidents, standards, and experimental data, and it speculated on open issues. It kept ASTM Committee G-4 apprised of its efforts and solicited its input.

Ultimately, the CGA published a position statement (PS-13) in the early 2000s (revised in 2007). The writer has not seen the final product but late drafts of it were largely consistent with traditional practices, which are deemed conservative. Most criteria like this do not elaborate on the bases for the position taken.

And that leads to a subplot for this paper dealing with the human factors involved in adopting technical practices such as the full body of CGA and ASTM G-4 work. In the mid 1970s, the writer bought into the practice of justifying safety (among other) technology practices, which prescribes the documenting and publicizing of bases for all positions and practices. The writer has been a harsh critic [***1***][3] of standards and especially codes that do not defend their bases and are not open to examination. In that spirit, this paper recapitulates, revises, and updates the technical data and some of the human speculations that were a part of the CGA Task Force early effort and attempts to elaborate upon them and give them an improved context.

A part of this subplot is a proposal to ASTM G-4 in 2000 that went wrong. The writer sought back then to pursue a standard on defining and estimating fire limits in homogeneous mixtures to be supported with a computer utility for making such estimates from empirical or theoretical data. ASTM G-4 (among others) declined such effort citing as bases the complexity (and it is a complex subject that is poorly documented), lack of energy, and lack of pertinence to the oxygen compatibility subject (the latter disputed by the writer [***2***]). The subject of defining and assessing the hazards of cleaning threshold concentrations is a powerful example of why ASTM G-4 and oxygen safety practitioners need both this knowledge and capability.

Justifying Safety Technology

Even if there are many settled oxidant safety practices, oxidant compatibility is by no means settled science. The foundations for many oxidant safety practices are surmised, based on “what has always been done”, “what has worked”, and ‘what is probably going on.” Today, ASTM G-4 does far better at justifying safety than most. It includes numerous technical notes in its standards and cites extensive references, and many of its standards are based upon and buttressed by a significant public body of technical analysis and discussion in its own series of oxygen safety publications: *Flammability and Sensitivity of Materials in Oxy-*

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[3] Italic numbers in brackets refer to the reference list at the end of the paper.

gen-Enriched Atmospheres, Volumes 1-11.

The ASTM body of work is impressive but there is no concerted effort to provide a basis for each and every criterion or design principle that the Committee advocates—an effort that would be well undertaken.

The argument to justifying safety is that those who manufacture, design, use and operate oxygen systems will better fulfill their duty if they know the significance of each task, each rule. There are many historical incidents that could be cited to exemplify the philosophy. In the writer's case, his first exposure involved an incident in which a small chemical plant was lost when the operator failed to realize the relative critical nature of certain of his duties. While diligently performing some required functions, other functions went haywire and were not monitored nearly as closely as needed. There is a big difference between controlling a valve *because failure to do so will cause an explosion or fire*, and failure to maintain a clean workspace *because failure to do so may cause slips and falls*. The writer could try to make a case (on the basis of reports in the perhaps too-often unreliable news media) for the NASA Challenger incident being in this same category. While the hazard was known to some, and while some were diligently doing their duties, some didn't perceive or didn't know the critical nature of other events. And finally, the writer would certainly cite the National Highway Traffic Safety Administration (NHTSA) and its abominable stewardship of car safety in the United States as a grievous offender but has already elaborated on them elsewhere.

And so for a time, the writer worked in an environment and contributed to a philosophy that no safety rule should be prescribed without giving a basis for it. And in cases where guesses are being made in a data vacuum, even knowledge of that can be valuable.

This paper will attempt to overview some of the issues of oxygen concentration thresholds above which special cleaning is needed against the perspective of the literature review assembled for the CGA Docket 96-86 Task Force. It will examine traditional practices and the controversial differing practices and try to defend and support both. It will seek to provide the writer's opinion (his speculation) of the bases for cleaning recommendations such as the CGA PS-13, ASTM G 94 and others documents, although only the originating sources could correctly and properly do that, and perhaps they will choose to offer their own commentary on portions.

Oxygen Concentration Cleaning Thresholds

ASTM Standards itemize numerous bases by which one might adopt specific oxidant safety practices, including:

- Whether a fire can occur at all
- The probability of ignition being acceptably low.
- The consequence of a fire being tolerable

The most conservative approach is to operate under conditions where fire is not possible, that is outside of the fire limits, and this is used whenever realistic. But often it is not. Indeed, the largest amount of engineering material on a mass basis in oxygen applications is that of pipelines which are almost exclusively made of carbon steel which is usually capable

