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Scientifically speaking

Paul White gets into the technical nitty-gritty to reveal the shortcomings both of screwcaps and of the theories seeming to support their use

It may be that 2005 proves to be the year when the screwcap bandwagon lost a little momentum. New Zealand's wine industry has been the staunchest supporter of screwcaps in the world up to this point; screwcap uptake there has risen to 70–90% of production. Currently, however, around 110 wineries in New Zealand have either shifted entirely to 100% TCA-free (supercritical CO_2 washed) Diam agglomerate corks or are trialling Diams alongside what had previously been screwcap-only portfolios. Estimates by NewPro Packaging's Vinko Rakich, who happily distributes both screwcaps and Diams, indicate that current momentum will probably drive the Diam figure much higher by harvest time 2006. This suggests a major shift in some producers' previous belief in screwcaps as 'the perfect seal'.

The reason is that practical experience with screwcaps over several vintages has led some very competent winemakers to a realisation that the underlying chemistry and winemaking practices professed by the leaders of the screwcap movement may have been seriously misunderstood. Additionally, screwcaps' tendency to produce 'reduced' SLO (sulphur-like odours) faultiness may be more real than initially postulated by screwcap proponents.

In fact, the problem is not screwcaps; rather, it is the airtight, tin-foil seal inside the current form of screwcaps. The problem centres around sulphide compounds in wine, called thioacetates and disulphides, which reduce to stinky compounds (thiols) under an anaerobic closure. For the past four years, screwcap proponents have been saying that any smelly sulphide problems that appear after bottling are not the fault of the closure. Instead, they argue, winemakers have not properly cleaned problematic sulphides out of their wines with copper sulphate solution before bottling. The closure simply reacted with 'dirty' wine that was the result of incompetent winemaking, whereas properly cleaned wine would have posed no problem. As it turns out, both the problem and solutions are much more complex than that.

Oxygen or none?

The bone of contention is the need for oxygen ingress during bottle maturation. Up to this point, the screwcap lobby has steadfastly contended that wines need to age in an oxygen-free environment, based on tendencies observed by Emile Peynaud. Their position has been that poor corks leak air up their sides (but not up their middle) and cause oxidation, spoiling the wine. They describe a perfect cork as one that is absolutely airtight, like a screwcap.

Early in the developmental stages of the New Zealand Screw Cap Initiative, spiritual leader Michael Brajkovich MW discussed these matters with one of New Zealand's top winemaking chemists, Hawke's Bay's Dr Alan Limmer of Stonecroft. Limmer suggested there was likely to be some serious sulphide reduction issues under screwcaps' anaerobic post-bottling environment. He suggested a minute but steady ingress of oxygen would ameliorate this problem and offered to help the screwcap lobby navigate through any developmental issues with the closure. His input was rejected on what appear to be ideological grounds – simply put, his warning about oxygen ingress did not fit with the screwcap lobby's absolute belief in the superiority of anaerobic bottle maturation. Perhaps even more troubling to them, they would have to admit that corks might have got something right.

Looking back to those initial encounters between Brajkovich and Limmer in 2001, it appears that Limmer, from the start, had a far superior understanding of the subtleties of post-bottling chemistry than anyone else actively commenting on screwcaps anywhere in the world. I first raised the question of possible reduction issues under screwcap with Brajkovich at the inaugural New Zealand Screwcap Initiative (in November 2003) and was told it wouldn't happen under screwcap. As late as February 2005 he still had 'yet to see a problematic reductive wine' under screwcap, while at the same time oddly explaining away the problem as something to do with corks scalping sulphides (in a letter printed in *The World of Fine Wine* issue 4, 2005). Disturbed by the lack of accurate scientific reasoning behind much of the public relations pushed out by the screwcap lobby through a largely uncritical media, Limmer published four important papers aimed at systematically explaining sulphide problems in post-bottling chemistry. So far, every bit of science he has put forward has been confirmed as correct either by known scientific principles, peer-reviewed research or other wine scientists with PhDs in chemistry. The following papers recently earned Limmer election as a Fellow of NZ Institute of Chemistry: 'Redox reactions, sulfides, and general

