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Antifreeze for Use in Noncontact Heat-Transfer Fluids in Oxygen Systems[2]

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ABSTRACT: Heat-transfer fluids are occasionally required in oxygen systems, typically for vaporizing and warming vaporized oxygen or cooling compressed hot oxygen. Similar fluids may be needed for damping fluids or hydraulic or seal functions. When outdoors, these baths often require use of water with an antifreeze, and typically a glycol is the most common antifreeze. Although commonly used glycols are flammable and not oxygen compatible per se, some glycol/water solutions are much less flammable than others and have been used successfully in combination with a series of hardware and operational precautions to prevent or cope with inadvertent oxygen exposure and the evaporation of the water fraction.

KEY WORDS: oxygen, oxygen compatibility, flammability, ethylene glycol, propylene glycol, ethanol.

Oxygen is often stored as a liquid and vaporized for use. For low rates of use this commonly employs ambient air vaporizers (e.g. star-fin aluminum arrays) installed near the LOX tank. However, where high draws are required heat exchangers with non-contact fluids have been used to provide the necessary heat transfer. Other cases exist where similar heat exchanges are needed.

Over the years, a number of considerations have been identified to control the fire risk. The writer has been tutored on this issue by Larry A. Nuesslein, James G. Hansel, Robert Sherwood, Howard Master, and other coworkers and recapitulates much, perhaps not all, of that counsel as a record. This topic was contemplated as a submission to an ASTM Committee G4 symposium on many occasions in the 1990s yet never obtained, and in 2003 some of those hardware teachings were factored into a revision of ASTM Standard G88.

Most common non-contact heat transfer fluids are by definition in a class of materials ASTM G4 refers to as indirect service meaning not normally in contact with oxygen, but which might contact it through reasonably foreseeable malfunction, error, or disturbance.

Examples of non-contact heat-transfer fluids in oxygen hardware include liquid oxygen vaporizers and coolers on compressor discharges. Similar hazards and risks are present with other fluid applications such as hydraulic or damping fluids in instrumentation and liquid seals on rotating shafts and similar consideration may be pertinent. The most common heat-transfer fluid in use is water, a material eminently compatible in oxygen systems due to

[1] Retired, "As is , Use at your own risk" commentator.
[2] This paper was prepared to avoid loss of these insights.

non-flammability with oxygen at all conditions. However, when water baths are used in cold climates or in heat exchange with cryogenic fluids, one must provide an antifreeze or other fluid to preclude the loss of circulation and/or over-pressurization of the system should the water freeze, obstruct the passages, and/or expand. To a lesser extent, when baths are used at high temperatures, an additive is desirable to elevate the fluid boiling point and reduce evaporative losses.

Among the antifreeze materials that one might consider, the most prominent are the glycols, alcohols and ionic salts (sodium and calcium chloride). The glycols are the most established and well known. However, glycols are organic liquids and exhibit significant flammability although they are not as flammable as similarly used alcohols nor as corrosive as the much less flammable ionic salts.

Note that at one time, ionic salts were the principle antifreeze and their mixtures with water were called brine (meaning a "strong saline solution" or a "water of a salt or sea lake"), however, in many instances low freezing-point mixtures (including glycol/water) have also come to be referred to as brines, even though they do not contain ionic salts.

Antifreeze Options

Ethylene glycol (EG) and propylene glycol (PG) are both widely available antifreeze solutions, Although alcohols, typically ethanol (EtOH) were popular in automotive applications in the past (1940s, 50 and even 60s), the high operating temperatures of modern combustion engines and other factors have resulted in the present perhaps exclusive use of glycols. Figure 1 exhibits the much lower vapor pressures of the glycols in comparison to EtOH, which is both a factor in evaporative loss rates and less tendency to form flammable mixtures in oxygen or air.

In most cases specialty formulations of glycols with an assortment of corrosion inhibitors are used. In addition, glycols have always been favored because, contrary to EtOH (boiling point 173°F [78°C]), the boiling point of EG (387°F[197°C]) is above that of water (212°F [100°C]) and the principal evaporation loss in mixture with glycol is water rather than the alcohol (leading to glycols frequent appellation as "permanent" antifreeze).