TABLE 1—*Examples of Cleaning-Threshold Criteria Circa 1998*

CGA G-4.1	Clean for oxygen	Clean for oxygen as specified in G-4.3
CGA G-4.3	Oxygen specification	Oxygen is in the high 90% range.
CGA G-4.4	Piping for oxygen	Oxygen is >23%
CGA G-4.6	Oxygen compressors	Oxygen is >90%
CGA G-4.7	Electric LOX pumps	LOX is >95%. Care needed at 25% to 99.5%.
CGA G-4.8	Structured packing.	Incidents are all at >99.5%
CGA G-4.9	Heat exchangers	Applies to 80% to 99.9%.
CGA P-8	Working atmospheres.	Safe at 19%-23% oxygen.
CGA P-14	Accident prevention.	O_2 enriched is >23% or >175 torr partial pressure.
CGA P-25	Flat bottom tanks	O_2 enriched is >23% or >175 torr partial pressure
ASTM G-4	All standards	O_2 enriched is >25%.
NFPA 53	O_2 enriched atmospheres	O_2 enriched is >21% or >160 torr partial pressure.
NFPA 99	Healthcare facilities	O_2 enriched >23.5%
NFPA 99B	Hypobaric facilities	O_2 enriched >23.5%
US DOT	Oxidizing NOS mixtures	O_2 >23.5%
US OSHA	Confined spaces	O_2 >23.5% is hazardous.
US OSHA	Commercial diving	Oxygen service is >40%, clean of flammables.
EIGA 33/86	Cleaning Guideline	Clean for oxygen and mixtures with O_2>25%

of combustion if ignited. However, practices have been developed to limit the probability of steel ignition to acceptably low levels in many cases and to a low consequence in others.

Historically, most oxygen safety practitioners have applied special cleaning to most oxygen-enriched systems. Some elected to specify cleaning of simply oxygen-enriched air, while most specified cleaning at enrichment levels beginning at from 23% to 25% oxygen. These were apparently all single-sided criteria. That is, cleaning was required above the threshold, but it was not intended to exonerate systems below the level from any cleaning. Indeed, many systems can experience fires, and indeed, numerous incidents have resulted in systems exposed to actual air and sub-air oxygen concentrations.

What Are the Pertinent Data?

CGA Task Force 96-86 searched the literature in the late 1990s and found numerous valuable information. Numerous documents cited thresholds of their own applicability that defined and distinguished "oxygen" from other gases in terms of purities near 100%. Some defined thresholds of applicability for oxygen without being specific to cleaning thresholds. And some were explicit as to when special cleaning was needed. Table 1 lists clear thresholds that were identified, some of which affect cleaning.

However, these thresholds are not typically predicated upon the exact boundary at which fire or ignition is possible, nor separated from it by either a safety margin or safety factor. In the writer's experience and view, these are largely based on jurisdiction. These may all be based on the existence of the fire hazard at the lowest level of some jurisdictions. In the case of the ASTM Committee G-4 criteria, a major factor was the desire to concentrate on oxygen enrichment and to avoid addressing air systems. However, some are based on incidents that might happen in some equipment without exemption for other similar equipment at similar conditions that might not experience the same hazard. That is to say, a more conservative approach was taken with cleaning than was taken for other thresholds that define fire hazards resulting from polymers or metals.

Test Data

The following literature is a subset of the literature reviewed by the CGA 96-86 Task Force, as prepared originally by the writer, thinly revised and in some cases expanded.

Burgoyne and Craven [***3***] treat a primary hazard of air systems as when an oil film is removed from a surface and either dispersed or vaporized with the air. Mechanical effects (flow and shock wave) may remove the film. Adiabatic compression or other heating may vaporize the film.

They appear to apply the traditional approach used with lower fire limits for hydrocarbon fuels which finds that the limits for a wide range of hydrocarbons is at a constant heat loading and temperature, and because most hydrocarbons are basically chains of two hydrogen atoms for each carbon atom, the limit is at a near-constant density of the fuel in the oxidant gas.

This is equivalent to saying the oil achieves a fire limit when:

$$t = CDP/4d \tag{1}$$

where: t = film thickness; P = absolute pressure in atm; C = min. weight of oil per pipe volume at the oil's lower flammability limit at one atmosphere pressure in g/m^3; D = pipe diameter in m; and d = oil density in g/m^3 .

Since thorough mixing of a dispersed or evaporated oil film would be more likely to occur in smaller tubing than in larger pipes, this formula appears to be more appropriate to smaller inside diameters (providing they are not smaller than the quench dimension). If evaporated oil were to be concentrated near the wall of a large pipe, it might yield an envelope of flammable mixture in the affected sub-volume at lower than apparent bulk or average fire limits that might be predicted with this equation for a uniform mixture.

Presti and DiSimone [***4***] rapidly compressed oxygen into oil-coated dead-end pipes. Their work suggests that an incoming pressure wave might strip oil from piping and transport it to the dead end, yielding a greater concentration locally than would be calculated based on average bulk conditions. Even though their work suggests fires are possible locally at conditions below those predicted by the equation in Burgoyne and Craven, their work also appears to support the notion that the oil may burn only when it has been removed from the surface by mechanical gas actions or evaporation rather than through liquid-phase reactions.

