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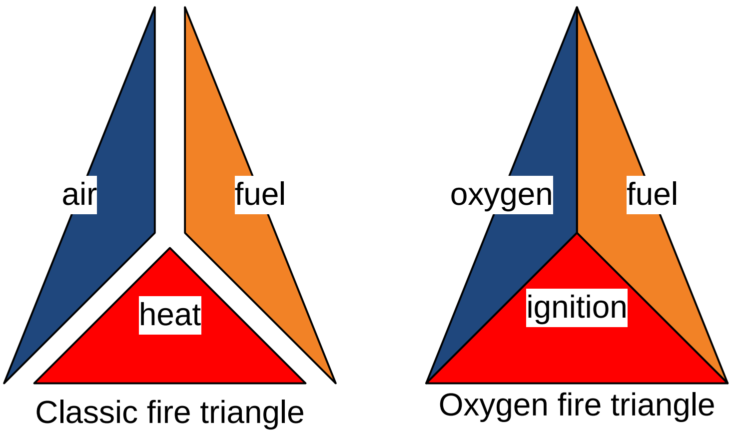
# Tech talk #9: (Oxygen) Cleanliness is next to godliness

Maybe it's been all those years working on yachts – shammy in the back pocket - that permanently damaged my brain. I can't stand a mess, I have to keep the workshop clean, all has to be organized... my special way of dealing with OCD. Most likely this will be the reason as well why I don't mind the tedious process of oxygen cleaning.

Bearing in mind that oxygen is present in the atmosphere at a concentration of around 21%; life on our planet would be non-existing without it... what's the fuss about oxygen cleaning all about then? Therefore it makes sense to have a closer look at oxygen in the first place.

Although the diatomic molecule oxygen in itself is chemically stable, is not shock-sensitive, will not decompose, and is neither flammable nor inflammable. Its use involves a degree of risk that shall never be overlooked. This risk is that oxygen is a strong oxidiser that vigorously supports combustion. Oxygen is reactive at ambient conditions, and its reactivity increases with increasing pressure, temperature, and concentration. As most materials, both metals and non-metals, are flammable in high-pressure oxygen; therefore, systems must be designed to reduce or eliminate ignition hazards. The bottom line: in oxygen rich environments things will simply burn more easily and rapidly.

Ordinary fires can be prevented or extinguished by removing one of the 3 components of the fire triangle: air, fuel or heat. When air is replaced by oxygen the classic fire triangle reveals an entirely different story. The triangle becomes inseparable: the fuel contains the oxygen and the oxygen contains the source of the ignition energy. Furthermore, once a fire is initiated the oxygen continues to fan the fire as it is an oxidiser and lowers the ignition temperatures. The ignition energy can be provided – limited listing - by the heat of adiabatic compression, frictional heating, resonance and particle impingement.




Unfortunately this is not the right time or place to go into further details about the oxygen hazards, however it should be clear that if we're dealing with elevated pressures or concentrations of oxygen whether that is in a blending system, a cylinder or cylinder valve or scuba regulator something should be done to minimise the risks associated with it.

Nitrox divers should be familiar with the concept of oxygen service. The idea behind the terminology of ‘oxygen service’ is twofold: it refers to an item which is (1) oxygen compatible and (2) oxygen clean. In a way closely related to oxygen compatible, personally I like to add a third concept to the definition: designed and engineered for oxygen contact, but we’ll leave it at that.

(1) Oxygen compatible: refers to the material and configuration of the component and its suitability for use within an oxygen system. The material will not react with oxygen at the operational pressures and temperatures specified for the system. Some examples of not so oxygen compatible materials: Buna-N o-rings, silicone based lubricants (for those who are in doubt, may I suggest to read this article: https://www.diversalertnetwork.org/diving-incidents/trust-but-verify#.VX4XjDiJhMs), plated steel and so on.

(2) Oxygen clean: refers to a component or item to be used in an oxygen system, which has been specially cleaned to remove and/or substantially reduce the concentrations of contaminants to minimize the risks of fire and explosions occurring.

Let’s have a little more in depth look at the concept of clean. First of all let’s identify some possible contaminants in blending and scuba systems, to name a few: scale, burrs and metal filings; corrosion, rust dust and other metal oxides; fingerprints (grease); cuttings oils used in the manufacturing process; chrome plate chips; carbon dust from filtration systems; airborne dust; pipe thread sealants; cleaning solvents or detergents; lint from wiping cloths; silicone grease... and of course hydrocarbons.

