INFLUENCE OF DIFFERENT SCREW CAPS ON WINE QUALITY

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Introduction

Fruity white wines develop different sensory expressions of ageing. The best known of these is typical ageing, which is intensified by oxygen uptake via the bottle closure. Conversely, it is largely prevented by the widespread use of screw caps, in some cases with hermetically sealing inserts. However, such closure systems promote the so-called reductive ageing through the formation of reductive taints in the bottle. The development of a functionalised liner for screw caps opens up a way out of this dilemma.

From the moment a wine is bottled with different closures, the emergence of different wines from the same initial wine begins. In white wines, essentially four different sensory expressions of maturation and ageing develop:

- Typical or oxidative ageing,
- Atypical ageing (ATA),
- Petrol flavour,
- Reductive ageing.

Without any doubt, every white wine is subject to ageing. The only question is which of the above-mentioned types of ageing it is and how quickly it develops. In most wines, the bottle closure, and particularly its oxygen permeability, plays a prominent role.

Different chemical reactions and odour-active compounds are responsible for the formation of the various forms of ageing. Two of them are predetermined by viticultural factors. Petrol flavour, for example, occurs almost exclusively in Riesling wines obtained from physiologically ripe grapes grown under hot-climate conditions, whilst the development of atypical ageing is observed exclusively in wines obtained from stressed fruit. The occurrence of these two very specific types of ageing is not related to the availability of oxygen. Consequently, it is not influenced by the oxygen permeability (OTR) of the bottle closure.

Regardless of this, the development of petrol flavour is significantly increased with screw caps because, in contrast to internally sealing closures such as corks, these have little material that could absorb the compound responsible for petrol flavour (TDN).

Typical or oxidative ageing

The situation is completely different with oxidative ageing. It has always been known and is, globally speaking, the most common sensory expression of white wine ageing. It is mainly due to the oxygen ingress through the bottle closure. In this process, odour-active compounds are formed under the influence of oxygen, of which methional, benzaldehyde, 2-phenylacetaldehyde, 3-methylbutanal and furfural are the most important ones and are considered indicator substances (Escudero et al. 2002, Ferreira et al. 2003, Pons et al. 2015). They are higher aldehydes formed by oxidation of their corresponding alcohols. Their aroma notes of nuts, dry herbs, honey, cooked vegetables and boiled potatoes increasingly mask the fruity varietal aroma and cause a distinct madeirized aroma in extreme cases.

In contrast to the well-known acetaldehyde, which in its free form elicits its typical smell reminiscent of bruised apples and sherry and which can be bound by sulphur dioxide, these higher aldehydes barely react with SO_2. Therefore, their formation cannot be effectively prevented by bottling with increased levels of free SO_2. The reactions that lead to their formation are largely irreversible. They are controlled by oxygen supply and significantly accelerated by warm bottle storage.

Screw caps counteract oxidative ageing because they protect the bottled wine relatively well or even hermetically from absorbing atmospheric oxygen. This is one of the reasons for their almost universal acceptance in some countries. On the other hand, the assumption that the well-sealing screw caps protect the wine against any kind of adverse ageing is wrong.

Screw caps as an answer to oxidative ageing

In oxygen-sensitive white wines, differences in oxygen uptake of more than 5 mg/L O_2 can be discriminated by sensory means. This led to the initial assumption that the ideal closure for such wines would seal hermetically and prevent any oxygen ingress in order to preserve the fruity primary aromas for as long as possible. Since screw caps fulfil this requirement better than most other closures, there was initially nothing against their widespread introduction. This was especially the case when, a few months after bottling, the oxygen dissolved in the wine and the oxygen trapped in the bottle headspace has been completely bound and consumed by the wine, the closure takes control of oxidative ageing. With increasing bottle storage, the influence of the bottle closure comes more and more to the fore.

Significance of the sealing insert in the screw cap

Contrary to popular belief, however, screw caps are not a uniform type of closure, but are distinguished from one another by different sealing systems with different oxygen barrier effects.