Ignition temperature can decrease with increasing oxygen concentration. Hence enriching a system may enable a fire and explosion due to oils or contamination that was not possible before, but this effect is not addressed and may be small.

Werley [***5***] ignited oil films applied to thin vertical brass substrates at atmospheric pressure in oxygen/nitrogen concentrations near that of air and at oxygen-enriched levels. The combustion observed was local and candle-like and slowly moved along the surface.

Loison [***6***] studied two air compressor incidents and conducted related experimentation. He passed heated atmospheric-pressure oxygen or 100-psig air over oil. The hot oxygen led to spontaneous heating of the oil at approximately 150 °C to 160 °C (300 °F to 320 °F). Spontaneous heating occurred as low as 137 °C, and flaming combustion occurred as low as

151 °C. Flow rate was significant in limiting the self-heating.

Loison also studied air in contact with oil at room temperature and 100 psi. These test cases employed hot-wire ignition with a localized gaseous fuel/air or fuel/oxygen-enriched air mixture. Fuel air ignition led to extensive combustion and fuel/oxygen-enriched air ignition led to massive damage.

Perlee and Zabetakis [***7***] studied causes of ignition. They concentrated on the work by Loison and many others and review it, and they conclude that ignition and explosion in compressed air systems at pressures at least as low as 100 psi were most typically caused by combustible vapors resulting from the presence of oils. The cause of the vapor production and the vapor/oil ignition was less certain and almost certainly the result of several mechanisms.

These authors cite and examine:

- Oil vapor or mist abruptly introduced into a system as a result of seal or other failures.
- Exothermic decomposition of oil to produce spontaneous heating of oils.
- Oil decomposition to yield volatile constituents.
- Iron oxides that can catalyze oil reactions.
- Removal and dispersal of oil into a flammable state by shock waves.
- Prevention of air compressor fires and explosions by periodic cleaning and re-cleaning.

Coward and Jones [***8***] and Zabetakis [***9***] are time-honored references on "flammability limits" which this writer prefers to call “fire limits”. Traditionally experimentation and publication has focused on the lower flammability limit (LFL), the upper flammability limit (UFL) and the minimum oxygen for combustion (MinO_2). However, fire limits can be arbitrarily defined in many ways. The lower and upper limits vary the amount of fuel in an oxidant and seek to identify the lowest and greatest amounts, respectively that just allow a fire. The MinO_2 is defined much more subtly. To measure MinO_2, they vary the amount of oxygen in a two component mixture with a nonreactive gas, then test various mixtures of that two-component mixture with a fuel, and the MinO_2 is the minimum amount of the oxygen *in the two-component mixtures* that will just allow a fire for *any* mixture with the fuel. The MinO_2 is **<u>not</u>** the amount that is present in the three component flammable mixture including fuel and is numerically larger.

This definition is consistent with the parameter of interest regarding special cleaning needs. In the case of enriched air, one is interested in how much oxygen can be present in the (basically) two-component oxygen/nitrogen mixture that may pose a fire risk regardless of the oil or contamination that may be present in a system.

Fire limits will generally widen if the temperature or pressure of a system is raised. However, at room temperature and atmospheric pressure, simple hydrocarbons (namely the paraffin's, all tend to have lower flammability limits near 45-50 ml/l (but there are important exceptions, see Zabetakis [***9***], p. 20).

Early theories on fire-limit behavior are reviewed in Zabetakis, Lambiris, and Scott [***10***] and among the earliest is that the lower limit is fixed by heat liberated by a mole of lean-limit mixture (which is nearly constant for many mixtures), to the later perspective that the adiabatic flame temperature of lean-limit mixtures is approximately constant.

TABLE 2—*Oxygen Concentration Threshold Versus Pressure* (Benning [***14***]) and Ikeda [***12***]).

Material	Oxygen Index
Polyacetyl	14.7
Polypropylene	17.6
Poly(methyl Methacrylate)	17.7
Silicone Rubber	21-32
Buna N	22
Nylon 6	24
Polycarbonate	27.4
Poly (vinyl chloride)	38.1
Vespel	53
Viton	56-100
Polytetrafluoroethylene	100

The correlation between the pressure of an oxidant gas and the spontaneous ignition temperature of two oils is reviewed by Zabetakis, Scott and Kennedy [***11***]. This suggests oils not only have wider limits at higher pressures, but pressure may also make them easier to ignite.