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misconceptions', *New Zealand Winegrower* Vol 8 No 2, 2004; 'Do corks breathe?', *New Zealand Winegrower* Vol 8 No 3, 2005; 'Possible ways of mitigation of post-bottling sulfides', *New Zealand Winegrower* Vol 8 No 4, 2005; 'Do corks breathe? or the origin of SLO', *The Australian and NZ Grapegrower and Winemaker*, Annual Technical Issue 2005; 'Origin of post-bottling sulfides, or Do corks breathe?' *Practical Winery*, in press; and 'The chemistry of post-bottling sulfides in wine', *Chemistry in NZ*, Vol 69 No 3, 2005.

Contrary to this, the Stelvinists are batting closer to zero. Much of what the screwcap lobby has espoused since 2000 appears to stem from poorly or incorrectly understood chemistry. Or just plain wishful thinking.

Through his papers, Limmer has clearly demonstrated the fallacy of the screwcap proponents' belief that so long as wines are properly copper-fined before bottling, they will not develop SLO faultiness. The chemistry and scientific literature say it is impossible to rid a wine completely of all its thiol precursors in order to guarantee the wine will not accumulate reduced SLO characters post-bottling. Copper-fining will knock back simple thiols and H_2S (yeast-derived sulphides), but it cannot eliminate the more complex precursor sulphides (disulphides and thioacetates), which are impervious to copper-fining. These sulphides are a necessary by-product of yeast fermentation. The only way to eliminate the whole range of complex and simple sulphides is to eliminate yeast fermentation. It simply can't be done.

In time, these precursors have been shown to degrade to thiols, and under an anaerobic environment the nasty, stinky sulphides (thiols) bounce back with a vengeance. The bottom line is that no matter how much copper-fining is thrown at a wine, this approach cannot absolutely guarantee that the wine won't have reduced sulphide characters at some point in its ageing process. The Australian Wine Research Institute (AWRI) has noticed these are most likely to start appearing at 12–18 months, but, in fact, reduced characters can appear sooner and later, depending on the redox potential of each individual wine. The redox potential of a wine is strongly influenced, post-bottling, by the type of closure used. We also must assume that negative reduced characters don't suddenly appear at 12 months but have been slowly building at sub-threshold levels well before this. Negative characters will appear on the palate well before they show up as aromatics.

An additional consideration is that a whole range of good thiols derived from grapes (not yeast) that heavily determine a wine's flavour and aromatic profile are stripped out by copper-fining. Copper-fining is not a smart bomb – it takes out all the good and bad thiols; consequently, it is impossible to know whether some screwcapped wines that show well after bottling and copper-fining might have shown greater complexity if they had not had a dose of copper stripping out positive thiols.

Pre- and post-competition tasting

So, what of the screwcapped wines that have been copper-treated, looked good after bottling and have gone on to win gold medals or trophies? There are two considerations. First, if the judging took place within the 12–18-month post-bottling period, these wines could still develop sulphide problems at a later stage. Another consideration is that these same wines may have some sub-threshold sulphide issues and may have looked considerably better had they been produced under a low-oxygen-permeable foil rather than an anaerobic one. Recently, a high-scoring Gewurztraminer in New Zealand was put through copper-fining after the competition and was then retasted against non-treated examples. The post-bottle 'coppered' wine was deemed superior, indicating the actual winner had sulphide problems that were not detected by the judges previously.

For the past year I've been treating all screwcapped wines on my tasting bench to 'before and after' comparisons like this, and I've found substantial problems, even in relatively recently bottled wines. Many screwcapped wines look better with a little bit of added copper post-bottling; try adding a few pennies to a glass and see for yourself.

