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Corte: 1 de 4

Memorandum

Oxygen transmis

Natural corks are porous and screwcaps are air-tight. It's just oxidation and reduction, right? Jamie Goode says the facts are found between the two

Within the past year or two there has been a change in thinking in the closures field. It has not percolated through the entire industry yet, but that's just a matter of time. What is this shift in thinking? It concerns the old notion of the closure 'sealing' the bottle. It used to be thought that the better the seal, the better the closure. Of course, to a degree that is true: we want to keep wine in the bottle, and we want to keep air out. Hence the term 'closure'. The idea that the cork allows the wine to breathe is patently false: if oxygen were able to permeate the cork freely, the wine would oxidise rapidly.

But if we extrapolate the notion that the better the seal, the better the closure, we'd end up with a position that maintains a perfect closure would be one that seals hermetically, with no gas transmission at all. Indeed, advocates of screwcaps frequently cite the writings of the late Emile Peynaud, who stated in *Knowing and Making Wine* that, 'it is the opposite of oxidation, a process of reduction, or asphyxia, by which wine develops in the bottle', or those of Pascal Ribéreau-Gayon, who in the *Handbook of Enology* asserts that, 'reactions that take place in bottled wine do not require oxygen'. But another celebrated French wine scientist, the late Jules Chauvet, had this to say on the subject of closures when interviewed by Hans Ulrich Kesselring in *Le Vin en Question*: 'I believe that no one can ever replace natural cork, at least not currently. Cork is porous, enabling the realization of an equilibrium of oxidation-reduction in the bottle. If you want to bottle a wine and drink it 15 days later, the closure has no importance at all. But for wines which are kept for a few months or a few years, you must use a cork, and a good cork. ...

'We did an experiment in which we sealed some wine bottles with cork and some with ground glass stoppers. We noticed that three months later the wine sealed by glass had a better appearance but it was already reduced. The cork-sealed wine was still ailing from its "bottling sickness", and was still a little oxidised. Later on we saw the cork-sealed wine improve and the glass-sealed one get worse. The latter became undrinkable. We are sure that a microexchange of oxygen is needed to induce an equilibrium that allows a light and pleasant ageing'.

One of the major changes in the closures field over the last couple of years is that most people would now agree that a degree of oxygen transmission is needed for the successful development of wines in bottle. 'The point we've been making for a few years now is that it is possible to use different levels of oxygen – introduced into the wine either at bottling or post-bottling – in a creative way to manage the development of the wine so it is at its optimum when it is consumed,' says the Australian Wine Research Institute's Peter Godden. 'I don't think zero permeation is ideal for many, if any, wines. I wouldn't use

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such a closure to seal my wines. But this is perhaps missing the point: variable levels of oxygen ingress will create different wines. This is the key point from our closure trial: we took one wine and bottled it with 14 closures. Since then we have taken one wine and bottled it with various numbers of closures.

'You get different wines, and they look different after as little as three to six months. They are not all heading towards the same endpoint: they are going off in different tangents. We are past the question of whether or not the wine needs oxygen.'

So why is some oxygen transmission by the closure necessary? There are two possible scenarios to explain the process of wine ageing and the influence of the closure on this development.

First, it may well be that oxygen transmission isn't needed for a wine to develop, and that a wine will evolve in a pleasing way if sealed hermetically. In this scenario, oxygen transmission is needed solely to avoid problems with reductive characters (caused by reduced sulphur compounds).

In the second scenario, wines will age in the total absence of oxygen, but in a way that we don't really like. In this scenario, successful ageing requires some oxygen transmission not just to avoid reduction, but also to facilitate the complex chemical transitions needed to result in a wine ageing to an optimal outcome.