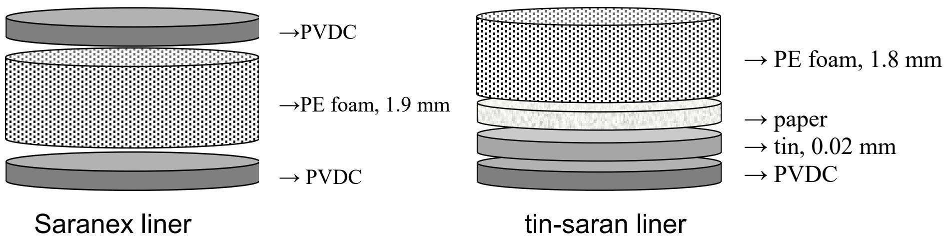
Each screw cap consists of an outer aluminium cylinder and a single or multi-layer sealing insert. The outer cylinder fixes the insert in the correct position and presses it onto the bottle rim with the required pressure. The sealing insert provides the seal between the product and the closure, seals the bottle and prevents the diffusion of gases and liquids. It determines the tightness and functional quality of the screw cap. The relative tightness to atmospheric oxygen is given as the "oxygen transmission rate" (OTR) in µg O_2/day or mg O_2/year.

Thanks to their specific characteristics, the inconspicuous sealing inserts are the central element of screw caps and their functional end. In other words: Screw caps are as good as their sealing inserts. The latter are produced by specialised companies. The multitude of screw cap manufacturers is supplied by only a few manufacturers of sealing inserts.

Originally, the sealing insert consisted only of simple elastomers such as PVC or PE, which were injected into the aluminium cylinder. In the wine business, such inserts are mainly found in the short-skirted MCA or roll-on pilfer proof screw caps, which are preferably used in the segment of simple and inexpensive wines. The OTR for injected PVC is 1.4 mg O_2/year (Müller and Weisser 2002).

The gold standard for screw caps is now considered to be the long-skirted (60 x 30 mm) variants such as "Stellvin" or "Longcap", which require a BVS bottle neck finish. Instead of injected elastomers, multi-layer sealing liners are predominantly used in these closures. Two main variants of such sealing liners are known (Figure 1):

Figure 1: Structure of common liners used for screw caps.



- The Saranex™ liner consists of a 2 mm thick layer of PE foam covered on both sides with a layer of PVDC (polyvinylidene chloride). The symmetrical structure of this liner can be described as "PVDC-PE-PVDC". Its OTR is 1.0 to 1.5 mg O_2/year with some dependence on temperature (Vidal et al. 2011).
- The tin-saran liner is designed asymmetrically, with one side of the PE layer in direct contact with the lid of the aluminium cylinder. In its traditional version, a thin tin foil with a thickness of 0.02 mm is applied to paper towards the bottom of the seal, as well as a PVDC layer that makes contact with the wine. The tin foil provides an additional gas barrier. As a result, the OTR of this liner is 0.0 mg O_2/year (Vidal et al. 2011), which corresponds to an absolute oxygen barrier. In the course of diversifying the range, designs deviating from this standard have since been developed in which the paper is omitted or the tin is replaced by aluminium.

It can be summarized that the traditional screw caps are characterised by a low OTR of only 0.0 to 1.5 mg O_2/year and thus by a high to absolute oxygen barrier effect. The exact values result from the sealing system used. To be able to classify them, a comparison with the OTR data of other closures is useful:

Technical corks have an OTR of approx. 1.0 mg O_2/year, which is roughly comparable to that of screw caps. Synthetic stoppers, on the other hand, have become known for their sometimes very high OTR of up to 20 mg O_2/year, however constant improvements and differences can be observed depending on the manufacturer and production process. The OTR of natural corks also varies in a wide range between 0.5 and 23 mg O_2/year, with strong fluctuations being observed between individual batches as well as between individual pieces within a batch (Godden et al. 2005, Lopes et al. 2006, Karbowiak et al. 2010).