All of which leads us to a much simpler solution: rather than throw copper at wine, why not try oxygen ingress? Oxygen creates a buffer that keeps sulphides from reducing into negative characters. Limmer thinks it is likely that sulphide reduction has always been a potential problem – it is just that previously all wines were under cork, and cork seeped in just enough oxygen to keep this at bay. The key reason why this difference under closures occurs is related to the ability of oxygen to oxidise the smelly thiols back to more innocuous disulphides. The disulphides can break down to thiols with the aid of SO_3 (a component of the SO_2 used in wine). But as the SO_2 content diminishes relative to the rate of oxygen ingress, corks show less accumulation of thiols than screwcaps, which retain their SO_2 for longer.

What is obvious now is that the chemists driving the screwcap movement have never really been up to speed with Limmer's chemistry, nor have they understood the implications it has for screwcaps in their current form. Several screwcap-sponsored papers published over the course of the past year have offered little more than a flimsy scientific response to many of the issues that Limmer has raised. One of the dodgiest – the so-called Australian Closure Fund paper – has been held up by many pro-screwcap journalists in Australasia as proof positive that red wines age under screwcap. Age they do, but 'positively' is highly debatable in this instance.

The paper found that a 1996 Penfolds Bin 389, bottled under both cork and screwcap, developed reduced sulphide characters under the screwcapped bottling. Oddly, the wine had been copper-fined and still developed SLOs – which, screwcap proponents claim, isn't supposed to happen. One obvious conclusion that the study doesn't draw is that, for the first time in Bin 389's decades-long history, the wine's overriding aromatic characteristics were determined by the closure, rather than by the vineyard and winemaking. So much for terroir as a function of place.

Jamie Goode, in his 'Close Call' article in *Wine International* (October 2005), has done an excellent job of carefully showing the authors' weaker points of analysis and incorrect conclusions. One of the most spurious claims is that corks have a thousandfold variability rate, which the authors appear to have concluded based on misinterpretation of a MOCON study using dry corks as a model. Unfortunately, writers such as Huon Hooke, Tyson Stelzer and James Halliday, to name but a few, have quoted this figure unchallenged – indeed, they continue quoting this figure – as a way of discrediting the viability of cork.

In fact, a recent peer-reviewed Bordeaux study by Lopez on oxygen permeability clearly demonstrates that corks do not have anywhere near thousandfold variability and are, surprisingly, comparable to screwcaps. One of the key issues here is that the study focused on wet corks in situ, which are less permeable and more consistent than dry ones. Rather than lumping together data from the cheapest-grade short corks to the highest-grade, ultra-long, high-grade flour, they

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compared like against like. Limmer explains: 'The natural corks had about a twofold variation between grades, and close to twofold variation within grades, while the technical corks had much lower rates of oxygen ingress and were approximately 10 times less variable in terms of oxygen ingress. These results are more in accordance with the AWRI trial results, and our commonsense experience of wine, than the MOCON thousandfold variation.

'Remember that the MOCON data for screwcap shows a fourfold variation. So, while some may say a twofold is too much, we have no concrete evidence that the screwcap is doing a whole lot better on permeability data. Although the AWRI closure-trial data, if interpreted correctly, suggests the screwcap is doing better than cork, it's not by much, and it depends which cork. In fact, Altec and Twin Tops are comparable or better in terms of variation.'

Prizefight: Tyson v Limmer

Another publication that has serious scientific problems is Tyson Stelzer's *Taming the Screw: A Manual for Winemaking with Screw Caps*. This has been touted by many pro-screwcap journalists as the bible for screwcap production. Paying around A$100 (£43) a book, winemakers should not expect it to be seriously flawed for its lack of scientific rigour, analysis and accuracy. It's most important chapter – devoted to sulphide issues under screwcap – makes significant scientific errors that will lead winemakers into a belief that following this manual will produce the results they hope for in their wines.

I, along with some others, was privy to a series of e-mails between Tyson and Limmer, in which Limmer took Stelzer to task for much of his poorly understood, erroneous chemistry. It is clear from this that the book had not been screened for accuracy pre-publication by a qualified wine chemist. Tyson has also admitted to some of the errors outright and appears to be thinking about other issues he hasn't quite grasped yet. Because the book was edited by key figures in the screwcap movement – Michael Brajkovich, Jeffrey Grosset, John Forrest, and reviewed by the AWRI's Peter Godden (a prime driver of closure study) – it seriously exposes this group as underqualified to comment on the fundamentals of wine chemistry.