But, as Godden points out, it is clear that the level of oxygen transmission will adjust the rate of ageing; it likely also will adjust the trajectory of ageing. Thus a wine sealed with a very low oxygen transmission closure might end up in a different place – never reaching the same destination – as one aged under cork in such a way that we

Some published levels of oxygen transmission by various closures

Closure	Mean oxygen transmission (cc O2/closure per day)	Source
Cork	0.081	Silva et al 2003
Cork	0.086	Hart & Kleinig 2005
Cork	0.0179	Godden et al 2005
Cork (45 mm, grade 1)	0.006	Quoted by Supreme Corq, a MOCON measurement by Impact Analytical
Technical cork (44 mm one plus one), grade 2	0.007	Quoted by Supreme Corq, a MOCON measurement by Impact Analytical
Zork	0.0078	Provisor trial
Screwcap (foil lined)	0.0002	Jim Peck's presentation at the 2005 ASEV symposium
Screwcap (foil lined)	0.0002–0.0008	AWRI measurements, Godden et al 2004
Screwcap (saran lined)	0.001	Jim Peck, 2005
Screwcap (polyethylene lined)	0.09	Jim Peck, 2005
Injection-moulded synthetic	0.0012–0.0015	Jim Peck, 2005
Extruded synthetic	0.001–0.009	Jim Peck, 2005
Nomacorc classic, 43 mm	0.0293 (in 100% oxygen) = 0.006 equivalent in air	Nomacorc (on own MOCON, SD = 0.0032, maximum = 0.0348, n = 30)
Nomacorc classic, 38 mm	0.011	Tested for Supreme Corq using MOCON, by Impact Analytical
NuKorc	0.016 (in 100% oxygen)	NuKorc
NuKorc	0.015	Tested for Supreme Corq using MOCON, by Impact Analytical
Supreme Corq Original, 38 mm	0.011	Tested for Supreme Corq using MOCON, by Impact Analytical
Supreme Corq Original, 45 mm	0.011	Tested for Supreme Corq using MOCON, by Impact Analytical
Sumpreme Corq X2, 38 mm	0.006	Tested for Supreme Corq using MOCON, by Impact Analytical
Supreme Corq X2, 45 mm	0.006	Tested for Supreme Corq using MOCON, by Impact Analytical
Integra	0.014	Tested for Supreme Corq using MOCON, by Impact Analytical
Neocork	0.018	Tested for Supreme Corq using MOCON, by Impact Analytical

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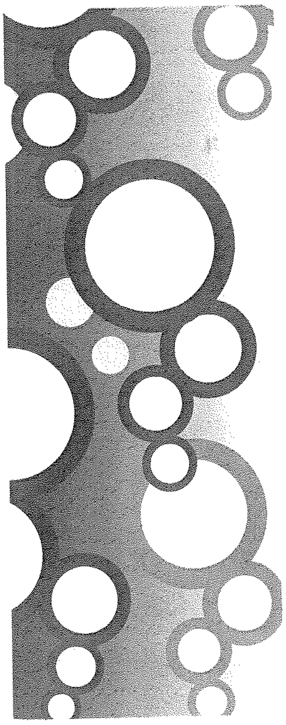
Memorandum

You can't just take a freshly corked bottle and measure the oxygen transmission rate through the cork, because we don't want to measure the oxygen *in* the cork



know and appreciate. Of course, it may be that low gas transmission closures will result in wines that are better than those sealed with corks. But then again, it may not. Be honest: would you suggest to the fine wine establishment that the way first growth Bordeaux from a good vintage develops isn't good enough, and they should, in an act of faith, switch closures because you are convinced the wines would be better after 20 years with the novel closure?

So, if oxygen transmission is the most important property of closures, this leads on to the subject of measuring it in a direct fashion. Most studies use a proxy, such as decline in free SO2 levels, OD420 (a measurement of browning in white wines) or sensory analysis. These correlate pretty well with the level of oxygen ingress through the closure. But direct measurement of oxygen transmission has proven tricky, mainly because such low levels are involved.

Jim Peck is one of the experts in the field, having spent 30 years doing research at Gallo and then the last three years with technical company G-3 Enterprises. At the 2005 ASEV symposium on closures, he made a presentation on oxygen transmission (OTR) measurement and variability. Peck explained that there are two components to oxygen transmission, microleakage and diffusion.