Reductive ageing

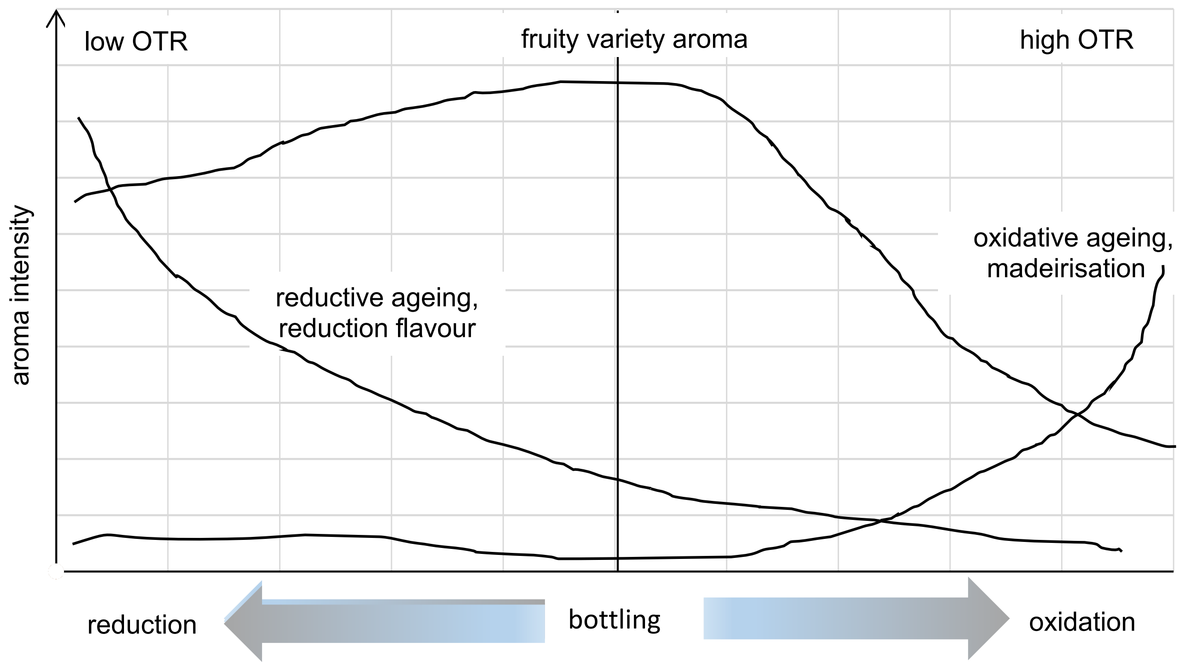
At the turn of the millennium, when the hermetically sealing screw cap with a tin-saran liner was introduced, Australia's and New Zealand's wine industries took a pioneering role. One of their reasons was the pursuit of better preservation of the fruity varietal aroma of white wines under absolute oxygen exclusion. After a short delay, the wine industry in several European countries also adopted this logic.

The initial euphoria 'Down Under' soon gave way to more sober reflection when a greater tendency of the wines to developing aromas described as reductive or sulphurous was demonstrated under conditions of absolute air exclusion such as under the tin-saran lined screw caps (Skouroumounis et al. 2005). The sensory data were supported by analytical data. The tin-saran airtight sealed lots showed higher levels of hydrogen sulphide (H_2S), methanethiol (methyl mercaptan), SO_2, and aroma thiols of Sauvignon blanc than the controls bottled with less airtight seals (Ugliano et al. 2009, 2011, 2013, 2015, Scrimgeour & Wilkes 2014). The elevated levels of methanethiol and H_2S, both volatile sulphur compounds (VSCs) relevant for reductive taints, have previously been associated with a lack of oxygen in absolutely airtight sealed bottles (Limmer 2005). They are formed under very reductive conditions by purely chemical pathways from less odour-active precursors. These include their forms bound to heavy metals ions, disulphides, thioacetates, and sulphur-containing amino acids (Ferreira et al. 2018, Kreitman et al. 2018).

