Sealing themes and variations

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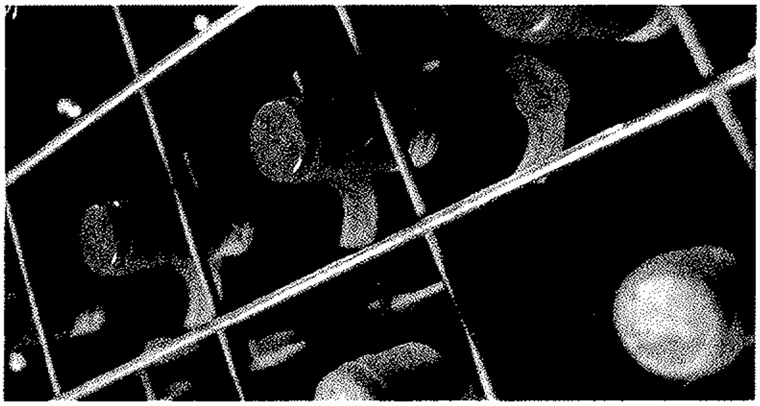

Natural cork closures perform best when bottles are laid down or inverted, but current Mocon methods cannot accurately measure oxygen transmission through wetted corks.

Once again, cork is under the microscope for supposed faults in its performance, but this time the criticism is based on a faulty interpretation of research.

With the support of the Australian Closure Fund, chaired by Jeffrey Grosset, members of the International Screwcap Initiative are promoting the view that wine corks are highly variable in their permeability to oxygen.

In a paper published by the Fund in February this year, Allen Hart and Andrew Kleinig quote internal research undertaken by then Southcorp Wines that reportedly shows a 1000-fold variation in the oxygen permeability of Reference 2 natural corks (A. Hart & A. Kleinig, 2005). The AWRI reported similar variability in cork's oxygen permeability from the 36-month mark of its long-term closure trial (P. Godden *et al.*, 2005).

Does it matter? Well yes, says Jeffrey Grosset, who rates variable permeability as one of the two main reasons why cork is flawed as a wine closure (the other being musty taints due to TCA) (J. Grosset, 2003). If, the argument goes, one cork will allow just one-thousandth of a cubic centimetre of oxygen a day into the bottle, but a seemingly identical cork from the same batch lets in 1000 times more oxygen, how can we ever trust cork to ensure the wine is not susceptible to premature oxidation?

According to Hart and Kleinig, this degree of variation is 'certainly not unusual for natural cork', but synthetic closures and screwcaps are far less variable.

Variability is the enemy of quality control and if it is true that oxygen permeability in cork can vary by as much as 1000-fold, then the cork industry has a problem. But was the interpretation of this research fair to cork? No, says Richard Gibson, manager of the Southcorp team that carried out the permeability research quoted by Hart and Kleinig.

According to Gibson, who is now an independent wine industry consultant, the Southcorp tests were undertaken

The numbers game: oxygen transmission rates for cork

Research conducted in 1999 by Richard Gibson at Southcorp Wines yielded oxygen permeability figures for 35 'randomly selected' 44 x 24mm Reference 2 natural corks ranging from less than 0.001 cubic centimetres of oxygen per day to more than 1.0cc oxygen per day (R. Gibson, 2005).

The AWRI tested 12 Reference 2 corks (44 x 24mm) at the 36-month mark of their long-term closure trial to arrive at a range of 0.0001 to 0.1227cc oxygen per day (P. Godden *et al.*, 2001; P. Godden *et al.*, 2005).

Both Gibson and AWRI used the Mocon method. The two sets of figures differ by a factor of 10 (0.001-1.0 compared with 0.0001-0.1227). According to New Zealand winemaker and chemistry PhD Alan Limmer, the tenfold difference between the AWRI's and Gibson's Southcorp figures, and the 1000-fold variation within each set of figures, along with other evidence, prove that the Mocon measurements 'should not be used as an absolute measurement of the oxygen transmission rate of cork in a bottle of wine' (A. Limmer, pers. comm. September 2005).

