Measurement of Oxygen Transfer Rates for Carboy Closures and Air Locks

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INTRODUCTION

The response of a phosphorescent sensor material to a light beam is the basis for new instrumentation that accurately monitors the concentration of oxygen in closed spaces.[1,2] This study utilized such an instrument to measure the extent to which oxygen permeates through, or leaks by, closures and air locks of the sort used in home winemaking and brewing. The study was undertaken to improve the understanding of conditions necessary for creating superior wines and beers and to enlighten the home winemaking and brewing conversation. All of the tested products have been selling in a competitive market for many years, so presumably each serves a useful purpose.

Though the oxygen measurements were quantitative, this study is essentially qualitative. In the first place, it was beyond the scope of the study to determine the exact composition, and consistency, of the materials used to manufacture all of the tested products. In many cases, the information was considered proprietary and, in several cases, it was not even possible to learn the name of the manufacturer. Secondly, the transfer of oxygen from one side of a closure or air lock to the other involves multiple factors: 1) Effusion (small leaks), 2) Porosity of rigid materials, 3) Flexibility of molecules in elastomers, 4) Solubility, 5) Diffusion, 6) Temperature, 7) Pressure, and 8) Surface tension. Controlling and quantifying the contribution of so many factors would have been daunting and, from a practical point of view, pointless.

SUMMARY

As was to be expected, rough sealing surfaces resulted in poor seals. It was also no surprise that the rate at which oxygen transfers through carboy closures made of materials known to be extremely oxygen permeable, silicone being a prime example, can be very significant, while carboy closures made of dense, low-porosity, low-permeability materials have oxygen transfer rates that are essentially negligible. It was also not surprising that air locks made of thin, relatively oxygen permeable materials and based on water-*trap* designs permitted the transfer of small, but significant, amounts of oxygen. Oxygen dissolves in and moves through water, especially when the water is stirred.

METHODOLOGY

Figure 1

Considerable attention was devoted to developing a gas-tight testing frame that would serve to test closures and air locks (Figure 1). The neck of a BetterBottle PET (polyethylene terephthalate) carboy was carefully cut from the carboy and the saw-cut surface was machined in a lathe to ensure a smooth surface. Care was taken to be certain the finish of the neck section was not scratched or distorted during this process. This neck section and two stainless steel, double-ferrule, 1/8” NPT X 1/4” tubing adapters were sealed to an anodized 6061-T6 aluminum channel with ResinLab EP1305LV epoxy.[3] This fixture and a stainless steel, 4-way, crossover flow path, 2500 PSIG (172 BAR) valve[4] were mounted to an aluminum pan for stability. Copper tubing was used to make connections for the flow of gas from one component to another. With the valve in an open position, the arrangement of the connections permitted purge gas to flow through the neck section to a vent. Closing the valve blocked all flow of gas in and out of the neck section. The design of the valve made it possible to switch quickly between these positions without increasing the pressure within the neck section or allowing back flow from the vent. When testing air locks, the testing frame vent was closed during purging, so the purge gas would pass though the airlocks. The vent was opened briefly before the valve was closed in order to eliminate any positive pressure within the test frame. The purge gas was ultra high purity, grade 5.0, argon (no oxygen).[5] A Mocon organoplatinum target was attached to the inside surface of the neck section and a Mocon OpTech O_2 instrument[6] was used to make oxygen concentration measurements (Figure 2).

Figure 2

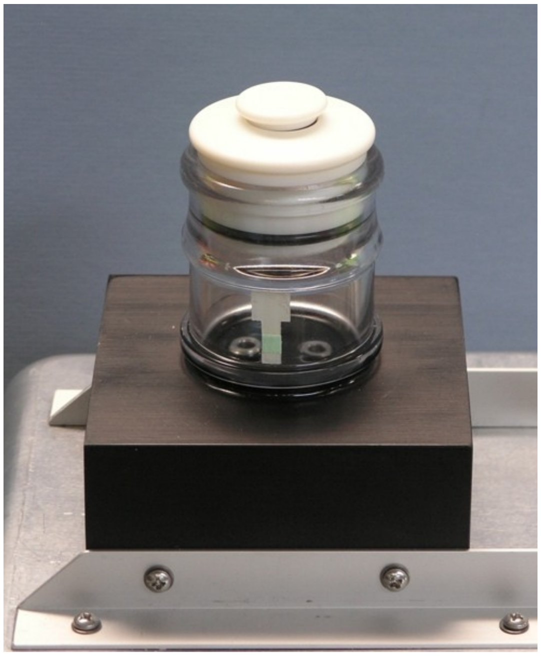
One sample of each type of closure or air lock was tested. The test closures and air locks were selected randomly and inspected visually to confirm that they were not flawed and would fairly represent the product lines to which they belong. Given the nature of the closures and air locks, it is unlikely that different parts of the same type and make would give qualitatively different test results.