The abiotic formation of malodorous VSCs and the resulting off-flavour (burnt rubber, rotten eggs, cooked cabbage, garlic, etc.) is called reductive ageing. This term is still little known in many countries. Reductive ageing is the opposite of oxidative ageing, which is due to higher aldehydes and their related aroma attributes of dry herbs, honey, cooked vegetables, etc.

The oxygen supply through the selected bottle closure determines whether the ageing of the wine is driven more in the oxidative or more in the reductive direction. This is illustrated in figure 2. This is a balancing act. In comparison with the tin-saran liner, increasing the OTR from 0 to 1.5 mg O_2/year by using a Saranex liner resulted in less reductive notes after two years of bottle storage, but at the same time also resulted in an enhancement of the typical aroma attributes of oxidative ageing (Lopes et al. 2009).

Figure 2: Influence of the oxygen transmission rate (OTR) of the bottle closure on post-bottling white wine ageing (adapted from Ugliano et al. 2009).



Such results underline the importance of the screw cap sealing insert and its OTR. Furthermore, they call into question the value of the absolute oxygen barrier provided by the tin-saran liner that is unilaterally preferred in many countries. In any case, they present the winemaker with the dilemma of having to choose between oxidative and reductive ageing. In real-world winemaking conditions he is hardly able to foresee the development of each individual wine.

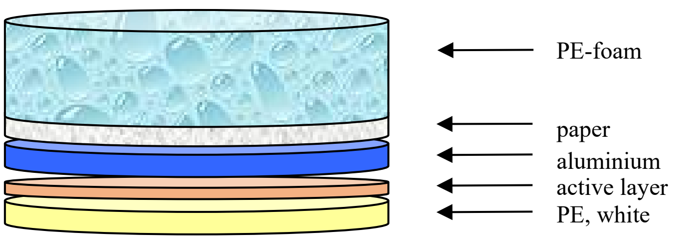
Reductive taints that do not appear until a few months after bottling are known as post-bottling reduction flavour. They have experienced a significant increase in many countries after the introduction of the screw cap. In contrast to New World countries, where this problem has been addressed and dealt with, such reductive taints are often still ignored or glossed over as mineral characteristics in more traditional wine growing areas. In other cases, attempts are made to avoid them by deliberately adding some copper sulphate before bottling. However, this procedure is criticised for ethical, toxicological, chemical or emotional reasons.

Concept of a functionalised sealing disc to prevent reductive ageing

For the aforementioned reasons, many winemakers do not use preventive pre-bottling copper dosing to avoid the occurrence of post-bottling reduction flavour. As a result, there has been no shortage of attempts to make copper available to the wine in an immobilised form in such a way that it does not come into contact with it or accumulate in it. One technical solution is to immobilise the copper on a carrier material and enclose it in a permeable polymer membrane. The thiols and H_2S responsible for reductive taints diffuse from the wine through the membrane to the immobilised copper and are irreversibly bound to it.

This concept was transferred to a liner for screw caps. Its structure is based on that of the conventional tin-saran liner, with the tin foil being replaced by an aluminium foil. The immobilised copper preparation is located behind the last layer of PE applied on the wine side. The permeability of this layer allows the migration of the molecules causing reduction flavour from the wine to the copper, but not the migration of the copper into the wine. At the same time, the absolute oxygen barrier of the tin-saran liner is still guaranteed. The aim is to preserve the fruity aroma by complete exclusion of oxygen and at the same time to reduce the molecules responsible for post-bottling reduction flavour. Figure 3 shows the structure of this functionalised, VSCs-absorbing liner.

Figure 3: Structure of a VSCs-absorbing liner for screw caps.