Furthermore, due to the extensive experience base, there is a vast body of modern corrosion inhibition technology that is vital to exchanger reliability that is not comparably available with many other alternatives.

However, EG is a toxic compound and exhibits a sweet taste, and spills yield a risk to life (especially to animals). PG, with properties similar to EG has a much lower toxicity and has gained popularity in automotive use for this reason.

Flammability of Glycol Solutions

Ethylene glycol (1,2 ethanediol)

Ethylene glycol (EG) is the organic molecule: $HOCH_2CH_2OH$, and it has a melting point of 9°F (-13°C) and boiling point of 387°F (197°C). Its heat of combustion is 4541 cal/g which is high (about half that of parafins) and is consistent with its molecular structure which is about half oxygen (that does not contribute to the heat of combustion). Several of its properties are listed in Table 1.

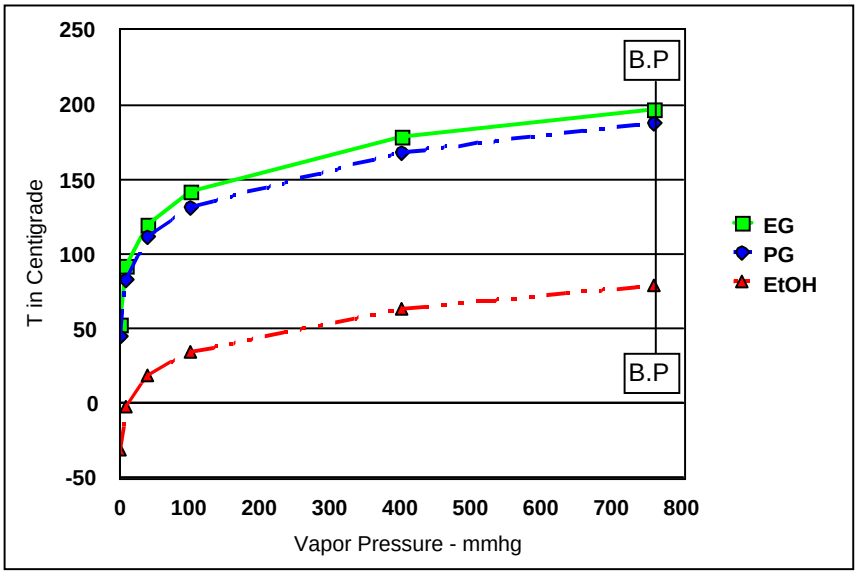

FIG. 1—*Vapor pressure of antifreezes*
(Weast, *Handbook of Chemistry and Physics*, 1967)

Pure liquid EG burns easily in oxygen and can burn in air especially if pre-heated. In mixture with water its can require elevated temperatures to vaporize a water fraction before ignition and fire can obtain. The higher the oxygen concentration in contact, the lower the temperature required for such fire.

TABLE 1-*Properties of bath components*

	EG	**PG**	**Ethanol**	**Water**
M.P. - °F(°C)	9(-13)[a]	-74(-59)[c]	-173(-114)[d]	32 (0)
B.P. - °F(°C)	388 (197.6)[a]	370 (188)[c]	172 (78)[d]	212 (100)
ΔH*c* cal/g (kcal/mol)	4542 (281.9)[b]	5664 (431)[b]	7116(327.6)[b]	0 (0)
Ign. T(air) - °F(°C)	748 (398)[a]	700 (371)[c]	685 (363)[d]	none
Flash Pt. - °F(°C)	232 (111) cc[a]	210 (99) cc[c]	52 (17)[d]	none
LFL (air) - %	3.2[a]	2.6[c]	3.3[d]	none
UFL (air) - %	15.3[a]	12.5[c]	19.0[d]	none
Spec. Gravity	1.1[a]	1.036[c]	0.79[d]	1.000
Molecular Weight	62.07[a]	76.09[c]	46.04[d]	18.0153

[a]Mallinkrodt Baker, Inc., MSDS Number E5125, 15 March 04.
[b]Weast, R. C., *CRC Handbook of Chemistry and Physics*, Forty Eighth Edition, The Chemical Rubber Company, Cleveland Ohio, 1967, pp. D-184 - D-189.
[c]Mallinkrodt Baker, Inc., MSDS Number P6928, 10 August 04.
[d]Fisher Scientific, UK, MSDS, 89619, 96% ethanol, March 04 download.