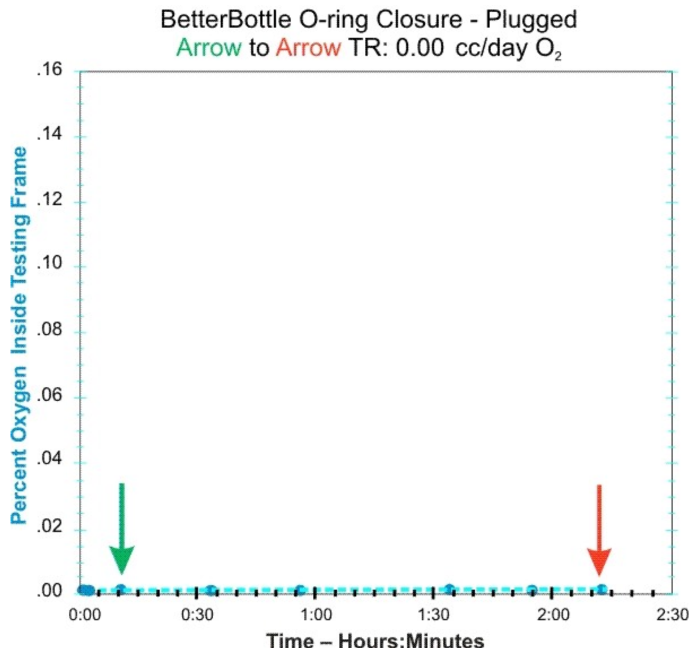
TEST RESULTS

The test data are presented in graphic format, so they can be more easily understood. Green arrows indicate the point at which the testing frame valve was closed and purging was stopped. The average transfer rate, TR, of oxygen between the point marked by a green arrow and the point marked by a red arrow is given in the legend at the top of each graph. Where applicable, a red slope line is provided as a reference for the average point-to-point rate of oxygen transfer. It is important to bear in mind that the straight lines connecting the data points are only visual aids and that sudden changes in slope are, in fact, highly unlikely.

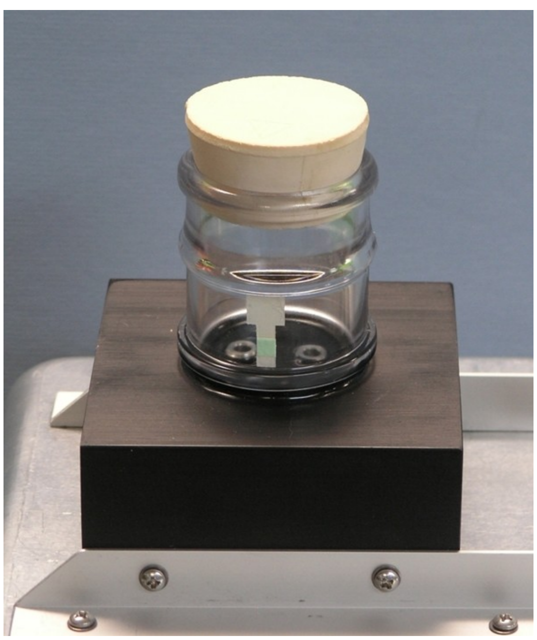
CLOSURES

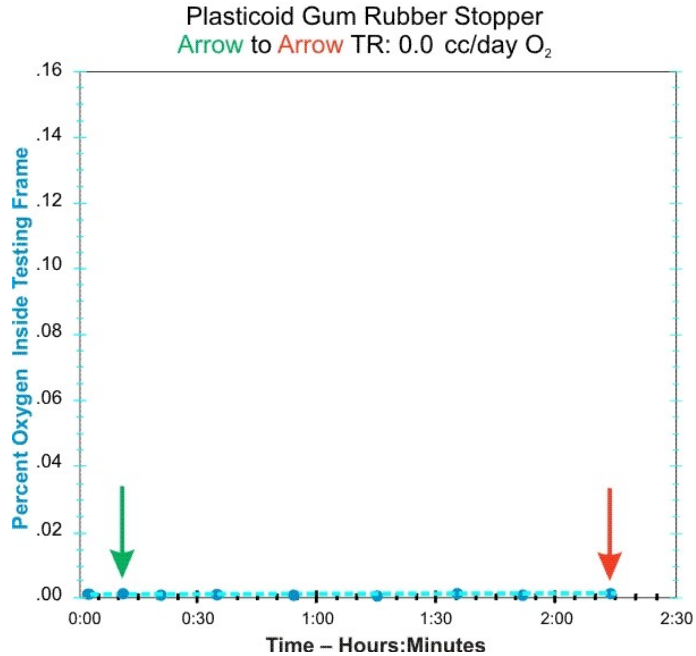
BetterBottle® PET O-Ring Closure – This closure is precision machined from solid (crystalline) PET. A Viton O-ring makes a tight elastic seal between the closure plug and the closure. A Teflon-encapsulated, Viton O-ring makes a tight, but slippery, seal between the closure and the inside of the carboy neck. With this closure installed, the volume of the enclosed test space was 86 cc. The oxygen TR for this closure was 0.00 cc/day over the test period – negligible.