So it’s all down to a cleaning process in order to remove those contaminants. Cleaning methods and techniques used to remove those contaminants include, and most likely will be a combination of: mechanical cleaning, vapour degreasing, steam cleaning, solvent cleaning, acid based cleaning, wiping, flushing, soaking... But most importantly, once the cleaning process is completed, how do we know the cleaning process was successful? Simply, we have to prove that contaminants have been removed and hence depend heavily on the use of a wide array of tests like: inspection under white light, inspection under UV-light, wipe test, water break test... Whenever a component fails any of these tests, the component is not considered oxygen clean and has to be re-cleaned. In some circumstances it is as good as impossible to achieve this clean state. Example: how can you be certain that no contaminants are left behind in corrosion pits inside aluminium cylinders?

Pretty elaborate and tedious isn't it? As you might have guessed, it just doesn't stop there. Performing the 'ritual cleaning' and inspection process also requires a suitable environment. Ideally the work area should be a designated oxygen clean room to handle and reassemble any cleaned component without risk of re-contamination. Unfortunately clean rooms will be out of financial reach for most but the largest service shops. However, simple measures can be taken in the workshop to improve the working conditions.

Within the recreational diving industry it is generally accepted that regulators, SPG's and alternate air sources can be used with enriched air mixtures up to 40% without modifications. On the other hand, equipment exposed to gas mixtures with more than 40% oxygen need to be cleaned to oxygen service specifications. To the latter, this will include cylinders and cylinders valves that will be used for partial pressure blending (introducing 100% oxygen).

As you would have guessed, I wouldn't have brought up the subject if there wasn't room for any controversy. Although the 40% rule 'seems' to have a proven safety track record, the 40% rule historically originates from a single entry in 29CFR910.430 by the Occupational Safety and Health Administration (OSHA) of the U.S. Department of Labour, which applies to "Commercial Diving Operations". Within the same set of rules, Commercial diver means a diver engaged in underwater work for hire excluding sport and recreational diving and the instruction thereof. Despite this clear exclusion, within the recreational diving industry this rule has been cited. Looking into more US legislation, a threshold of 23.5 or 25% seems more acceptable – see table 1 -. Worth mentioning here is NASA: their threshold is >21% />100 PSI (6.8 bar); got to be said, those chaps might have a little experience with oxygen handling and unfortunately learned that the hard way. To add to the confusion, the IMCA recommends a threshold of 25%, EN12021:2014 mandates the use of oxygen compatible air in mixtures containing an oxygen concentration greater than 22%. Furthermore, in Europe both EN 13949:2003 and EN144-3 state that scuba equipment sold in CEE (European Community) countries over 21% and up to 100% will be manufactured with the special M26 fitting.

| Organization | Oxygen threshold | Reference |
|---|---|---|
| U.S. Navy | >25% | Mil-Std-1330D |
| U.S. Compressed Gas Association (CGA) | >23.5% | CGA Pamphlet 4.4 |
| National Fire Prevention Association (NFPA) | >21 – 25% | NFPA standards |
| American Society for Testing & Materials (ASTM) | >25% | G126, G128, G63, G94 |
| National Aeronautical & Space Administration (NASA) | >21%/>100 psig | Various KSC & JSC |
| Occupational Safety & Health Administration (OSHA) | >23.5% | 29CFR1910.146 |
| OSHA | >23.5% | 29CFR1910.134 |
| OSHA | >40% | 29CFR1910.430 |

Not only in geographical areas where legislation is not as strictly enforced or present, I believe it is foolhardiest just to stick to the 40% rule. If large geographical areas or industries have significantly raised the bar, why should the recreational diving industry not follow? To be politically correct, at least 3 agencies I'm aware of, both RAID, ANDI and BSAC have already raised this bar and deserve by hereby an honourable mention.

Regardless of the above discussion, let not lose out of sight the manufacturer's position and recommendations for the use of their equipment in oxygen rich environments. I suggest you read carefully some of their manuals and you'll get some fine surprises there. Do a little research and you'll find that both major cylinder manufacturers' Catalina and Luxfer state that oxygen cleaning should be performed if their cylinders are used with oxygen concentration in excess of 23.5%.

Many factors contribute to an oxygen reaction. If one would express oxygen safety in terms of a poly-factor equation p * q * r * s * t * u * v * x * y * z and regard the oxygen percentage as one of many factors out of the equation, let's say factor q, it is clear that if factor q ought to increase, it is not that simple to control the rest of the equation in order to keep the same safety factor. Just by saying if you keep the oxygen percentage below 40%, you only control just one variable; it doesn't mean the whole equation will give you a positive safe result.