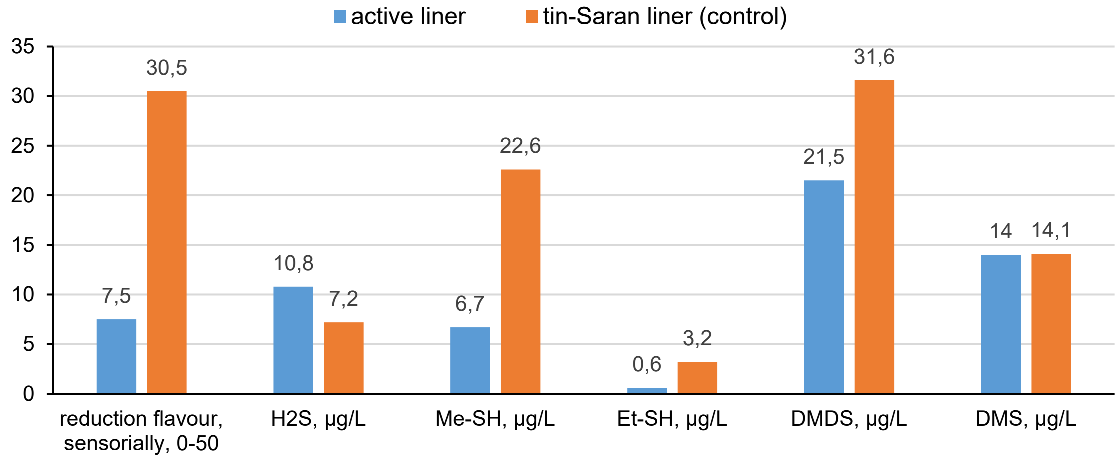


Find more information about ALKOvin™ active **here**.

Effect on thiols

In a first test, the effect of this liner was checked on a white wine (free SO_2 = 40 mg/L, Cu^{++} < 0.1 mg/L), which was bottled with a clearly perceptible reduction flavour, sealed after headspace inertisation with nitrogen, and stored upright. The traditional tin-saran liner served as a comparison. Figure 4 shows that the sensorially perceptible reduction taint disappeared after eight months of storage under the functionalised liner. The sensory perception is in line with the behaviour of the thiols such as methanethiol and ethanethiol involved in post-bottling reductive taints, whose contents were reduced to a fraction with the use of the active liner. The simultaneous differentiation of the content of dimethyl disulphide shows that the effect of this active liner also indirectly extends to disulphides.

Figure 4: Development of the contents of VSCs and of sensorially perceptible reduction flavour of a tainted wine (Chardonnay) after 8 months of bottle storage (upright, dark, 20° C) after sealing with screw caps fitted with different liners.



H2S = hydrogen sulphide, Me-SH = methanethiol, Et-SH = ethanethiol, DMDS = dimethyl disulphide, DMS = dimethyl sulfide.

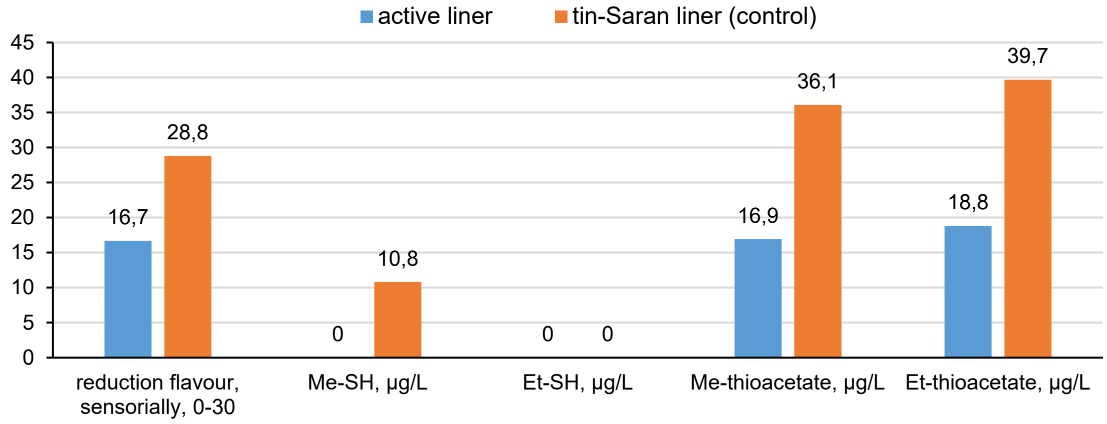
Effect on precursors of reductive off-flavours