A 2005 study by the University of Bordeaux 2, using a different method, found that the oxygen transmission rates for first-grade natural cork stoppers with diameters of 22-26mm ranged from 0.24mg per litre per month (equivalent to 0.002cc per day) to 0.50mg per litre per month (0.004cc per day) between two and 12 months after bottling. Over the same period, Twin Top® closures had an oxygen transmission rate of 0.02mg per litre per month (0.0002cc per day), similar to the AWRI's Mocon finding for screwcaps (0.0002-0.0008cc per day). The Bordeaux study used a non-destructive method to assess colour changes in an indicator solution in bottles stored lying down, i.e. bottles with wetted corks.

In 1994, John Casey, a former chief chemist with McWilliam's Wines, cited the oxygen pick-up of a cork-sealed bottle of white wine stored on its side as 0.067mL per month (J. Casey, 1994), equivalent to 0.002cc per day. This compares well with the Bordeaux results for natural cork stoppers. Casey's estimate was based on analysis of SO_2 losses in several dozen bottles of white wine over a period of 21 months and assumed that the loss of SO_2 was entirely due to permeation of oxygen into the wine.

using the so-called Mocon method. This method is widely used and accepted for measuring permeability in 'dry packages', but does not appear to be valid for corks in contact with wine.

Gibson advised an American Society of Enology and Viticulture (ASEV) seminar in June this year 'not to rely on dry cork Mocon data to predict wetted natural cork performance' (R. Gibson, 2005). More recently, he told this writer that, while Mocon is a good indicator of oxygen transmission in synthetic closures and screwcaps, 'there appears to be little relationship between the Mocon figures for cork and what actually happens in the bottle.'

'There is strong evidence that the oxygen permeability of cork is lowered considerably when wet. Oxygen transmission in a wet state cannot currently be measured by Mocon,' Gibson said.

Does this mean the claimed 1000-fold variation in corks is nothing more than an artefact of experimental design? Maybe so. The claimed variation is not supported by studies on oxidation and SO_2 loss in wines under cork. For example, the AWRI's closure trial shows that, after 63 months, wine under Reference 2 corks had a mean OD_{420} (an indicator of the extent of oxidation in wine) of 0.20 with a standard deviation of 0.014 (figures provided to Amorim by AWRI, July 2005). The ROTE (screwcap) closure had a mean OD_{420} of 0.17 with a standard deviation of 0.005. The standard deviations, which are a measure of variability, indicate that the Reference 2 cork was just two to three times more variable than the screwcap (Alan Limmer, Stonecroft Wines, pers. comm., September 2005). The one-plus-one closure used in the trial, (Amorim Twin Top®) performed as consistently as screwcap, with a mean OD_{420} of 0.20 and a standard deviation of 0.006.

Even more telling is fresh research undertaken at the University of Bordeaux 2. Using a different method to Mocon, the researchers have estimated the degree of variability in cork at less than a factor of three (P. Lopes, C. Saucier & Y. Glories, 2005).

As part of doctoral research supported by Amorim, Paulo Lopes and his colleagues in the Oenology Faculty of the Université Victor Segalen Bordeaux 2 developed a non-destructive colorimetric method to determine the diffusion of oxygen into bottles after bottling. The method depends on an indigo carmine solution that gradually changes colour as oxygen diffuses through the closure.

Nine different closures were investigated: a first-grade natural cork stopper with three different diameters, a natural colmated cork stopper, three technical cork closures (Twin Top®, agglomerate and Neutrocork®), an extruded synthetic closure (Nomacorc) and a moulded synthetic closure (Supremecorq). The bottles were stored lying down so that the closures were in contact with the indigo carmine solution. The colour of the indigo carmine was determined using a spectrocolorimeter, i.e. without opening the bottles.

Over the course of a year, the University of Bordeaux 2 team found that the full range of natural cork closures tested (three first-grade and one third-grade colmated cork) varied in permeability by a factor of less than three.

The two synthetic closures (Supremecorq and Nomacorc) were both found to have substantially higher oxygen permeability than cork. This is consistent with the AWRI closure trial which found that by 24 months, most of the nine synthetic closures in the trial had transmitted significantly more oxygen than corks and screwcaps, and that wine sealed with these closures was showing undesirably high oxidised aroma scores compared with the other closures (P. Godden, 2002; L. Francis *et al.*, 2003).