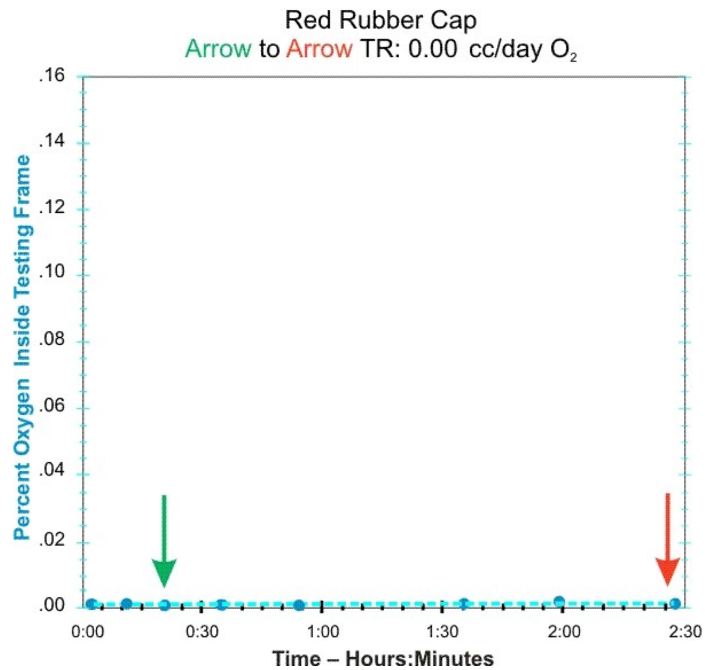


Plasticoid[7] Rubber Stopper – This stopper is made of natural rubber (polyisoprene) with proprietary additives and modifiers. With this closure installed, the volume of the enclosed test space was 89 cc. The stopper's oxygen TR was 0.00 cc/day over the test period – negligible.