Solid materials also exhibit a minimum required oxidant concentration in the gases they can burn in, defined as the oxygen index. Ikeda [***12***] reviews some of the experimental data, and Werley [***13***] reviews the correlation between the MinO_2 measurements for mixtures and blended gas streams. The lowest polymer oxygen index among those Ikeda reports is 14% for polyacetyl. Many polymers will burn in air and most will burn in less than 30%. Only a few require concentrations approaching pure oxygen or resist burning even there.

Table 2 exhibits the data presented in the CGA 96-86 Task Force report. When pressure and temperature are increased, polymers, like gases, become easier to burn (Benning [***14***] and Ikeda [***12***]).

Benning [***14***] reports that polytetrafluoroethylene (PTFE) experiences a decrease in index from nearly 100% to about 50% as pressure approaches 300 psig.

Metals also exhibit oxygen concentration limits, and among those that have been studied, the limits decrease with increasing temperature and pressure much as for polymers. In the case of carbon steel, Benning and Werley [***15***] report that that the oxygen concentration threshold in mixture with nitrogen fell from about 80% at about 1 MPa (132 psig) to about 50% at 8-20 MPa (1000-3000 psig).

A First Speculation

The CGA 96-86 Task Force confronted two speculations dealing with dissolved oxygen in oils and the role of moisture (the latter to be covered later).

Flammable liquid mixtures are always a concern. Often owing to their densities, they can exhibit exceedingly fast reaction and often fall into the category of “high” explosives. Among the materials in this category are granulated frozen or fine structured solid material in liquid oxygen, which can be awesome, sometimes erratic, explosives. The more uniform the mixture, the more explosive these materials tend to be.

What if oxygen gas were sufficiently soluble in oils at elevated pressure to pass through a fire limit condition? And if such a condition were possible, how long would it take to come to saturation? In some cases, incidents in oxygen cylinders have happened after long periods of time. Could a long dissolution time explain the delay?

However, most literature seems to suggest (perhaps unintentionally) that an oil contamination must become dispersed before a fire is possible. These analyses take the tack that the oil must filter into the oxygen and raise its fuel concentration above the lower flammability limit. In comparison, oxygen diffusing into a liquid oil would have to raise its oxygen concentration through the limit for a “fuel-rich” fire (that is, through the upper flammability limit from above).

At first blush, this is curious. For many hydrocarbon gases, it requires only a few percent of fuel in air or oxygen to achieve the lower fire limit, whereas it requires much greater addition of oxygen into gaseous hydrocarbons to achieve the upper limit. However, as pressure and temperature rise, both limits widen. Also keep in mind that in the condensed state the density of most materials is hundreds to a thousand times greater than for the gas. This increased density will render an oil film fire to be much more adiabatic (much less likely to have radiation escape for example) than would be the case for a gas-phase fire. This is to a large extent why condensed explosives can be so “angry”.

When oxygen is the limiting reactant, the heat produced (and therefore explosive energy) in an oil film fire would be related to the amount of oxygen present rather than the amount of fuel present. Hence the “upper” limit for an oil film may be at a much lower oxygen concentration than is required for fire in a corresponding gas-phase mixture.

There is a possibility, perhaps supported by anecdotal observation over the years, that even in the absence of an explosive fire between oil and oxygen dissolved into it, there might also be a lower-order exothermic release that might react the oxygen and evaporate some of the leftover oil to produce a gas-phase flammable condition.

Grumer [***16,17***] reports that dust layers require less oxygen for reaction than do the same dust layers when dispersed in air. Superior adiabaticity in the layer may be the cause. However, this may also argue that the level of dissolved oxygen in an oil film may be less than needed for a gas-phase limit.

Unfortunately, there do not appear to be any data today that would allow for meaningful assessment of liquid-phase fire limits. Much work has been put into predicting gas-phase fire limits, yet most limits that are employed are based on experimental data. Just what are the lower and upper limits for powder in LOX and for oxygen dissolved into oils? These data would be valuable to have.

The 96-86 Task Force examined data from an Air Products’ database that predicts solubility of oxygen and nitrogen in hydrocarbons. These data are fairly well established. Indeed the writer has heard of patents for the separation of air that employ preferential dissolution of oxygen and nitrogen in hydrocarbons (possibly unused today due to an explosive risk). At elevated pressures, the concentrations of oxygen possible were in the several percent range. This is high enough to lend credence to the fire possibility. A paper exploring the solubility patterns of oxidants among various hydrocarbons at various pressures would be worthwhile and is encouraged.

A second worthwhile paper would be an analysis of the fire-limit behavior of fuel-rich hydrocarbon-oxygen mixtures at elevated pressures approaching the density of liquids.

Today various Gibbs free energy minimization methods are used to make such estimates and if the required "lower flammability' limit for oxygen in hydrocarbon gas (which is the upper flammability limit for hydrocarbon gas in oxygen) tends towards the low percentage range (even ignoring any latent heats of evaporation), then this is a hazard that Oxygen Safety Practitioners need to address.