Propylene glycol (1,2 propanediol)

Propylene glycol (PG) is the organic molecule: $CH_3CHOHCH_2OH$, and it has a melting point of –74°F (-59°C) and a boiling point of 372°F (189°C).

Table 1 indicates many of the properties of PG are similar to EG. It also contains two oxygen atoms but additional carbon and hydrogen that yield a higher heat of combustion. This results in an expected lower lower-fire limit. Therefore PG would be expected to have a slightly lower autoignition temperature (which it does at 700°F[371°C] versus 752°F[400° C]) and to burn at lower bath temperatures in solution with water. However, the principal concerns of concentrating to pure PG still obtain if the PG/water solution is allowed to evaporate and concentrate.

Typical Applications

Among the applications for which glycol antifreeze agents have been considered are the following:

Compressors often warm due to adiabatic compression and friction and can have noncontact coolants in "water jackets", and they are often located outdoors. In the event of an unanticipated shutdown in cold climates, freezing and mechanical damage is a risk if a pure water coolant is not drained immediately and completely (and the geometry of the compressor coolant circuit must allow free draining for this approach). Cylinders and diaphragms have a risk (however small) of cracking .

Compressors are used with the oxidants: oxygen, nitrous oxide, fluorine and fluorine compounds and other materials on a frequent basis.

Oxidant vaporizers often require a heat transfer fluid. Some vaporizers are quite large. They typically have a separate heater apparatus where the bath fluid is heated and it is pumped through the vaporizer. Corrosion/perforation of the vaporizer itself is a primary issue, but mechanical failure of the vaporizer is a secondary prospect. Freezing risk is elevated here because of the cryogenic liquid temperature.

Although not functioning to provide heat transfer, other fluids can offer similar issues. Low-pressure waste-water-treatment facilities are often equipped with stirring/ circulating equipment. Rotating shafts may pass through "water seals" that retain the atmosphere in the treatment basins. Among the risks here are those of freezing or loss of seal. Seizing of the shaft is possible, especially if there is a protracted shutdown. This application has a high rate of evaporation often being open to atmosphere.

Non-heat-transfer fluids are also used to transmit pressure and damp oscillation in certain differential pressure gauges or other instrument. When located outdoors, freezing can prevent transmission of the pressure signal or produce false readings. This fluid is isolated from the oxidant by a diaphragm, and failure of the diaphragm is a primary risk.

Mechanical Considerations

Figure 2, reproduces and supplements early data from Carrier [**1**][3], and it exhibits the