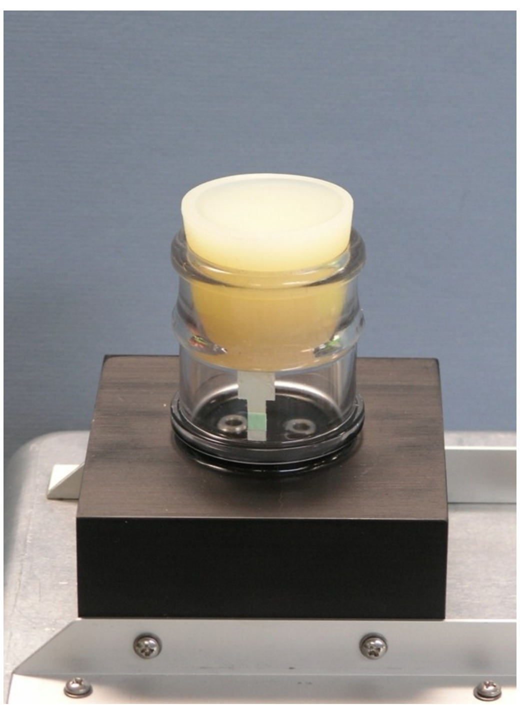


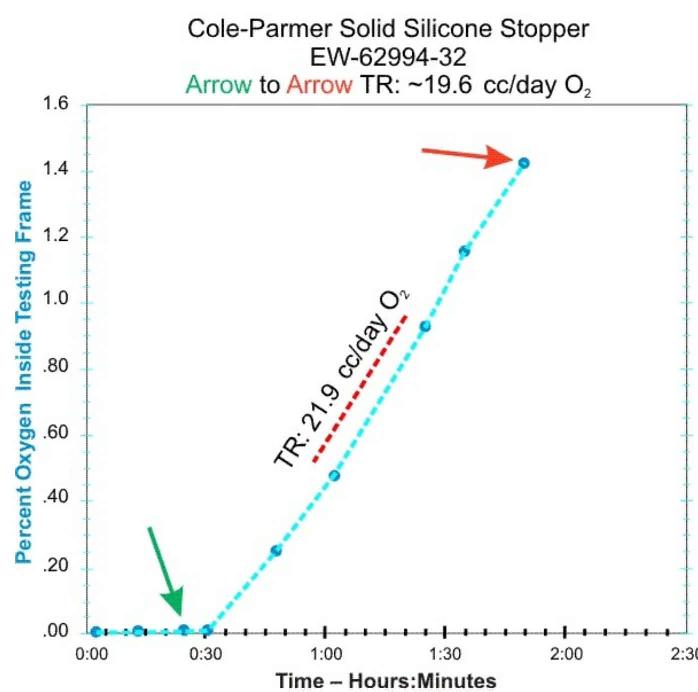


Red Rubber Cap – The type of rubber used to make this sleeve-style cap could not be confirmed, because despite considerable effort it was not possible to identify the manufacturer. The port in the cap was plugged with a solid PET rod. With this cap installed, the volume of the enclosed test space was 159 cc. The cap's oxygen TR was 0.00 cc/day over the test period – negligible.

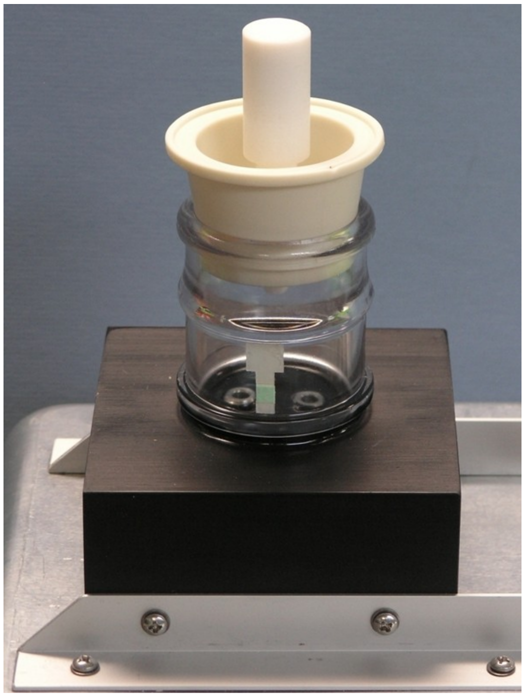


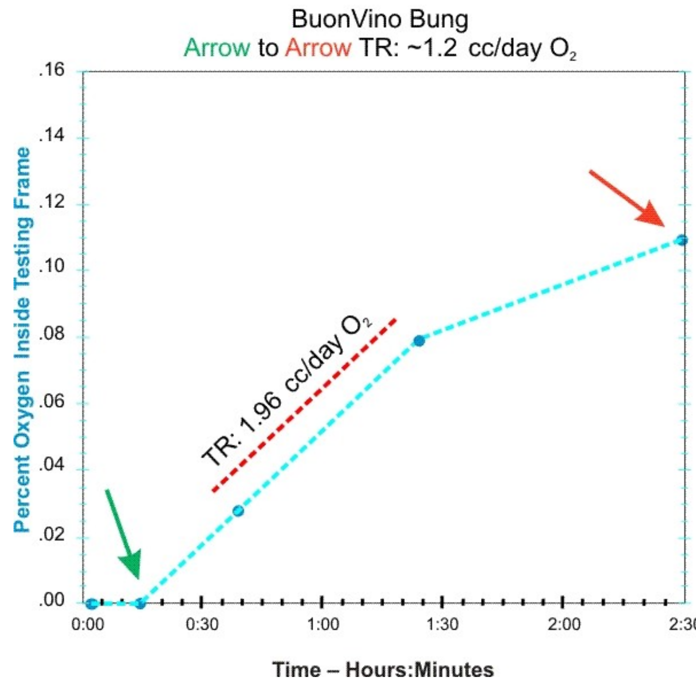
Silicone Bung – This 3.8 cm tall, 70 gm stopper was purchased from Cole-Parmer.[8] The type of silicone material could not be confirmed, because efforts to identify the manufacturer were not successful. The stopper fit tightly into the carboy neck. With this stopper installed, the volume of the enclosed test space was 81 cc. The stopper's oxygen TR averaged ~19.6 cc/day over the test period.