Limmer summarises the main problems with Stelzer's book thus: 'It contains a number of critical errors in the relevant chemistry. It confuses the terminology and identity of the compounds, and consequently attributes incorrect chemical behaviour of the compounds with respect to the pre-bottling preparation and post-bottling chemistry. It also tells us, among other errors of fact, that SO_3 in wine is non-existent. While the quantity may be small, the presence is significant and well documented. Consequently, it is not possible from the chemistry described by Stelzer to arrive at a cogent explanation for the observations as recorded and described by AWRI or my articles.'

Cracking the chemistry – or not

The AWRI's 'Towards offering wine to the consumer in optimal condition…' (*Australian and New Zealand Wine Industry Journal* Vol 20 No 4, July/August 2005) – essentially its final conclusions on its 63-month-long study of screwcaps and synthetic, technical and real-cork closures – is yet another recently published paper with shortcomings. Whereas in previous publications the AWRI appears to have been at a loss to explain the high incidence of reduced characters in screwcap wines, it now appears to be heading in the direction of Limmer's previously published explanations. Unfortunately, the authors still seem not to have cracked the underlying chemistry yet, continuing to espouse the old red herring that reduced faultiness is a winemaking fault, not a closure issue.

Limmer explains the disconnect. 'The AWRI paper discusses the results of the closure trial and the reductivity issue under the screwcaps. It does note that low-ingress closures are more prone to this problem, and [it] cites an accumulation of thiols as the cause of the character attributed to post-bottling SLO. This is what I have been writing about for a few years now, although in more detailed chemistry than described in the AWRI report. The report does note, "For wines with a propensity for this to happen, increased oxygen permeation through the closure, whether it is a screwcap or any other closure, would be advantageous." However, the report also goes on to say that the problem is caused by the winemaker rather than the closure, and that the winemaker needs to be prepared to adopt new winemaking practices if they are going to use the closure. The specified practices are the same ones recommended to minimise sulphide issues at ferment generally.

'The difficulty with this approach is that it does not seem to recognise the earlier research (10–20 years ago) that has been done on sulphides formed at ferment. This work, by Rauhut particularly, shows us that the formation of the post-bottling thiol precursors is, to a large extent, out of the winemaker's hands and [is] controlled by the yeast as a genetic trait. All yeasts have this trait, and although it does vary between yeast strains and can be mitigated or exacerbated to a slight extent by winemaking techniques, it cannot be eliminated.

'The report also concludes that the link between the occurrence of SLO and SO_2, as demonstrated in their trial work, is coincidental rather than causal of the problem. The chemistry gets a bit complex here, but, again, this seems not to recognise earlier work on this issue, which has shown SO_3 (a component of SO_2) to be the cause of the degradation of one of the thiol precursors and one of the key determining factors in the thiol–disulphide balance in the wine. The connection between SO_3 and the chemistry we are talking about here has been cited in the literature over 50 years ago and [was] more precisely analysed 20–30 years ago. This mechanism also gives us a good explanation why the SLO peaks at about 24 months post-bottling (it was first noted in the trial at 18 months) and why it slowly diminishes with time, to the point where long-aged wines under screwcap do not display this trait. It is very hard to explain this behaviour without resorting to the SO_3 mechanism.'

One can't help but sense a bias towards screwcaps in this report, even though screwcaps in the study developed significantly higher levels of reduced flint/rubber/H_2S/cabbagy characters than other closures – what used to be called 'dirty' winemaking. What is not often noted is that the reductive characters were assessed aromatically, not by taste and feel, so there is no input on wine quality regarding these other important markers of quality for any closure. Given that the study's screwcaps showed reduced characters, it is probable that negative palate characters existed on all these wines as well.

