

The 'random oxidation' myth

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Introduction

The term 'random oxidation' was invented in Australia in the 1990s in response to a perceived increase in sporadic oxidation in some bottled white wines. As bottled wines usually have very limited or no contact with air, the onset of sensory symptoms of 'oxidation' indicates a malfunction of some sort.

It has been known for at least several decades that packaged wines are affected by sensory symptoms of 'oxidation' if the concentration of sulfur dioxide (SO_2) in the wine falls below a certain 'critical' level; this was confirmed experimentally in bottled white wine by Godden *et al.* (2001). Thus the onset of sensory symptoms of 'oxidation' in a bottle of wine shows that the level of SO_2 at filling and sealing was insufficient to counteract the oxidising effects caused mainly by oxidants and oxygen in the bottle at sealing and, to a much lesser extent by any ingress of very small amounts of atmospheric oxygen in the years after bottling (Figure 1). The sources of oxidants and oxygen in a freshly sealed bottle are inadvertent contact with air in the days before bottling, and also the contact the wine inevitably has with air during bottling operations. Because the sensory symptoms of oxidation may not become apparent until several or more months after bottling, the cause of the problem is not immediately obvious and can elude an inexperienced investigator.

The term 'random oxidation' is a misnomer because it implies an inscrutable, independent propensity of individual bottles of wine to succumb to oxidation. In reality, the causes of post-bottling oxidation

are known, and they can be controlled. Attributing the problem to the oxygen permeability of some corks is based on misunderstandings about the mechanism of the oxidation processes in bottled wine, and about the nature of the oxygen barrier properties of cork stoppers. These misunderstandings are conducive to the acceptance of circumstantial evidence which would otherwise be treated more sceptically.

The inadvertent inclusion of additional air increases the pressure in the sealed bottles - this is air dissolved or emulsified in the wine, plus that compressed in the headspace by the incoming cork. The elevated hydraulic pressure results in an excessive uptake of liquid vapour by the cork, a premature softening of the cork tissue and a decline in its sealing pressure. When this occurs, it might seem to the casual observer that a 'soft' cork has allowed the loss of wine and the ingress of air. Surprisingly, it is the increased air content and the excessive headspace pressure which are responsible for a degree of oxidation, damage to the cork and expulsion of some wine.

I first encountered sporadic post-bottling oxidation in the mid 1960s. Over the next year or so, the causes were identified, and preventative measures were established. They were not completely successful, and it soon became apparent that the price of freedom from post-bottling oxidation is eternal vigilance and occasional confrontations with production staff. Blaming the corks is just 'scapegoating'.

This article focuses on acceptance of the myth as a phenomenon and only deals cursorily with the technical details. Various aspects of the chemistry of SO_2 in wine, sensory oxidation, the sources of oxygen and the oxygen barrier properties of corks have been described in a number of previous articles by the author, (see bibliography).

The genesis of 'random oxidation'

Active steps to prevent sporadic post-bottling oxidation became necessary in the early 1960s as the increasing speed and mechanisation of bottling and corking operations disrupted traditional methods. In order to prevent uncontrolled contact with air, industrial scale packaging of wine requires supervision of the preparation and delivery of wine to the filler, and continuous monitoring of the filling and sealing operations. It is also essential to ensure that the wine contains sufficient SO_2 to counteract the effects of the likely maximum air contact (Figure 1).

The reported increase in the occurrence of post-bottling oxidation

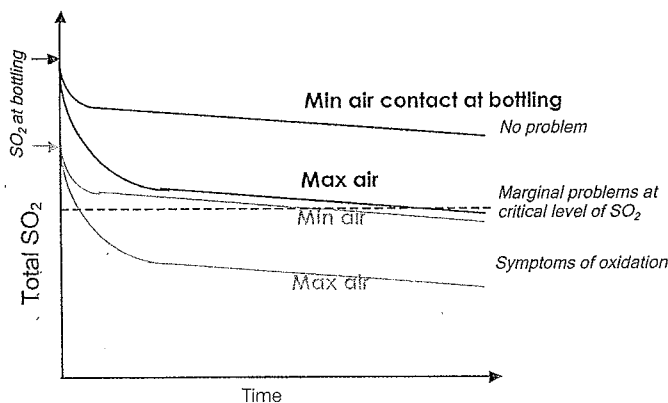


Fig. 1. Schematic representation of post-bottling changes in SO_2 levels. The extent of sensory 'oxidation' depends predominantly on the initial levels of SO_2 and the amount of air contact before and during bottling.

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in the early 1990s has its origin in the earlier encouragement given to winemakers to reduce the levels of SO₂ in their wines. Lee (1989) reported and applauded a reduction in mean levels of SO₂ in Australian bottled wines, and also a putative industry consensus to reduce by 50mg/L, the maximum allowable level of SO₂ in wines with <35g/L of sugar. He urged the wine industry to talk about these reductions because, "... it has beneficial implications for health and for wine quality."

At the 1992 Wine Industry Technical Conference, Sneyd *et al.* (1993) also concluded that the maximum allowable level of SO₂ under Australian food law could be lowered. They acknowledged that the concentration of acetaldehyde is the controlling factor in determining the most appropriate level of SO₂, but they gave no precise details of how acetaldehyde concentrations could be restricted or reduced, or what levels of SO₂ were required at the time of bottling. Other attendees at the Conference expressed reservations about the need to reduce SO₂ levels.