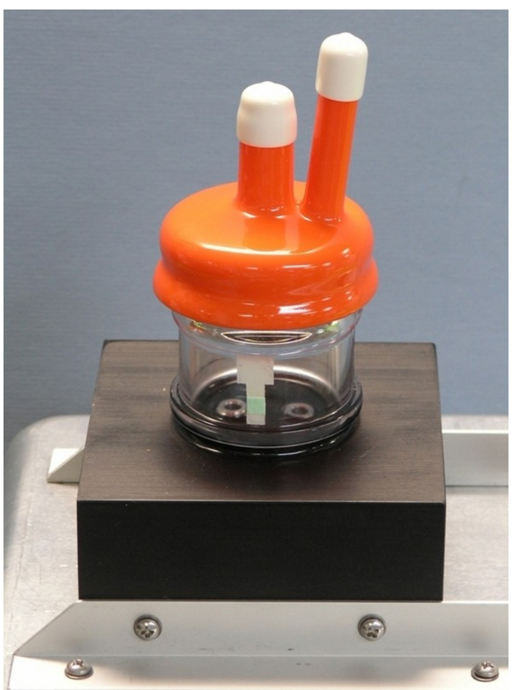


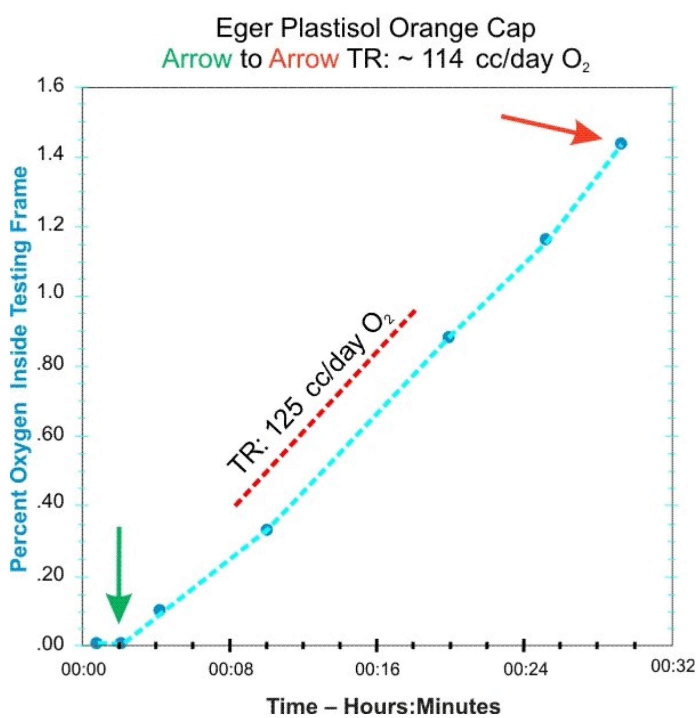
Buon Vino[9] Bung – This bung is made of a thermoplastic elastomer. The port of the bung was plugged with a tight-fitting, solid PET rod and the bung fit very tightly into the carboy neck. With the bung installed, the volume of the enclosed test space was 131 cc. The bung's oxygen TR averaged ~1.2 cc/day over the test period.





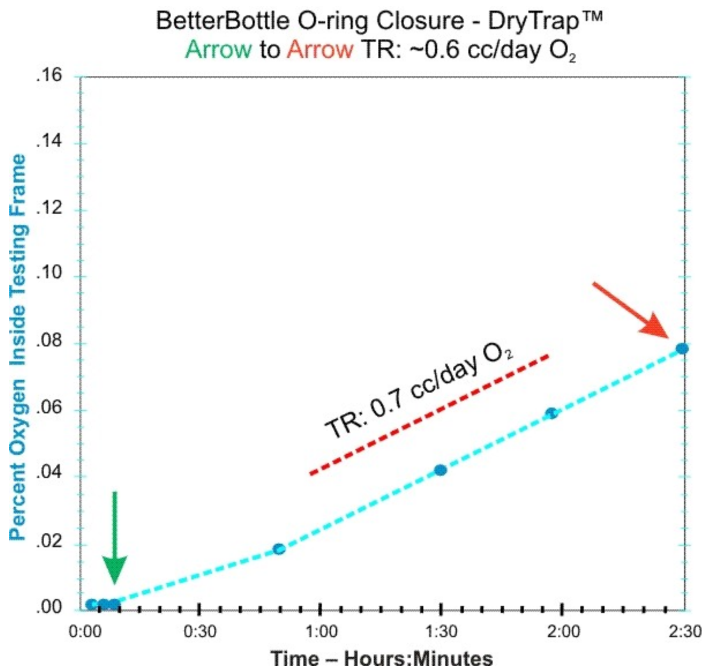
Eger Products[10] Plastisol Topper – Plastisol is highly plasticized PVC. The plasticizer used to make this product is the orthophthalate di-isononyl phthalate (DINP). The molding process results in a relatively rough inner surface (see photo to right). With this topper installed, the volume of the enclosed test space was 129 cc. The topper's oxygen TR averaged ~114 cc/day over the test period.





AIR LOCKS

BetterBottle PET DryTrap™ – DryTrap air locks are mechanical, ball-style check valves that are designed for use with plastic carboys, which flex when they are moved. The water in water-*trap* air locks is likely to blow out or suck back under those conditions. DryTraps are precision machined from solid (crystalline) PET, utilize stainless steel hardware, and are designed to mate with BetterBottle PET O-Ring Closures – though they can be used with other types of closures that have sufficiently large or elastic openings. A BetterBottle PET O-Ring Closure was used to adapt a DryTrap air lock to the testing frame, because the oxygen TR for this type of closure is negligible (see above). With the DryTrap installed, the volume of the enclosed test space was 86 cc. The oxygen TR for the DryTrap did not exceed 0.7 cc/day over the test period and would likely be significantly lower if carbon dioxide, produced by fermentation, were drafting (not diffusing) outward through the tiny mechanical opening of the check valve.