Disulphides and thioacetates are essential precursors of the malodorous VSCs and the resulting post-bottling reductive off-flavour. In order for the innovative concept to actually work, a liner functionalised in this way must also be able to scavenge VSCs to the same extent as they arise in the bottle from their precursors. Therefore, in further trials, wines were spiked with these precursors, bottled under inert conditions, sealed using screw caps equipped with the respective liners, and stored upright.

Figure 5 shows the results for thioacetates. After eight months of bottle storage, their contents in the bottles sealed with the active liner were only 47 % of those under the tin-saran liner. However, thioacetates cannot react directly with copper. Their depletion is explained by a shift in the dynamic equilibrium between them and the corresponding thiols during storage. The resulting thiols are then adsorbed by the active liner. This adsorption of the thiols accelerates the decay of thioacetates and finally leads to their effective decrease. With the tin-saran liner, on the other hand, the thiols formed accumulate and the thioacetates remain on a higher level, which results in a twofold higher intensity of the sensorially perceptible reduction flavour.

Figure 5: Development of the contents of VSCs and of sensorially perceptible reduction flavour after 8 months of bottle storage (upright, dark, 20° C) after sealing with screw caps fitted with different liners.

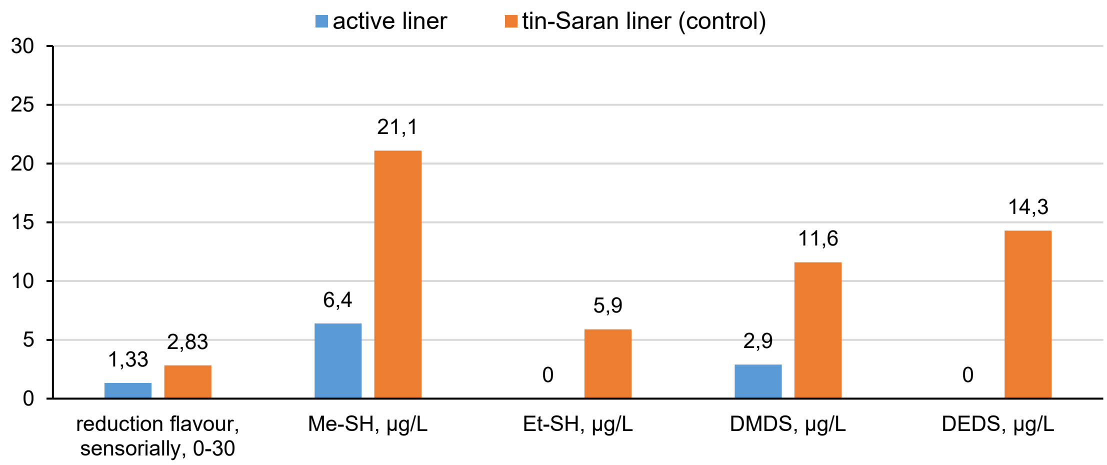
Wine spiked with 50 µg/L methyl thioacetate and 50 µg/L ethyl thioacetate before bottling.



Analogous experiments were performed after spiking a wine with disulphides. Figure 6 shows the results after eight months of bottle storage under conditions of oxygen exclusion. In comparison with the tin-saran liner, the functionalised liner led to a 75 % decrease of dimethyl disulphide and a 100 % decrease of diethyl disulphide. At the same time, methanethiol accumulated under the tin-saran liner, which did not occur under the active liner, with the result that it almost halved the intensity of the sensorially perceptible reduction flavour. Since disulphides cannot react directly with copper, it can be assumed that they are first reduced to thiols and as such are subsequently bound to the active liner.