Incident Experience

Contamination may be the most frequently cited factor in oxygen-enriched system fires. Sufficient oil that burns will rupture many a system. In lesser amounts it can burn and wreak widespread heat damage. In still lesser amounts it may ignite other components or metals which may then provide a major heat source. And in still lesser amounts, it might just possibly sensitize other materials and render them more vulnerable to direct ignition by traditional ignition processes.

Only a very small fraction of the incidents that occur are ever reported in the literature. However, among the few are several of great interest here [**6,7**].

There is no doubt whatsoever that compressed air in combination with a fuel material and ignition can be destructive and has on occasion ruptured pipes and blown the sides off of buildings. Cars compress actual air, mix it with gasoline and with high reliability produce power.

Ball [***18***] elaborates on the data of Zabetakis, Lambiris, and Scott [***10***] and Zabetakis, Scott and Kennedy [***11***] and describes actual incidents involving impure nitrogen compressors which experienced fires and explosions at oxygen concentrations as low as 3.5-5%. One of these incidents was in the second stage of a high-pressure compressor and occurred at 180 psig. These events are attributed to wide flammability limits that result at elevated pressures and/or elevated temperatures.

And yet these incidents are most significant, because they are the seeming exceptions that test the rule. Events like this are rare despite the massive numbers of both large and small compressed actual-air systems and blended air systems. Such events *can* happen but seldom do.

Setting Thresholds

The review above presents the cold hard data. Now what about the human factors that go into selecting a threshold concentration for cleaning?

How does one go about setting a threshold concentration for the cleaning of oxygen or other oxidant systems? At first blush, a conservative approach would say to clean every system exposed to any oxygen or oxidant concentration above the lowest at which an incident or experiment has shown the possibility of a fire developing. And this would be the conservative initial approach. However, as life became complicated, this approach would suffer.

This approach is comparable to encouraging use of nonflammable polymers and metals in every system at any concentration, pressure or temperature above which any incident or experiment has indicated a fire limit could be exceeded or was exceeded in the past. Needless to say, this is not how polymers and metals are always selected (though *sometimes* they are selected this way). They are perhaps more often selected on the basis of whether a fire limit is crossed, but also on whether a probability of ignition is too high, or whether there is an unacceptable fire-consequence possible. This is a much more sophisticated and flexible approach. However to date there has been no known effort to adopt "limits" of approval for situational cleaning requirements that are dependent functions of not only percent concentration but pressure, temperature, phase, and contacting materials, etc.

As the writer among others has noted [***5***], oils also tend to migrate throughout a system in very complex ways. They collect into puddles. And so very quickly one would come up against the issue of "How clean is clean?" "Completely clean" is not a realistic goal and so there would soon arrive (as there has) a whole spectrum of cleaning levels that are acceptable. And all of them are considered to be "clean". But clearly they are not equal.

So specifiers must then specify both an oxidant concentration threshold and a threshold contamination-level. On the basis of the above data, fire is possible in oxygen concentrations at least as low as 3.5 percent. However, 3.5 percent does not qualify as "oxygen enriched" which clearly starts at concentrations above that of air, and so such a specification would quickly lead to demands for more sophisticated criteria. This is a strong incentive for those interested in oxygen to forego the adoption of criteria for systems at and below the composition of air.

Is it really a problem for the oxygen safety community to specify cleaning for systems above 3.5 percent when it knows of incidents that have occurred at 3.5 percent? What is the impact of requiring cleaning of systems at 25 percent but not at 21 percent? Today, the 21 percent case is outside the oxygen-enriched region. Don't we need to avoid fires at 21 percent? And even at 3.5 percent? Should those who demand cleaning of 23 percent oxygen systems also similarly clean their own compressed actual-air systems (many may not)?

Although there have been severe incidents in air systems and even at lower concentrations, there is also a compelling body of experience that would argue that many air systems even ones not specially cleaned are indeed safe (at least up to a 100 psig or so). Why is that? Are the air incidents being ignored? Are the air users more careful?

The 96-86 Task Force contemplated an issue that the data do not resolve. Although, speculation, there is a vast assortment of generic compressed actual air in use and it may be significantly different from industrial gas-blended air and selected compressed actual air. The vast majority of compressed air systems in use are indeed actual-atmospheric-air that has been compressed. As a result, it contains small, but perhaps not insignificant, amounts of assorted gasses besides oxygen and nitrogen, except for selected, typically larger, systems that employ driers. Its largest tertiary constituent is water. And if one performs fire limit study on the effect of water on the flammability of other materials, for example gases, water (the most widely employed of extinguishers as a liquid) often (but not always) has a fire inhibiting effect even as a gas.