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

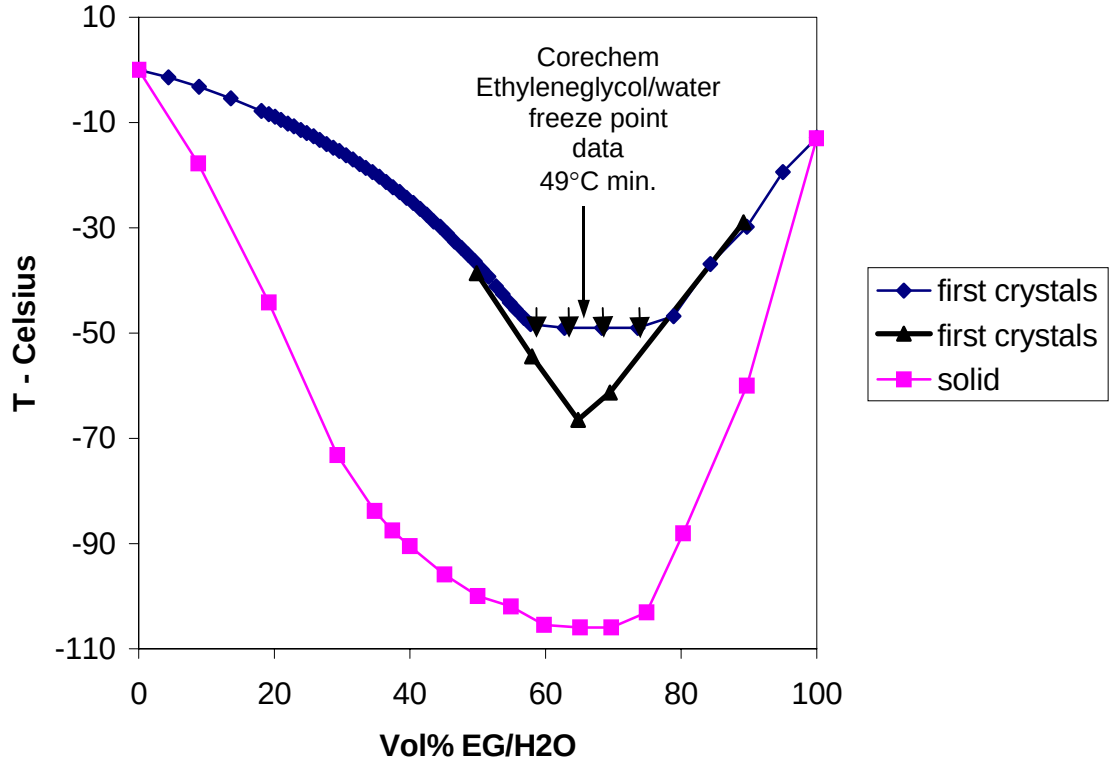

FIG. 2—*Glycol freezing and pumping points [x.y.z]*

freezing points of various EG/water solutions. There are three curves shown, because EG/water solutions exhibit a freezing-point range. As the first crystals form, they initially trap a greater amount of water in them than the bulk coolant and so the freezing point of the bulk has a lower freezing point. This continues until the whole mass is frozen solid. The upper two curves are for the dated Carrier data and more recent data from Corechem [***2***]. This point of first formation of crystals is taken as the freezing point. At the freezing point, the vast majority of the coolant is liquid and can still be pumped to vaporize LOX. However if the heat being added to the coolant is less than the heat being extracted to vaporize the LOX the coolant will form more and more crystals ultimately becoming a slush and then a solid plug that may prevent vaporization and may expand and rupture components.

The lower curve exhibits the point at which the entire solution is solid. These data should be taken as approximations for it is challenging to detect when the first and especially the last crystals form. Note that these mixtures are eutectic, having lower freezing points than either of the pure constituents. In this case, the eutectic point is at approximately 65% EG.

Below the eutectic point, the first crystals that form during freezing are rich in water leaving a higher concentration of EG in the remaining liquid and lowering its freezing point. Above the eutectic point, the first crystals are rich in EG leaving a more dilute liquid solution behind and raising its freezing point.

In most common applications, EG/water mixtures in the range 35%-50% EG have

typically been used. There are several reasons for this. One is to exploit the low freezing points that are possible. However, another important consideration is that many commercial antifreeze solutions contain corrosion inhibitors that will be in the adequate-concentration range only if the fraction of EG is in the 35-50% level. When one is adding corrosion inhibitors themselves, this latter issue does not apply.

Finally, in cases where the solution is being pumped at temperatures below its freezing point, the presence of a large population of crystals increase viscosity and may cause pumping losses that cannot be tolerated. However, when the desire is simply to prevent the solution from becoming solid and expanding (which can develop "hydraulic" pressure capable of failing piping), concentrations of EG as low as 20% are apparently often acceptable in many winter climates. Mixtures much greater than 60-70% EG (the "eutectic" point) offer less benefit, because the freezing point is higher than for the lower concentration.

Even in systems that do not face the threat of low temperatures, but instead face very high temperatures, EG can be beneficial. In solution with water it raises the boiling point in comparison to pure water. This reduces the need to contain high vapor pressures and provide make-up water to cope with evaporation.

PG is used in automotive applications very much as a equivalent to EG, but it is not similarly equivalent for oxidant applications. PG is unlikely to gain favor in oxygen systems because it requires incrementally greater concentrations for the same for protection up to the eutectic point, incurs slightly greater flammability and cost, and the toxicity issues are much easier to cope with in comparison to automobiles. Very importantly the viscosity of PG is much greater than EG near the freezing point.