Figure 6: Development of the contents of VSCs and of sensorially perceptible reduction flavour after 8 months of bottle storage (upright, dark, 20° C) using screw caps fitted with different liners.

Wine spiked with 33 µg/L dimethyl disulphide (DMDS) and 33 µg/L diethyl disulphide (DEDS) before bottling.



Effect on aroma thiols

The influence of the functionalised liner on aroma thiols was of particular interest. These are aromatic substances containing sulphur and eliciting a smell reminiscent of passionfruit, guava, grapefruit, and black currants. They are sensitive to copper and oxygen similarly to the thiols responsible for reductive off-flavours. They are present in sensorially significant concentrations in wines from Sauvignon blanc and a few other grape varieties.

Table 1 shows the results on a Sauvignon blanc after 12 months of bottle storage in comparison with the tin-saran liner. The percentage losses of the aromatic thiols were barely measurable and not significant. They were disproportionately lower than those of the compounds responsible for the reductive off-flavour. Apparently, the PE layer separating the active layer of the new liner from the wine acts as a kind of molecule filter. It allows the low-molecular thiols methanethiol and ethanethiol causing reductive taints to pass more easily than the higher-molecular aromatic thiols.

Table 1: Impact of the active liner on the contents (µg/L) of aroma thiols in Sauvignon blanc after 12 months of bottle storage.

	active liner	tin-Saran liner (control)	Difference as compared to tin-Saran liner
4-mercapto-4-methylpentan-2-on	1.53	1.52	+ 0.7 %
3-mercaptohexan-1-ol	1018	1042	- 2.3 %
3-mercaptohexyl acetate	3.37	5.4	- 17.9 %
benzyl mercaptan	2.27	3.18	- 28.6 %

Results on an industrial scale

In a comparative large-scale trial with 21 wines in Australia and New Zealand (Schneider et al. 2017), the functionalised liner showed a hardly measurable OTR of almost 0.0 mg O_2/year, which is comparable to that of the traditional tin-saran liner. Accordingly, the SO_2 losses during storage were also comparably low.

Over a period of 24 months, no increase in copper content was observed in the bottles sealed with the functionalised liner and stored laid down. The data obtained for OTR and copper prove that the VSCs sensorially perceived as reductive off-flavours are reduced exclusively by irreversible binding to the copper immobilised in the new liner. The sum of the results obtained indicates that despite storage conditions under a hermetically sealing screw cap, reductive ageing caused by the formation of malodorous thiols can be significantly mitigated without enriching the wine with copper. At the same time, the exclusion of oxygen provided by these screw caps is able to completely prevent oxidative ageing. Oxidative ageing and reductive ageing as opposing problem areas lose their significance under these conditions.

Wines that are not prone to develop post-bottling reduction flavour behave in the same way under the functionalised liner as under the tin-saran liner. In such cases, a decrease of methanethiol levels of only 27 % on average is observed, which precludes sensory differentiation.

The functionalised liner against reductive ageing is now commercially available under the trade name ALKOvin active®.

Summary

Screw caps differ in the oxygen barrier effect of their sealing inserts. Too much oxygen promotes oxidative ageing, too little oxygen promotes reductive ageing. Reductive ageing under hermetically sealing bottle closures is due to the formation of increased levels of volatile sulphur compounds, in particular thiols and H_2S, whose odour causes reductive taints. Their prevention by the addition of copper salts before bottling is commonly opposed due to a variety of concerns. As an alternative, a functionalised liner for screw caps has been developed. It traps the thiols responsible for the occurrence of post-bottling reduction flavour and at the same time protects the fruity varietal aromas from oxidative ageing through its perfect oxygen barrier effect.

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