Adapting water-*trap* air locks to the testing frame – Creating a smooth hole in a rubber stopper is difficult and the walls of holes in rubber stoppers are often quite rough (see Figure 3) and could potentially be a significant cause of oxygen leakage. Liquid nitrogen can be used to harden rubber stoppers in order to facilitate the machining of smoother holes. A drilled Plasticoid rubber stopper with an especially smooth hole was chosen to adapt the liquid-filled air locks to the testing frame. This type of stopper tested well as a solid stopper (see above) and made a consistently tight seal with the carboy neck. The hole in the selected stopper fit the air locks so tightly that it was necessary to wet the hole and the stems of the air locks in order to insert and withdraw them without risk of breakage.

Figure 3

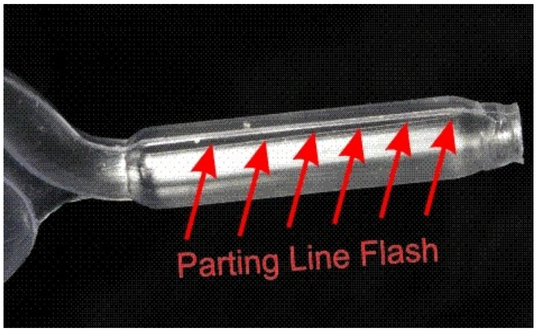
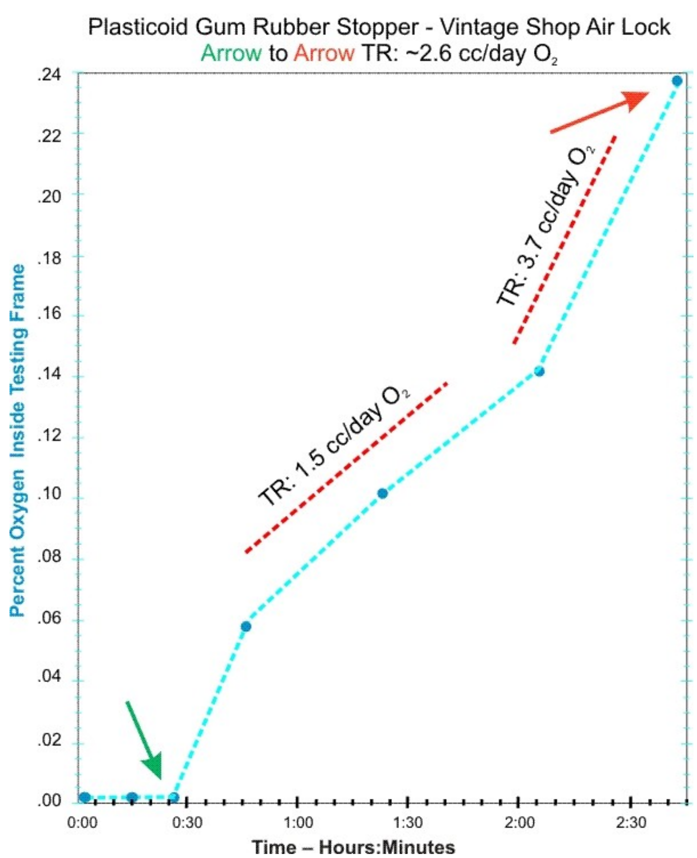