Oxidant Compatibility Issues

Because of its flammability, pure EG is not compatible, per se, in oxidant systems. However, mixtures of EG with substantial amounts (25-66%) of water do not appear to be flammable at atmospheric pressure even in pure low pressure oxygen. Nonetheless, an EG/water mixture would be highly undesirable in a oxidant system, because the typically bone-dry oxidant atmosphere would quickly evaporate the water fraction and leave a highly incompatible pure EG contaminant behind. Therefore, the introduction of EG/water in any proportion should be avoided scrupulously in oxidant circuits. However if an amount of a mixture were to be inadvertently introduced in an oxidant circuit, the lower the fraction of EG, the better. Dilute EG solutions will concentrate more slowly, be easier to detect, and leave less mass of pure EG behind, but significant principal efforts should be directed to keeping EG/water solutions out of oxygen circuits.

Oxygen introduced into EG/water systems is less of a problem. Because of the large mass of EG/water present, evaporation of the water fraction to the point of flammability would be a very slow process. However, if the bath were configured so that trapped pockets of oxygen could form under the bath or so that the ullage in the bath (say at an expansion tank or reservoir, could concentrate to pure oxidant, one would have to consider the prospect of a flammable gaseous mixture forming. The following hierarchy can be useful for coping with heat transfer baths:

- When realistic, encourage the use of a nonflammable (for example, water) or

compatible fluids (fro example, PFPE or CTFE) suitable for direct oxygen exposure. Discourage glycols.

- When glycols are needed, use reliable hardware, most preferred is a multiple-barrier exchanger.
- Use careful reliability design and corrosion control, and minimize introduction of the bath fluid into the oxidant circuits and also control the prospect of oxidant introduction into the bath circuit.

These will be elaborated upon in order.

Use Nonflammable or Compatible Fluids Where Realistic

Whenever realistic, the use of pure water or other inherently nonflammable material in oxygen is the most conservative tactic. This is the case in warm climes, including reliably warm indoor systems.

Typically, the only practical nonflammable fluid is water. Compatible oils are prohibitively expensive and less effective heat transfer fluids. Mechanical refrigeration/heat pumping is impractical and uneconomic (and many of the fluids are not compatible or are only marginally more compatible than the glycols).

However, even these systems must face the prospect that a system (even one indoors) may still face freezing if power is lost. In some cases, this can be dealt with by automatic shut downs and immediate (fail-open) draining of the bath before it can freeze. However, the geometry of the system must allow for complete draining.

Use Reliable Isolation

If the probability of contact between the bath and the oxidant can be sufficiently limited, then the bath need not be treated as being oxygen exposed, despite being physically close to oxidant molecules. In this case, the mean-time-between-failures of the exchanger may need to be enormous, but this level is achievable with some systems.

One reliability technique is use of multiple-safeguard exchangers. FIG. 3 exhibits several. designs in order of preference. These are shown as design examples in ASTM G 88-05, in a section on avoiding unintended exposure to oxygen.

Example A is of two separate, highly reliable circuits, each fabricated of seamless tubing and bonded together. This configuration prevents contact of the fluids unless there is simultaneous failure of both seamless tube barriers, a highly improbable event on a mechanical scale. Further, if the bonding material and piping materials are carefully selected with regard to corrosion concerns, there can be an acceptable use of any glycol concentration in the bath circuit.

Example B is less conservative, because there is only one boundary (one pipe wall) between the two fluids albeit a usually very reliable barrier if carefully selected.

Examples C, and D exhibit progressively less conservative hardware employing a shell and pressed tube design. Example C is less conservative than B, because the tubes to the two circuits are installed in a less reliable fashion and will be more prone to corrosion and pin-hole leaks at the tube-to-sheet joint. However, the construction exhibits some of the