Regardless of the above, sometimes I feel like putting things in a different perspective. As mentioned before, when talking about oxygen we have to consider the oxygen pressure. An approach in terms of percentages has its flaws, the pressure (partial pressure of oxygen) in a mixture should be considered. In order to calculate the partial pressure of each gas in a mixture a derivative of Dalton's Law can be used: it states that each partial pressure of a gas in a mixture is determined by multiplying the fraction of the gas by the total pressure of the mixture. In a cylinder filled to 10 bar of pure O2 the oxygen fraction has a partial pressure of 10 bar. On the other hand, a cylinder filled to 200 bar with an EANx mixture of 36% has a oxygen partial pressure of 72 bar. Although 100% is a higher percentage; the 36% mix exerts a higher oxygen partial pressure. A second stage at the surface would typically be exposed to an average intermediate pressure of 9.5 bar. If this regulator would be used for 100% O2 during decompression, this regulator would be exposed to a oxygen pressure of 9.5 bar- ignoring the increase of the intermediate pressure at a depth of 6 m -. Would it ever cross your mind to decant 9.5 bar of pure oxygen into a non-oxygen cleaned cylinder? As both would be exposed to the same oxygen pressure, it would make sense to me to treat both pieces of equipment the same way wouldn't it?

The table 2 below illustrates this concept a little more. The table clearly shows that a 2$^{nd}$ stage will exposed to a much lower oxygen pressure then first stages or cylinders, and therefore the hazard will be less. In this particular example this 'safety factor' is 21 times. Although there is a greater safety factor, proper engineering practise would dictate to treat any components in an oxygen system the same way in order to eliminate cross contamination and possible compatibility errors.

| EANx % | Partial pressure of O2 at the cylinder, cylinder valve and 1st stage regulator with a supply pressure of 200 bar | Partial pressure at the 2nd stage subjected to an intermediate pressure of 9.5 bar |
|---|---|---|
| **21** | 42 | 2.0 |
| **23.5** | 47 | 2.2 |
| **25** | 50 | 2.4 |
| **32** | 64 | 3.0 |
| **36** | 72 | 3.4 |
| **40** | 80 | 3.8 |
| **50** | 100 | 4.8 |
| **60** | 120 | 5.7 |
| **70** | 140 | 6.7 |
| **80** | 160 | 7.6 |
| **90** | 180 | 8.6 |
| **100** | 200 | 9.5 |

We've mentioned some contaminants before, but hydrocarbons (an organic compound existing entirely of hydrogen and carbon) and especially those in breathing air deserve a little more attention as it is not specifically the hydrocarbon content of air that exist the compressor that causes the problem but accumulation of those hydrocarbons on internal surfaces over time. Once those hydrocarbons have contaminated the cylinders it goes without saying that it will in turn contaminate the regulators used. Therefore to reduce the accumulation of hydrocarbons, the content of hydrocarbons in breathing air for oxygen serviced equipment should be kept as low as possible and not exceed 0.1 mg/m3 or air. The latter statement is in line with both what is known as oxygen compatible or modified grade E air and oxygen compatible air in accordance with EN 12021:2014. To achieve this, especially when oil lubricated compressors are used, proper compressor maintenance and filter husbandry will be required, but even strictly adhering to this, it is unlikely that this low value will be obtained and additional filtration or hyper filtration will be required. How can we establish that the air used meets these required standards? There is only one way: air quality testing on a regular basis.

Eventually all pieces of equipment that once were oxygen cleaned will degrade and become contaminated. The problem is that we just don't know when the contamination threshold has been crossed to create a potential dangerous situation. So regular servicing of your equipment is a must and it is recommended that any time contamination is suspected, to have the equipment serviced. Hoping that a piece of equipment is still clean enough is a thought that only belongs in utopia and fantasy land.

I hope this tech talk gave a 'brief' introduction to the concepts, ideas behind and the importance of oxygen servicing. Understanding that oxygen servicing is important is one thing. In the big picture it plays only a partial role:  the fraction of oxygen, maximum pressure, temperature, equipment design, contamination, material compatibility and ignition sources – just to name a few - are all connected. When dealing with systems exposed to elevated oxygen concentrations, it comes down to controlling all of those different variables, in which case the outcome will not be based on guess work but on proven facts.