Water vapor also has the effect of preventing static electricity (unless it freezes to form crystals in which case it can aggravate static electricity). It narrows fire limits and can even swamp a fire. There is appreciable water vapor present in a massive majority of those air compressors in auto service facilities. In all those home air compressors. In all those compressors used to power tools and spray paint. In all those compressors that are seldom maintained, many of which are likely to suck organic materials and dust and solvents and paints into their intakes. To the designer of oxygen-enriched systems, this scenario would be a nightmare. And yet it appears there is seldom if ever a fire. And this experience is vast.

The CGA Task force recognized this prospect, and the ASTM Committee G-4 in 1998 posted a potential proposal [***19***][4] to suggest studying the effect of water on oils in contact with oxygen. However the experiments were not conducted (or at least not made public). Nonethe-

[4] ASTM G-4 posted a draft ISP (Industry Sponsored program) proposal for potential study of water on ignitability and of dissolution of oxygen in oils on its web site.

less, it begs the question whether the humid oxygen in some air compressors is less hazardous (even to dissolved oxygen in oils) than the dry oxygen in oxygen/nitrogen mixtures, or possibly even to dried compressed actual air, that are both similar to air in concentration but have produced fires in industrial systems and even in crude (albeit warm) nitrogen that still contained only 3.5 percent oxygen from its original air.

Enter The Recreational Diving Dilemma

As reviewed by Gabel and Janoff **[*20*],** in the 1990s, oxygen-enriched air came into common use by recreational SCUBA divers. Previously enrichment had only been used by small groups such as the Navy. Concentrations used were divided (perhaps arbitrarily) into two classes, up to 40 percent and above 40 percent. The historical base of experience was therefore small and there may have been incidents, but this commentator is not aware of any. However, spreading this practice widely to potentially less thoroughly trained divers raised the specter of a new hazard. In addition, as a new industry, its promoters were entrepreneurial to a high degree and were enthusiasts, as well as vendors. However, they were also largely outsiders to the subject of oxygen safety as it was being promoted by the CGA and ASTM G4.

The equipment and practices observed in these systems at up to 40 percent oxygen were little different from those used with commercial compressed actual air, however, the pressures used for diving were well above the pressures in most compressed actual-air systems. There was little or no special cleaning. Gabel and Janoff [***20***] lament the industry's arguments that it had had no incidents to date (which was relatively weak because the statistics were so small). But there was another factor operating that was subtle. The Occupational Safety and Health Administration (OSHA) had published a "presumably single-sided" criterion (CFR §1910 Subpart T Commercial Diving Operations, §1910 430i Oxygen Safety) which dictated that

> "(1) Equipment used with oxygen or mixtures containing over forty percent (40%) by volume oxygen shall be designed for oxygen service" and (2) Components (except umbilicals) exposed to oxygen or mixtures containing over forty percent (40%) by volume oxygen shall be cleaned of flammable materials before use."

Clearly cleaning was mandated above 40 percent but that was *probably* not intended to imply that it was totally unnecessary below 40 percent. But that is how it was apparently interpreted. The groups that were used as a model for the legislation apparently reverted to high pressure air standards below 40% for which they still employed some degree of contamination control. This is the same issue as for the single-sided threshold for enriched air. Cleaning that is required above 21-25 percent does not mean to imply that incidents can not happen below 21 percent (and they have happened down to at least 3.5 percent). But this single-sided subtlety is easy to misinterpret.

So there were two dilemmas. Industry cleaned above 21-25 percent because it was oxygen-enriched and capable of fire or explosion but was much less cautious with cleaning below this threshold (at least at lower pressures) even though there were few if any technical data defending that boundary as a fire limit. And now here was an industry, using a similar single-sided criteria to justify the omission of cleaning at higher levels than 21-25 percent, which also apparently had no compelling relation to any local boundary as a fire limit.

If at least some generic actual-air compressors can be safe (and statistically they apparently are) without special cleaning, then why can't recreational diving systems (albeit based on much flimsier statistics and for higher pressure systems)?

These dilemmas become much more problematic when one considers that in many cases (perhaps not all of the time) the recreational diving industry was employing breathing gases with much higher levels of moisture than were present in industry systems or in the previously blended mixtures used for diving. In some case, they were using the reject stream from membrane nitrogen generators which contain the atmospheric humidity (nitrogen apparently filters through the membrane leaving the oxygen, water and all the other gases behind in enriched quantities). This was (and maybe still is) a very economical way to obtain oxygen-rich respirable gas. In some cases, oxygen from pressure swing adsorption plants (another lower cost source of oxygen enrichment that also apparently has much higher levels of moisture present) may have been used. In comparison, all of the mixtures used by the previous generation of divers may have employed bone-dry cryogenically produced blended-gas mixtures of nitrogen and oxygen alone.

