Wine screw cap closures: The next generation

One of the perceived issues of screw cap closures has been the apparent occurrence of reductive taints, ascribed to a lack of oxygen ingress. **Volker Schneider**, **Martin Schmitt** and **Rainer Kroeger** explain a concept of a new screw cap liner capable of overcoming these issues.

THE QUALITY AND VALUE of fruity white wines strongly depend on their typical varietal flavour. After bottling, the rate, extent, and sensory outcome of wine ageing are primarily driven by temperature and exposure to oxygen. Depending on oxygen availability, we can differentiate between oxidative ageing and reductive ageing.

For preservation of fruity aroma, the ideal closure would be one allowing as little oxygen ingress as possible. This is one of the main reasons why screw caps have been introduced, in particular those containing a tin/Saran liner. Screw capped wines keep fruity freshness and retain sulfur dioxide (SO_2) extremely effectively.

Since the widespread deployment of screw caps, an apparent increase in the occurrence of reductive taints has been observed and ascribed to a lack of oxygen (Limmer 2005). Ground-breaking closure trials by the AWRI in 1999 provided evidence for a tendency: The less oxygen ingress, the more likely the development of reductive character. Reductive wines were described as having a discernable struck flint / rubber aroma in contrast to the more advanced oxidised aromas, lower SO2 levels, and higher browning rates in wines sealed with closures providing a higher oxygen ingress (Godden et al. 2001, 2005, Skouroumounis et al. 2005, Lopes et al. 2009, Ugliano 2013).

The appearance of post-bottling reduction taint is ascribed to the conversion of sulfur containing compounds of low odour intensity into more odour-active volatile sulfur compounds (VSCs). Pathways comprise the hydrolysis of thioacetates to thiols (Rauhut et al. 1994), the reduction of disulfides to thiols (Limmer 2005), and a light-induced degradation of methionine giving rise to the formation of methanethiol and dimethyl disulfide (Maujean et al. 1978).

PRE-BOTTLING COPPER ADDITION

Some winemakers add copper prior to bottling, expecting thus to mitigate the formation of post-bottling reduction. However, while sometimes this is successful there are numerous drawbacks to this practice. Under conditions of low oxygen ingress, the copper complexes initially formed with VSCs may serve as a latent source of free hydrogen sulfide (H_2S) and other odorous VSCs during later storage (Viviers et al. 2013, Franco-Luesma and Ferreira 2016, Bekker et al. 2016). Copper can also affect the varietal aroma profile of Sauvignon blanc and other varieties where poly-functional thiols play a major role in overall aromatics (Ugliano et al. 2011). Furthermore, since copper is a heavy metal subject to legal limits, many wineries are reluctant to willfully add it to wine for health or ethical reasons.

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CONCEPT OF A SCREW CAP LINER CAPABLE OF BINDING VSCS IN BOTTLED WINE

Considering the problem of post-bottling reduction as well as the drawbacks of prophylactically added copper prior to bottling it was reasoned to devise a liner being capable of inactivating VSCs during bottle ageing.

The makeup of this liner has been inspired by the traditional tin/Saran liner but with the tin layer being replaced by an aluminium layer. Furthermore, the new liner contains an additional acceptor layer consisting of immobilised copper, capable of irreversibly binding VSCs after diffusion of the latter through a polyethylene layer in contact with the wine. The objective was to entirely relocate the interactions between VSCs and copper as they are known to occur in wine from the bottle into the liner. The result was the patent pending ALKOvin™ liner (Patent No. WO 2015/000901 A1) manufactured by Meyer Seals.

The basic objective of this new liner is to reproduce the effective oxygen barrier inherent in the tin/Saran liner, protect fruity aroma compounds against oxidative degradation, and simultaneously control the concentration of VSCs without copper or reaction products dissolving or getting into contact with the wine. Figure 1 depicts the makeup of this new ALKOvin™ active liner.

OTR OF THE ALKOVIN™ LINER

Prior to any work on wines great attention was paid to the OTR of the new liner. It was ensured in various tests that the ALKOvin™ active liner possesses an OTR indistinguishable from that of the tin/Saran liner. As a consequence, post-bottling SO_2 losses under the new liner would be comparable to those under the tin/Saran liner.

EFFECTIVENESS OF THE ALKOVIN™ ACTIVE LINER IN MODULATING REDUCTION TAINT

Based on the encouraging results obtained in our initial study (data not shown), it was decided to have these results confirmed by the AWRI, where a broader study was performed from Sept. 2015 – Sept. 2016.