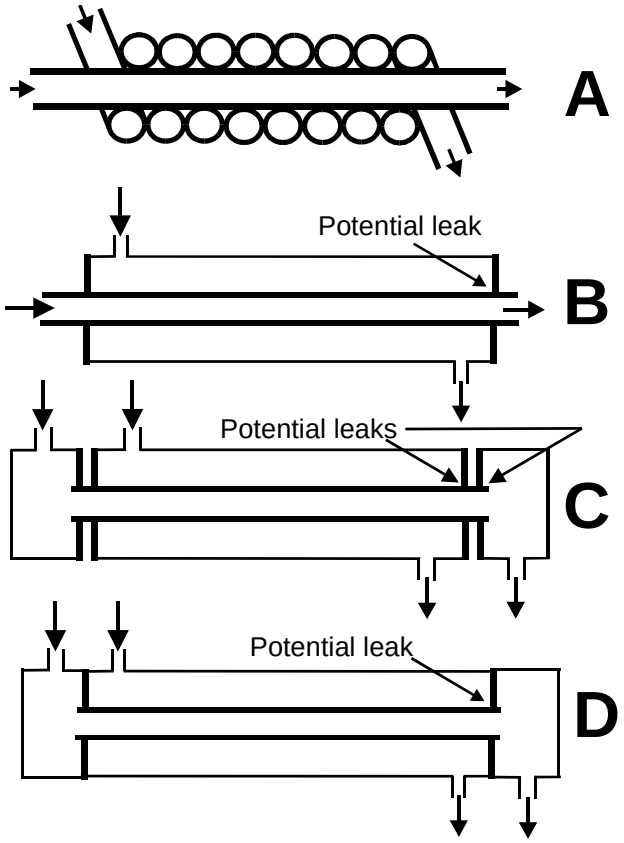

FIG. 5—*Heat exchanger designs (ASTM Standard G 88-05).*

features of a double-block-and-bleed valve isolation, because if corrosion were to breach both circuits the only contact between oxidant and bath would be at low pressure and unconfined.

Finally, example D exhibits the least conservative of these designs in which the fluid is isolated by only one barrier which contains a joint not likely to be highly reliable. If any leak develops, there is contact of the fluids at pressure. Clearly, the most reliable joints are preferred (welded versus pressed) and corrosion prevention would be paramount in these systems.

Minimize and Control Communication

Regardless of the system design, additional precautions are possible to control contact of the fluids. These precautions are progressively more important as the mechanical reliability of a system decreases.

Since oxidant entry into the bath circuit is less of a hazard than bath fluid entry into the oxygen circuits, oxygen pressure can be maintained above the bath pressure (the greater the ratio the better). For many types of leakage this will preclude or minimize entry of the bath into the oxygen system, provided the pressure bias is reliably sustained throughout the system service. This can mean administrative or automated precautions must be applied

whenever there is a shutdown to prevent gravity or capillary flow of bath into the oxygen circuit. Strategic sight-glasses and drain points can be used to determine whether shutdown has resulted in leakage into the oxygen circuit prior to startup and while the leaked solution will still contain water sufficient to render it nonflammable.

Bath circuits can be designed so that there are no pockets or areas that would trap gases and allow a flammable gas-phase mixture to form. The ullage of the bath receiver can be analyzed for elevated oxygen or purged to prevent accumulation of flammable mixtures. Level gages and low-level alarms can indicate when topping off is needed to preserve the water fraction from falling.

In all cases, careful maintenance is needed to ensure that the bath does not concentrate in glycol from normal water evaporation to where it would be a great risk upon exposure to oxygen in either circuit.

Summary

Some basic concerns of using heat-transfer, and also hydraulic and seal, fluids with oxygen systems have been described. The mechanical demands on these fluids have been listed and the flammability properties of candidate fluids have been reviewed. All should be evaluated in the context of any specific system, however, with careful selection of fluids, design of exchangers, control of corrosion, and operation of the system, oxygen system heat exchangers, vaporizers and other equipment with antifreeze fluids can be safely operated.

Acknowledgment

As noted in the text, former associates: Larry A. Nuesslein, James G. Hansel, Robert Sherwood, and Howard Master were key in tutoring the author on these issues.

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[1] Technical newsletter, Shell and Tube Condenser Performance with Ethylene Glycol, Carrier Air Conditioning, date unknown.

[2] Corechem data sheet: corecheminc.com, https://corecheminc.com/wp-content/uploads/2020/06/Freeze-Point-Chart-GlycoChill-Ethylene-Glycol-Heat-Transfer-Fluid.pdf

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