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In the end, the AWRI concludes that 'it is clear that the gap between our desired specifications of closure performance and what closures are currently able to deliver is smaller with screwcaps than with other closures'. But the AWRI's own trials show that Diam corks equalled or beat screwcaps on all parameters. Most importantly, they did not produce reduced characters in the same wines bottled under screwcaps.

Stepping back from all this, one can't help but feel that the leaders of the screwcap movement had not really mastered the chemistry they needed to know before going to market with their product. If perhaps they had listened to Limmer four years ago, at the beginning of the screwcap movement, and looked seriously at oxygen-permeable foils, they wouldn't be in the difficult position they are in today. Nor would they have provided the cork industry a four-year breathing space to clean up its act.

Why there has been an unwillingness by the screwcap movement to admit that it got the oxygen-permeability issue so wrong is perplexing. Perhaps the profits from the dollar per case to dollar per bottle saved in converting to screwcaps is not easily given up. Or perhaps there is a fear that consumers might demand their money back for the screwcapped wines currently being cellared for the longer term.

More at risk with screwcaps

So, what effect has all this had on winemakers? New Zealand's Kate Radburnd of CJ Pask in Hawke's Bay is a highly competent winemaker, senior wine-show judge and one of the most respected players within the New Zealand wine industry. After having used screwcaps on Pask wines for several years now, she found herself unhappy with the way some of her wines were developing under screwcap. She now appears to be leaning towards Limmer's view that the New Zealand wine industry could be more at risk with screwcaps – in their present form – than most winemakers were led to believe.

As a senior judge at Air New Zealand shows, I asked if she had encountered faultiness under screwcaps while judging over the past few years. 'Certainly there are wines that are reductive,' she responded. 'And speaking honestly, there are more now than before the advent of screwcap.' Increasingly, she has noticed these faults 'clearly from the aromas, but more so now as bitterness at the back palate and a dulling of fruit'.

This last perception of faultiness is the most worrying, because the science of reductive post-bottling chemistry suggests that wines will begin to suffer low-level, sulphide faultiness progressively on the palate much sooner than the 'burnt-rubber, firecracker, cabbage, rotten-egg, H_2S-like' aromatics that spoil a wine's true varietal expression.

In its effect, this sub-threshold sulphide faultiness equates to the way sub-threshold TCA taint knocks back fruit and crimps a wine's finish. Ironically, this is one of the reasons why many screwcap users moved away from cork closures.

Previously, in the event of any sulphide problems under screwcaps, winemakers have been blamed by the screwcap lobby for not properly 'preparing' their wines. Clearly, Radburnd is a competent winemaker, and she has done everything humanly possible to ensure her wines are bottled clean. She explains, 'We rigorously copper-trial throughout production and ensure that [the wines] are bottled clean. And generally they are clean after fermentation, so most don't need copper. The norm is to copper-fine only once as wine goes in at bottle.' Following recommended practice, problems still cropped up under screwcap, just as they have with many other winemakers who have adhered to 'correct' procedure.

Like most winemakers, what Radburnd wants from a closure is something that consistently shows her wines in the best light. Consequently, Pask is now trialling ProCork (cork covered with a Gore-Tex–like membrane that filters out TCA) and Diams, as well as looking at oxygen-permeable foils under screwcap. They are 'continuing to use screwcap on whites because these are predominantly drunk within a year to 18 months' (when SLOs are most likely to start appearing).

Radburnd believes 'screwcaps are here to stay, so let's learn more about them and perfect them. We know a lot more now about screwcap than we did previously.' And she still believes that screwcaps offer the best opportunities: 'We will probably end up with a slow-permeable membrane eventually, and that will help.'

Limmer agrees with the potential of low-ingress closures, and as head of the research programme for the New Zealand industry he has work on these issues under way now.

Meanwhile, 100% TCA-free Diams have already been developed, offering two grades of closure with consistent permeability that eliminate both reduction and bottle-variation problems. And with that, Diams appear to have already beaten screwcaps to the draw. ■

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