The less than three-fold variability in cork's oxygen permeability found by the University of Bordeaux 2 is in fact similar to the variability in oxygen permeability found for screwcaps.

Gibson's belief in the Mocon method as a reliable indicator of oxygen transmission in synthetic closures and screwcaps is supported by the degree of consistency found between the AWRI and Southcorp results for screwcaps. Gibson found an oxygen transmission rate of less than 0.001cc oxygen per day for screwcaps and AWRI found rates of 0.0002 to 0.0008cc oxygen per day. In *Taming the Screw*, Tyson

Stelzer explains that the four-fold variation in oxygen transmission rate for screwcaps is 'suspected' to be the result of bottle finish variability, 'which the AWRI has measured to be considerable' (T. Stelzer, 2005, p81).

The high degree of consistency claimed for screwcaps actually depends to a large extent on eliminating all other sources of variation. Stelzer spends many pages of his book (*Taming the Screw*) describing potential faults in screwcap components and bottles, not to mention the winemaking process. Other pages are devoted to listing the precautions that winemakers must take in order to achieve an acceptable result with screwcaps. Bottles, for example, must be checked for variation in 'perpendicularity, slope of mouth (mouth sag), smoothness of sealing surface, angles, diameters and other critical parameters' (ibid., p81).

The 'array of faults' associated with the capping process is "extensive and the implications are far-reaching" (ibid., p157). Stelzer's six-page 'quick reference guide for capping faults' lists 28 bottling line faults and 74 possible causes.

Potential risk factors (in terms of wine variation) associated with winemaking include variable levels of dissolved oxygen in wine – which can result from contact with air prior to bottling, contact with air during bottling, bottling line stoppages, turbulent flow during filling – and variation in headspace volume, pressure and gas composition. The optimum level of SO_2 is 'a somewhat complex function of a number of variables: headspace, pH, dissolved oxygen, oxidants, and other wine elements such as carbonyls, anthocyanins and in particular acetaldehyde levels' (ibid., p105).

Apart from the capping process, many of these factors are also relevant to bottle variation in wines under cork. However, despite the evidence from a range of sources that the oxygen permeability of corks varies by a factor of just two or three, it is almost invariably the cork that is blamed.

From their research at the University of Bordeaux 2, Lopes *et al.* concluded that 'the rate of oxygen diffusion through the natural cork stoppers into commercial wine bottles during post-bottling storage is more important' than indicated by the findings reported by J. Ribéreau-Gayon in 1933. Ribéreau-Gayon used a similar colorimetric method, but did not record the characteristics of the closures, the bottles or the storage conditions, factors that Lopes *et al.* believe would help to partially explain some of the differences between the results of the 1933 and 2005 studies.

The Lopes study confirms that natural cork allows a tiny quantity of oxygen to permeate into the wine bottle after it has been sealed. While the impact of this permeation is still unclear, many winemakers believe that the oxygen that can enter bottles through natural cork closures is beneficial for wine development. There also appears to be a level below which the relative lack of oxygen can lead to the formation of undesirable reductive characters.

For cork to maintain its relevance in the modern age of winemaking, technical performance is paramount. More research is needed to improve the wine industry's knowledge of the range of factors that affect the development of wine in the bottle.

Where cork industry research and development has already produced tangible results is in the reduction of Grosset's other main objection to cork, i.e. TCA (2,4,6-trichloroanisole) contamination. The ROSA steam distillation process developed and implemented on a routine industrial basis by Amorim reduces releasable TCA levels in contaminated cork by 70-80%, according to independent validation trials. To further reduce the risk of cork-related taint in wine, Amorim has also implemented measures that screen out contaminated raw material and prevent contamination during processing. The company is currently developing an enhanced version of the steam process, named ROSA Evolution.

Judging by recent developments, the cork industry has accepted the challenge of ensuring that its products can continue to meet the demands of winemakers and consumers.

To ensure that winemakers have the information they need to select the best closure options for their wines, research into the factors that affect closure performance must keep pace with product development. Only in this way can the cork industry dispel the doubts raised by the anti-cork lobby.

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