Microleakage, also known as permeation, relies on pressure differences and bulk transfer of gases. Diffusion occurs through the body of the closure, and is dependent on concentration differences. Diffusion can therefore occur against a pressure gradient: for example, oxygen can get into a pressurized Champagne bottle through the closure because its diffusion occurs with the concentration gradient of oxygen, and the pressure in a Champagne bottle is caused by carbon dioxide.

Several manufacturers of OTR equipment exist, including Systech, Illinois Instruments, PBI-Dansensor and the best-known, MOCON from Minneapolis. Peck says that he was looking at Illinois Instruments at one stage, but couldn't get the results to correlate with the MOCON work, so he gave up and paid the premium for the MOCON.

MOCON involves taking a wine bottle, inserting a cork into it, cutting off the neck and sticking it to a small plate with epoxy resin. Compression fittings are used to attach this plate to the instrument. So the system is set up with air containing oxygen on the outside of the cork and humidified nitrogen with some hydrogen (carrier gas) on the other side (inside the bottle). The latter comes in, picks up any oxygen that has entered via the closure, and then goes out to the sensor.

'It's more complicated than it looks,' explains Peck. 'You can't just take a freshly corked bottle and measure the oxygen transmission rate through the cork, because we don't want to measure the oxygen *in* the cork. When you stick the cork in the bottle it is full of air, and when it is crammed in you have a cork full of compressed air.

'You have to give that air time to come out through the bottom part of the cork until it reaches an equilibration point. This takes at least a month, and can take as long as three months.' This is why closure trials consistently show a rapid initial decline in measures such as free SO2 levels, followed by a steady, slower rate of decline.

Peck also identified some of the difficulties with equipment or analysis, which included: (1) microleaks at fittings/valves; (2) stuck/plugged valves; (3) inadequate (diffusion) equilibration; (4) temperature variability (a controlled temperature environment is needed); and (5) sensor fatigue/failure.

According to Peck, the mean measurement of oxygen transmission by a closure isn't the most useful: for wine, it's the high numbers – the maximums – that matter because this will be reflected in oxidised bottles on the shelf.

While there's not a huge amount to report yet, Peck and his team have several current and future projects that look set to yield important data in the near term. These include: (1) the development of 'inverted' cork OTR tests; (2) a screwcap OTR model looking at film type, thickness and hardness, plus foam type, density, hardness and depth; (3) bottle bore effects on OTR.

'We have taken a synthetic cork and inserted it in a small bore tube,' says Peck. 'The OTR dropped from 0.01 to 0.007,' he explained. 'At the moment we are studying the effect of bottle bore on the OTR of natural cork', says Peck. 'As the bore decreases some interesting things happen. We are also performing some tests on the effect of capper setting on the performance of screwcap wads of different materials, but I don't think any determination has yet been made about whether this will be published or will be kept in-house as a consulting tool for our customers.

'We are also in the planning works of a test to compare OTR of several closures using three different measurement tools, MOCON, Orbisphere and Oxysense which we are definitely planning to publish jointly with Oxysense.'

It's interesting that Peck and his colleagues are working on inverted cork

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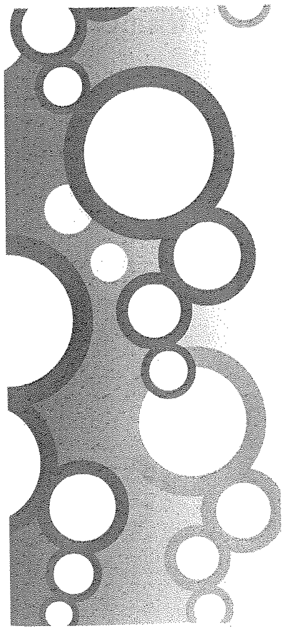
Memorandum

Red and white wines will respond differently to oxygen ingress because of their rather different chemical composition, and studies on one type of wine are not necessarily applicable to another



OTR tests, because one of the big problems with MOCON measurements on dry corks is that they don't reflect reality very well. 'Testing a cork upright gives some information if you want to apply it to bottles that are stored upright', says Peck, 'but it doesn't apply well to bottles that are inverted'.