A commercial Chardonnay wine (free SO2 = 40 mg/L, Cu++ < 0.1 mg/L) was spiked with three different concentration levels of ethanethiol, dimethyl sulfide, and H2S to achieve concentrations corresponding to several times the threshold limit. Methanethiol was present at a level above the sensory perception threshold in the unspiked Chardonnay wine, so this was not adjusted in any of the sample treatments.

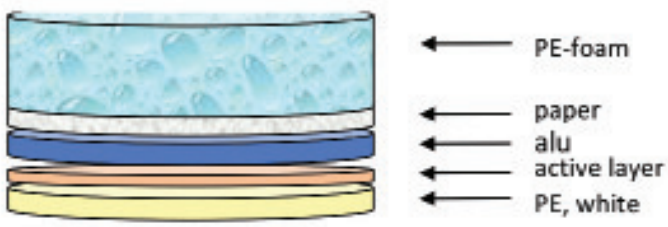

Figure 1: Design of the ALKOvin™ active liner adsorbing VSCs in bottled wines.

Table 1: Concentrations of VSCs as affected by ALKOvin™ active liner in comparison to tin/Saran liner in samples spiked at high concentration level after 12 months of bottle storage (upright, dark, at 17°C). Storage trial conducted in Australia.

	tin/Saran	ALKOvin®	percentage change caused by ALKOvin®
methanethiol, µg/L	10.13	7.10	- 30.6 %
ethanethiol, µg/L	7.23	3.50	- 51.6 %
hydrogen sulfide, µg/L	2.57	2.67	+ 3.9 %
dimethyl sulfide, µg/L	185.0	226.3	+ 22.3 %

(Full report on the AWRI study is available upon request.)

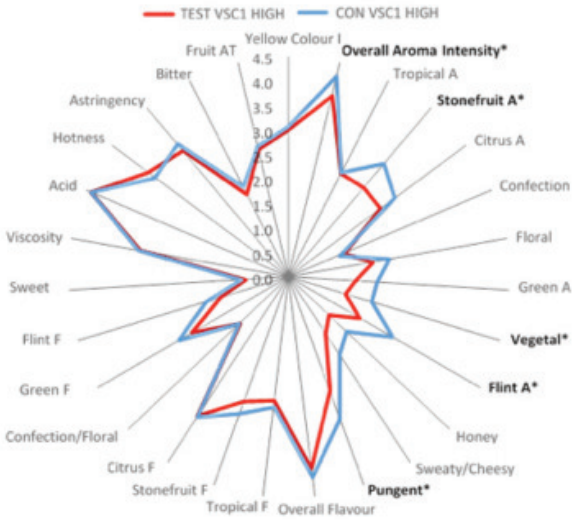

Figure 2: Mean values for all sensory attributes for Chardonnay after spiking with thiols, H2S and dimethyl sulfide and 12 months' bottle storage under both tin/Saran (CON VSC1 HIGH) and ALKOvin™ active liner (TEST VSC1 HIGH) liner.
Means found to be significantly different from each other (LSD = 5 %) are marked in bold with *

Table 1 depicts the impact of ALKOvin™ active liner after 12 months of bottle storage as compared to the tin/Saran liner.

Table 1: Concentrations of VSCs as affected by ALKOvin™ active liner in comparison to tin/Saran liner in samples spiked at high concentration level after 12 months of bottle storage (upright, dark, at 17°C). Storage trial conducted in Australia.

Thiols relevant for post-bottling reductive attributes show a drastic decrease under the ALKOvin™ active liner with the concentration differences generally increasing over time. The complex chemistry involved in the fate and formation of VSCs makes it difficult to explain the lack of effect on H2S and dimethyl sulfide concentrations.

The AWRI trials also studied the impact of the new liner on the concentrations of various precursor compounds, i.e. on sulfur compounds, out of which reductive VSCs develop. Remarkably, concentrations of almost all VSCs measured are lower under ALKOvin™ active liner, as compared to the tin/Saran liner. Only H2S and dimethyl sulfide show a deviant behaviour, which cannot be explained conclusively.

The decrease of precursors is caused by a shift in the equilibria established between the primary thiols and their corresponding precursors. When thiols are scavenged by the new liner, the equilibria favour conversion of the precursors to their primary thiols, resulting in a lower concentration of both precursors and thiols (data not shown).

Sensory evaluation was carried out at the end of the 12 months' bottle storage using the AWRI's expert sensory panel. Figure 2 summarises the attribute scores under tin/Saran and ALKOvin™ active liners for Chardonnay previously spiked with thiols, H2S, and dimethyl sulfide.