Suddenly the two dilemmas are joined. The recreational divers may have had good but small statistics to defend their practice, and they may have also had moisture (and in most cases other gases) present that is also one of the potentially most significant differences that might explain a difference between industrially blended "air" and compressed actual air.

If the moisture effect (or other gas effect) is real and significant, it may not only be of great importance but of great value to understand ….and to exploit.

Fire Limits and FLLAME

Contamination in oxygen service is one of the first hazards identified and one of the most important. Special cleaning is one of the first and most widely practiced safety measures. In some systems in which no other precautions may be needed, cleaning can still be crucially important.

Throughout the preparation of this paper, as is the case in many instances in the oxygen safety literature, one encounters citation of the "fire triangle" concept to simplify (the writer likes to think over-simplify) and explain traditional fire-limit hazard analysis. The fire triangle cites three factors necessary but not sufficient for a fire to obtain. The fire triangle is a useful tool for introducing a few of the key factors in the occurrence of a fire, but it is much less useful for the actual evaluation of a fire risk for the sake of prevention. Nonetheless, the fire triangle is very popular.

The fire-triangle level of sophistication is best characterized as a blunt tool, a bludgeon, when applied to oxidant systems. The writer apologies for previous writing (2000) [***21***] which discussed (with perhaps a tad too much sarcasm and mocking) the fire square, fire pentagon, fire hexagon, fire heptagon and fire octagon[5]. One can design systems based on the absence of one or more of the three triangle legs (fuel, oxygen and ignition) or other "legs" (up to at least eight in number) that can be assigned to a more complex, but more powerful, symbolic figure,

[5] In the 1970s or before, a slightly more sophisticated artifice was created, the Fire Tetrahedron—a pyramid in which each of the four triangular sides were the key factors, three representing the usual fire-triangle legs, and adding a forth in the form of "chemical reaction" or "chain reaction". Apparently for some time there has also been another formulation of a "fire square" that used "extreme weather" as it fourth factor. All of these however appear to derive from the firefighting industry and seek to itemize factors which allow for the extinguishment of a fire. The fourth side was added because of Halon fire extinguishers which do not employ any of the first three factors (legs or sides) in their operation.

but in an oxygen system there is always a fuel (the system), and oxygen (the stuff being contained) and preventing ignition actually demands a pretty steep knowledge of fire theory. To a large extent, practical prevention of fire often demands more detail from the discipline within the body of fire practice known as fire limits.

In evaluating fire limits, the fire triangle is an extremely and excessively simplified model[6]. But there are few oxygen safety practitioners who are steeped in fire-limit analysis. Indeed, in many cases, fire-limit practice is such a complex and empirical subject that theoretical analysis of systems proves flawed. Few today would calculate a fire limit and trust it solely. As a result, today much and perhaps most fire-limit analysis is based on empirical data that is interpreted and interpolated and the larger theoretical context is used to validate and buttress empirical data. Often fire limits are not even referred to as fire limits but instead employ less intimidating terms like “threshold” or “boundary” or “index”. Prediction of fire limits is still not attempted for many materials, and fire limits that are calculated are seldom taken as certain. And once fire limits are estimated or actually measured, the interpretation of the importance of those data is still a challenging task, still a real mountain to climb.

The writer has climbed on that mountain for decades, with only limited success and a lot more frustration. The fire triangle, useful as it is for step one in a training process, has not held him in good stead thereafter. In retirement for nearly a decade, he still struggles to convince ASTM G-4 to build a body of standards and tools to deal with the practices for fire limits. G-4 has demurred so far based on the complexity of even the basic material that would be initially tackled, but they have also cited low levels of available energy and interest.

However it is the commentator's conviction that the subject of oxygen compatibility can not be complete nor adequately addressed without practical (if somewhat complex) tools to address basic fire limit issues and much more. It can be surprising how little use it can be for one to know that a lower fire limit of a fuel in oxygen is “x” per cent, or that an oil film of “y” thickness could produce a fire-limit concentration, or that a polymer will burn in “z” percent oxygen in nitrogen.

In reviewing the data in this paper, one should be impressed at how dependent the physical hazards for threshold concentrations for cleaning are on fire-limit perspectives. These are some of the most crucial safety measures Oxidant Safety Practitioners face. The oxygen safety community needs to deal in some detail with fire limits, needs to take on standards in the area, and most of all needs to simplify the material but to a level far more sophisticated than the basic fire triangle.