At the same symposium, Richard Gibson (*see his Synthetics feature on page 14*) presented five theories to explain the difference between MOCON measurements between corks in upright bottles and the actual performance of cork in bottles lying down:

1. Wetting swells the cork, reducing porosity and the transmission properties;
2. A smaller interface surface area between the gas phase and the liquid is available with a wetted cork, limiting oxygen entry into the wine;
3. When the cork is wet oxygen can react with the cork phenolics, thus scavenging the oxygen before it meets the wine;
4. The wine dries out at the wine/air interface in the cork, blocking oxygen ingress;
5. Temperature changes cause expansion and contraction of the wine. The headspace in upright bottles can release and take up gas through a porous cork when internal bottle pressure changes. This can't happen when the cork is in contact with the liquid.

Whatever the explanation, it seems clear that MOCON measurements of dry corks in bottle necks don't reflect the real world experience of closure performance. This must be borne in mind when looking at the data in the table on page 21.

In truth, if we want to get a good picture of closure performance, when we see such data we need to ask the following questions: (1) how many replicates were there?; (2) what was the standard deviation?; (3) what was the highest reading?; (4) was the measurement made in air or pure oxygen?; and (5) what was the bottle neck bore?

Another technique is non-destructive colorimetry. Lopes et al (2005) recently published about this interesting technique, which involves the use of an indicator dye, in this case indigo carmine, to estimate the diffusion of oxygen into a bottle of wine through the closure.

It's not a new idea, but what they have done is calibrate the technique properly to make it useful. The authors found that synthetic corks allowed more oxygen diffusion than natural corks, and that technical corks allowed still less. They also noted that the ingress of oxygen is much higher during the first month after bottling than it is over subsequent months, which tallies with the comments made by Jim Peck in the previous section. This seems to be a consistent feature in all closure trials: an initially high rate of decrease in free SO2 (or whatever measurement is made), followed by a more steady decline phase. The important bit of data is the rate of this steady decline: the initial loss may be due to factors such as diffusion of oxygen from the closure into the wine, or the effect of oxygen pick-up during bottling. Frustratingly, screwcaps were not included in this trial.

The important thing about dye studies is that the dye should be part of a model wine solution, or the results won't be indicative of what happens in real wine bottles, where components of the wine will react with the oxygen as it enters. From this it follows that red and white wines will respond differently to oxygen ingress because of their rather different chemical composition, and studies on one type of wine are not necessarily applicable to another. The advantage of this technique is that analysis is simple, and it can be done repeatedly at time intervals on the same bottles, because it is a non-destructive method.

Final thoughts

The emerging picture is that the important properties of closures, assuming that they are taint-free, is how much OTR they permit. If this is the case, winemakers need access to reliable, independent measurements of closure OTR if they are to make informed choices, together with some knowledge of how their wines are likely to respond to differing OTR levels. But the possibility remains that there's something special about the way cork permits post-bottling development of wines that can't easily be replicated by alternative closures. Celebrated Australian winemaker and wine scientist Brian Croser points out that, 'Apart from the deficiencies of the screwcap, which are real but not fatal (my masters thesis was on sulphides and thiols), the benefits of cork, indeed the necessity of cork to provide the right oxygen regime over time to facilitate ageing, have not been properly elucidated.'

Croser continues: 'It is dangerous to opt for either an anaerobic bottle ageing regime and even more foolish to opt for a consistent oxygen ingress over time as in permeable screwcaps. The cork pattern of oxygen ingress is likely to be very complex over time and including oxidised components acting as oxidisers in their own right.' If Croser is right, then the reality is a lot more complex than the still rather technical picture painted here. More work is needed on this important topic.