The wines stored under the ALKOvin™ active liner exhibited significantly lower perceived levels of reductive aromas such as vegetal and flint. Samples were also presented at a workshop focused on "The impact of packaging on wine development and shelf-life",(workshop #13 at the 16th Australian Wine Industry Technical Conference), where most participants were observed to prefer the wine under the ALKOvin™ active liner .

AT A GLANCE

- An innovative screw cap liner capable of modulating the concentration of volatile sulfur compounds (VSCs) in screw capped wine has been subjected to performance trials;
- The innovative liner includes a layer containing active copper capable of immobilizing VSCs, present in the bottle headspace. Essentially their scavenging by copper takes place within the liner;
- OTR of the new liner is indistinguishable from that of a tin/Saran liner;
- Tests have shown that none of the active copper leaches into the wine during storage, even when bottles are stored horizontally; and
- In storage experiments performed by the AWRI using commercial wine spiked with VSCs, a distinctive decrease in their concentration was observed in bottles sealed with the active liner, in comparison with those sealed with a tin/Saran liner.

IMPACT OF THE ALKOVIN™ ACTIVE LINER ON VARIETAL THIOLS OF SAUVIGNON BLANC

Varietal thiols of Sauvignon blanc such

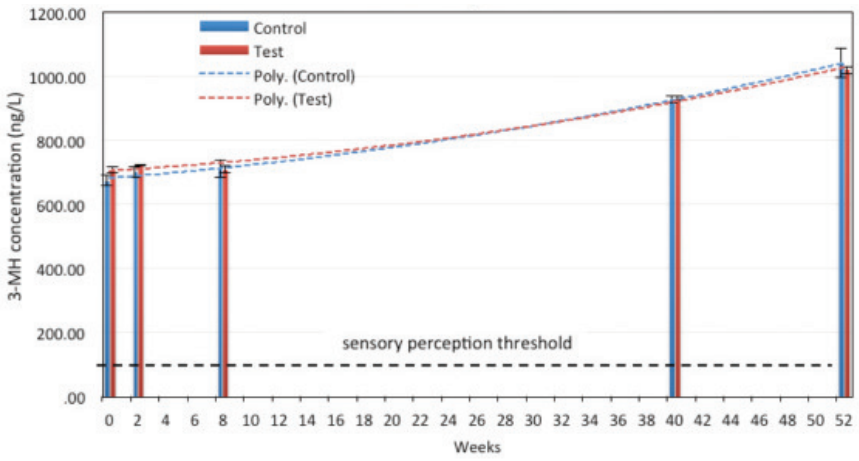

Figure 3: Concentration of 3-MH in Sauvignon blanc under tin/Saran (Control) and ALKOvin™ active (Test) liner at different time points during 12 months' bottle storage.

as 3-MH, 3-MHA, and 4-MMP possess –SH groups and hence are reactive towards copper. Consequently, it was investigated to what extent aroma thiols could become compromised by the new liner.

A commercial Sauvignon blanc wine (free SO2 = 40 mg/L, Cu++ < 0.1 mg/L, no spiking) was bottled and stored as outlined before. Varietal thiols were measured at different time points during bottle storage under both tin/Saran and ALKOvin™ active liner. Figure 3 shows the concentration profile for 3-MH under both liners over a 12-month period. The concentration profiles for 4-MMP and 3-MHA showed similar patterns under both liners.

Evidently, the difference in concentration of the individual varietal thiols under the ALKOvin™ active liner and tin/Saran liners was minimal across the 12 month storage period. The only significant difference was observed for 3-MHA from 40 weeks onwards, with the concentration under the ALKOvin™ active liner being slightly lower than under the tin/Saran liner.

The insensitivity of aroma thiols may seem surprising in consideration of the definite impact of the ALKOvin™ active liner on VSCs. However, one has to keep in mind that a thiol, prior to interact with the active layer, has to diffuse through a polymer film. Diffusion rate in polymers depends (among other parameters) on the molecular weight of the diffusant. The molecular weights of aroma thiols are distinctly higher than those of VSCs. It is believed that this is the reason for aroma thiols only being marginally influenced by the new liner.

IMPACT OF ALKOVIN™ ACTIVE LINER ON COPPER CONTENT

Thorough checks of copper in wines stored under the ALKOvin® liner have shown that no copper leaches into the wine during storage.

THE FUTURE

Extensive field trials with leading AUS and NZ wineries are under way to confirm the impact of ALKOvin™ active liner on wines bottled under real world conditions.

Results of the field trial will be published in a future article.

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