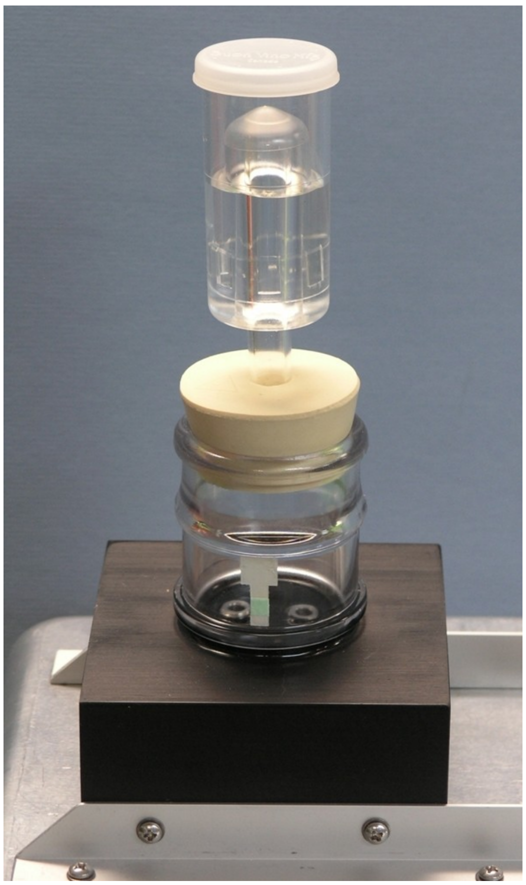
Figure 4

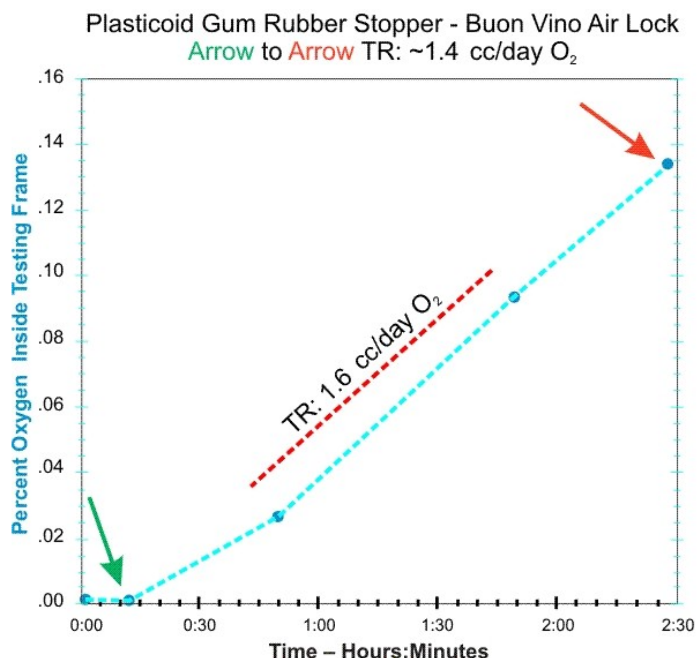
Blow-molded air locks are likely to have a thin, sharp *fin* of plastic, referred to as “flash”, where plastic squeezed between the halves of the mold (Figure 4). If this flash is not carefully removed from the stem of these air locks, it will cut into the edges of the hole of whatever type of closure is used. The flash could also push the edges of the hole away from the stem. In either case, the result will be an air leak. When removing the flash care must be taken to avoid cutting away too much plastic or scratching the stem, which would also result in leaks.

Vintage Shop[11] Air Lock – This blow-molded air lock utilizes a water-*trap* design and appears to be made of a high-impact polystyrene (HIPS) plastic. The surface area of the water on both sides of the water-*trap* is about 3 cm^2. The path length of the water is about 6.3 cm and narrowed considerably over half the distance. The surface area of the plastic that is in direct contact with air on the test frame (carboy) side of the water-*trap* is about 8.2 cm^2. The wall thickness of the plastic in this area ranged around 0.05 cm and was as thin as 0.03 cm in some places. The molding flash was carefully removed from the test air lock. With this air lock installed, the volume of the enclosed test space was 104 cc. The oxygen TR averaged ~2.6 cc/day over the test period. The oxygen TR would likely be higher if carbon dioxide (produced by fermentation) were stirring (bubbling through) the water.



Buon Vino Air Lock – This three-piece air lock utilizes a water-*trap* design. The body and inner bell are injection molded using what appears to be polystyrene plastic (crystal styrene). The surface area of the water on the air side of the water-*trap* is about 3 cm^2 and about 2.7 cm^2 on the carboy side. The path length of the water is about 4.4 cm. The surface area of the plastic which is in direct contact with air and which is on the test frame (carboy) side of the water-*trap* is about 6 cm^2. The wall thickness of this area ranged around 0.04 cm. The stem of the test air lock was carefully inspected to be sure it was free of scratches. With this air lock installed, the volume of the enclosed test space was 101 cc. Following an initial equilibration period, the oxygen TR for this air lock averaged ~1.6 cc/day. The oxygen TR would likely be higher if carbon dioxide (produced by fermentation) were stirring (bubbling through) the water and bouncing the floating bell off the inner stem. The flow of the carbon dioxide would not be sufficient to flush oxygen away as the bell float bobbed above the large opening at the top of the inner stem.





CONCLUSION

The fact that the tests for three of the carboy closures showed no transfer of oxygen is evidence of the integrity of the testing frame and the stability of the monitoring system. The results for the other carboy closures and the air locks were illuminating; though not unexpected. Of course, oxygen will move through the openings of a leaky seal. And the fact that gases can move through solids, elastomers, and liquids is common knowledge and has been extensively studied and documented (Table 1). Helium balloons made of metalized nylon float for much longer than natural rubber (latex) balloons, because the former is much less permeable than the latter. Contact lenses are made of silicone materials, because these materials *breathe* oxygen. The high flexibility of the silicon-oxygen polymer chain provides molecular-scale openings through which oxygen can easily diffuse.