Reconciliation

It is meaningful to recommend cleaning of oxygen systems starting at 21-25 percent as has been done. This may have been done, probably was done, more for human than for technical reasons but nonetheless it will provide safety. For the same reason, it is meaningful to recommend “complete cleaning”. And it is also meaningful to recommend making all oxygen sys-

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[6] The writer is loathe to condemn any efforts at simplification, having recently used simplification as justification for a massive effort of his own to make adiabatic compression processes in oxidant gases more comprehensible to the ordinary Oxygen Safety Practitioner. But incongruity arises when one scans the body of ASTMG-4 work and some of its extreme esoteric analysis then confronts diametrically extreme efforts to simplify fire limits. Perhaps a fair and balanced approach might be to allow some additional complexity regarding fire limits and strive to simplify more of these other topics.

tems of copper and using only minimal amounts of PTFE polymers at strategic regions. This too will usually provide safety. However today the oxygen safety community provides rather complex situational and circumstantial strategies for employing metals other than copper and polymers other than PTFE, and it even provides so-called weasel room on certain dimensions of cleaning, too.

Similarly, it is meaningful to recommend cleaning of systems starting at 3.5% oxygen and yet this is not done, and the writer believes for good reason. This paper has elaborated on what the writer sees as dilemmas in the practice of oxidant safety. If indeed (as can be argued), many compressed actual-air systems up to some pressure that can not be precisely identified are safe without special cleaning, then recommending cleaning at 3.5 percent would be an overly conservative and wasteful limit, because not every 3.5 percent system is at risk.

If moisture or any of the other constituents of actual air provides any degree of protection to actual-air compression systems (as statistics may suggest) or to some range of actual-air based oxygen-enriched gases, then it would provide a valid basis for the practice of using these systems with reduced or no special cleaning.

Indeed in the distant past, there was a time in the air separation industry when high pressure compressed oxygen was compressed using soap/water lubricated compressors. The oxygen was much more humid and there were corrosion issues in the steel cylinders. But there may have been (and the writer surmises there was) a reduced risk of fire, but here again documented experience is smaller and less reliable to assess.

In the medical industry, there is concern for the use of halogenated polymers in oxygen systems. They resist burning but when they do burn they can produce highly toxic chemicals (like phosgene, the WWI WMD gas) and can poison patients downstream. Less fire-resistant materials that produce less toxic gases offer a way to balance the risk, by reducing a fire’s toxic consequence at the cost of increasing its potential frequency. If water is protective, then perhaps medical oxygen should contain a water constituent as a safety measure. Although this would not appeal to the users of steel cylinders because of potential corrosion, the medical industry also likes aluminum cylinders (despite their own fire risks) and much of its hardware may be more able to tolerate moisture. Indeed, since aluminum itself is capable of spectacular fire, the water might also serve to mute the hazard therein (but this is speculation and one must also consider that at some high pressures moisture may freeze into crystals during gas expansion that promote static electricity and an increased potential for ignition). Humidity, even in small amounts might even change the fire limit of aluminum cylinders (as do some other diluent gases even in very small amounts), or might change the fire limit of lubricants and contaminants. And since bone-dry oxygen is often not desirable for the patient, moist oxygen might have multiple benefits. But the writer is unaware of any analysis of how much humidity might be possible or how much might be needed in various applications, or data that would allow for real insight into these apparent dilemmas. These data would be worthwhile to have.

What the writer thinks he knows is that the reported incidents at 3.5 and 5 percent are sufficient to prove that the fire limit is that low in at least some systems. He also thinks he knows that the body of home and industry compressed actual-air use at common pressures is so huge and public (and therefore so challenging to careful use principles) that it is unlikely to prove that actual compressed air is a hazard in those systems even with some degree of lubricants and contaminants present, and this effect is likely to extend at some higher-than-air oxygen concentrations, as well.

Human factors may ultimately dictate whether any benefit of moisture or other minor constituents is too small or complex to warrant modification of current practices. Any inconsistency or dilemmas in the oxygen concentration threshold recommendation may therefore be sustained for human-factors reasons unrelated to safety, fire limits, or other fundamental and technical safety issues, and it is important for the OSP to be aware of these bases.

Summary

Data that relate to the oxygen concentrations at which fire or other hazard limits are crossed were reviewed. The data do not appear to establish a fire limit, or ignition boundary, nor consequence threshold in the vicinity of the composition of air. Some fire limits may be crossed at much lower concentrations, and for some systems, the risk of fire due to fire limits or ease of ignition or even consequence may be low at significantly higher oxygen concentrations than that of air.

As a result, the cleaning of systems at or above the approximate concentration of oxygen in air is a conservative approach well taken because the knowledge of fire limits and ignition behaviors above this level is scant. However, numerous air systems provide a solid statistical proof that cleanliness is much less an issue in many compressed actual-air systems at common pressures, and it may be due to moisture or other low level gases present in these systems. When systems are drier or purer or warmer or at high pressures, the fire hazard may extend down to very low oxygen concentrations of even just a few percent.

The importance of knowing this background and the bases for choosing practical thresholds of special cleaning has been asserted both to aid those who may someday wish to establish the safety of higher thresholds, and to avoid misleading those who operate at the conditions of air or less-than-air.

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