Carbonated beverages are bottled in PET plastic, which has extremely low permeability, so they do not lose their carbon dioxide and go *flat*. Fish and plants thrive in water, because water transfers oxygen and carbon dioxide. At 20°C (68°F) and 1 bar of pressure (standard atmospheric pressure), a liter of water will dissolve 6.8 ml of oxygen[12] and though the diffusion rate of oxygen is very low in still water ($2.3/10^{-9}$ m^2 s^{-1} at 20°C)[13], considerable oxygen will move through water when it is mixed.

Given the results of this study, it seems likely that many, perhaps even most, home winemakers and brewers have been fermenting and aging under conditions involving considerably more oxygen than they imagined. This is important information, because without knowledge of how much oxygen is likely to be present and how to control it, there is no way to evaluate its possible advantages or disadvantages and to learn from experience.

Table 1
Permeability of Plastics and Elastomers

The larger the O_2 permeability coefficient (PC) the more rapidly oxygen will pass through a material. Different formulations and production conditions result in a range of PCs for some of the materials. The values listed in this table are selections of data published in Permeability Properties of Plastics and Elastomers, 3rd edition.[14]

Plastics	**O_2 Permeability Coefficient** cm³ mm/m² day Atm 20°-25°C	**Elastomers**	**O_2 Permeability Coefficient** cm³ mm/m² day Atm 20°-25°C
Polyethylene Terephthalate – PET	<1-1	Fluoroelastomers – FKM (Viton)	98
Ethylene Vinyl Alcohol Copolymer – EVOH	<1-1	Butyl Rubber	132-141
Polyvinylidene Fluoride – PVDF	2	Thermoplastic Polyolefin Elastomers – TPO	280-500
Polyvinyl Chloride – PVC	5	Chlorobutyl Rubber (Neoprene)	298
Polyacrylics - Poly methyl methacrylate – PMMA (Plexiglas)	6	Ethylene-Propylene Rubbers – EPDM	1735
Polyamides – Nylons	1-18	Polyisoprene – Natural Rubber	2600-2800
Acrylonitrile-Styrene – ASA	15-55	Thermoplastic Polyurethane Elastomers –TPU	16200
High Density Polyethylene – HDPE	44-91	Silicone Rubber (dimethylsilicone)	40700
Polypropylene – PP	35-373		
Polycarbonate – PC	71-81		
Acrylonitrile-Butadiene-Styrene – ABS	79-102		
Low Density Polyethylene –LDPE	98-138		
Polystyrene – PS	140		
High-impact Polystyrene – HIPS	162		
Ethylene Vinyl Acetate – EVA	157-263		
Fluoropolymers copolymers – PTFE [Teflon]	180-255		
Fluorinated Ethylene Propylene – FEP	222-255		

References

1 Papkovsky DB, Ponomarev GV, Trettnak W, O'Leary P, Phosphorescent complexes of porphyrin-ketones: optical properties and application to oxygen sensing, Anal. Chem., v.67, p.4112-4117 (1995)

2 Borisov SM, Nuss G, Klimant I, Red light-excitable oxygen sensing materials based on platinum(II) and palladium(II) benzoporphyrins. Analytical Chemistry 80 (24):9435-9442 (2008)

3 Ellsworth Adhesives, W129 N11687 Morese Drive, Germantown, WI 53022

4 Swagelok SS-43YF2-125 – Chicago Fluid System Technologies, 360 Windy Point Drive, Glendale Heights, IL 60139

5 The BOC Group, Inc., 575 Mountain Avenue. Murray Hill, NJ 07974

6 Mocon, Inc., 7500 Mendelssohn Ave. N., Minneapolis. MN 55428

7 Plasticoid, 249 High Street, Elkton, MD 21921

8 Cole-Parmer, 625 East Bunker Court, Vernon Hills, IL 60061

9 Buon Vino, 365 Franklin Boulevard, Cambridge, ON N1R 8E8

10 Eger Products, Inc.,1132 Ferris Rd.,Amelia, OH 45102

11 The Vintage Shop, Unit 17, 8333-130th Street. ,Surrey, BC V3W 7X4

12 *http://www.engineeringtoolbox.com/oxygen-solubility-water-d_841.html*

13 Verhallen, P et al., The Diffusion Coefficients of Helium, Hydrogen, Oxygen and Nitrogen in Water Determined from the Permeability of a Stagnant Liquid Layer in the Quasi-steady State, Chemical Engineering Science: Vol. 39.11 pp 1535-541 (1984)

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