Some pragmatic wine-bottlers were opposed to indiscriminate reductions of SO₂ levels at bottling. They were concerned that lowering the existing levels of SO₂ at bottling would decrease the safety margin and increase the risk of oxidation and microbial problems in the bottled wine. By contrast, the prevailing mood at the 1992 Conference appeared to display more enthusiasm than good sense about reductions in the use of SO₂ and other 'additives'.

At the time, the cause of the reported increase in post-bottling oxidation of white wines seemed clear; that is, insufficient SO₂ at bottling and/or incorporation of more than usual amounts of oxygen at bottling and sealing. This was also indicated tentatively in some AWRI Technical Reports (1992) dealing with specific instances of post-bottling oxidation. Some other unpublished analytical data showed that 'oxidised' bottles examined by the AWRI were significantly lower in carbon dioxide than the 'un-oxidised' bottles of the same wine. The lowered carbon dioxide levels indicated that

the 'oxidised' bottles had had significant pre-sealing contact with air.

Despite this evidence, industry and research personnel persisted in their belief that bottling operations could not be the root cause of oxidation which only became apparent some months after bottling. It later transpired that this reluctance to accept the logical explanation was not just because of the delay in the onset of symptoms, but also because in some occurrences of post-bottling oxidation, the extent of oxidation of SO₂ required amounts of oxygen that exceeded the solubility of atmospheric oxygen in the wine. However, this is not a valid objection. In addition to oxygen dissolved in the wine (8mg/L at 20°C, more at lower temperatures), additional oxygen pick-up by air contact before and during bottling can easily raise the total amounts well above the air saturation value as follows:

- oxidant formation from air contact in the days before bottling, (0-6 mg/L)
- emulsification of air and wine by the filling machine, (maybe 1-2 mg/L)
- air compressed in the headspace when the cork is driven into the bottle without effective application of vacuum, (3-6mg/L).

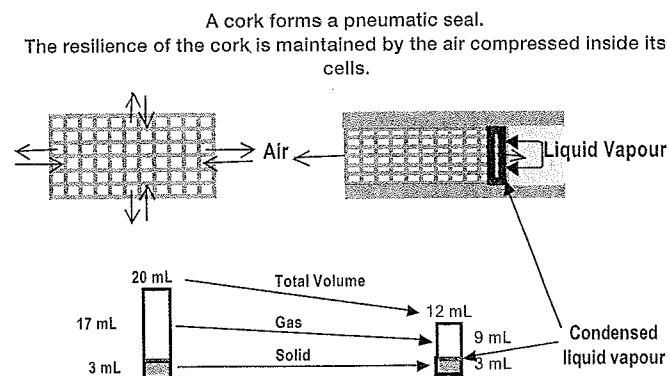
The possible total amount of oxidants and oxygen included at bottling may seem improbable, but it nevertheless remains a possibility that can account for SO₂ declines of up to 60-80mg/L. Murphy's Law tells us that "If it's possible, it will happen", and presumably, large amounts of oxygen pick-up had happened at one or more wine bottling plants. Some published accounts of post-bottling oxidation cite maximum SO₂ declines of 40-70mg/L, (Waters *et al.* 1996), and 45-65mg/L, (Gibson, 2005).

Cork as a scapegoat

The belief that cork could be responsible for sporadic post-bottling oxidation rested on three unproven assumptions.

- that atmospheric oxygen can diffuse through the cork into the wine against the higher concentration of oxygen compressed in the cork cells (Figure 2).
- that some corks contain a volatile agent of oxidation
- that despite a 40% compression in the bottle neck, there are still significant differences in the intrinsic sealing performance of individual corks.

Assumption No 1 is physically impossible (Figure 2). Assumption No 2 is purely speculative as 'residual oxidants' [*sic*] have never been detected in commercial corks. Although Assumption No 3 may seem plausible, any difference would be slight, and its effects would be obscured by the much larger variations in headspace pressure produced by the corking machine.



After insertion:

- The volume of the cork is reduced by some 40%
- In round terms, the gas pressure in the cork cells is doubled. The only possible permeation of oxygen is from the cork, mostly to the infinite volume of the atmosphere. At the same time, several hundred milligrams of liquid vapour permeates from the wine into the cork.

Fig. 2. Air compressed in the cork cells acts as a barrier to the net entry of atmospheric oxygen.

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It was then surprising that papers by Waters *et al.* (1996) and Caloghiris *et al.* (1997) claimed to have demonstrated that oxidative spoilage of bottled white wines could be attributed to the corks. However, neither of these papers demonstrated 'cause and effect', but simply assumed that unexplained declines in SO₂ must be a result of either 'oxygen permeability' or the presence of 'residual oxidants' in some but not all of the corks. Apart from ignoring the implausibility of both hypotheses, the authors did not take into account the variable oxygen pick-up which occurs inevitably at bottling, or the possibility of larger amounts caused by malfunction at bottling. Waters *et al.* (1996) demonstrated a slight oxidative effect in some bottles stored in an atmosphere of oxygen, but this effect is not exclusive to corks, and it has been demonstrated for screwcaps (Matthews & Vale, 2009).

Trials that fail to take into account the extent of air contact just before and during bottling cannot make any valid conclusions about the cause of post-bottling oxidation. It follows that the papers by Waters *et al.* (1996) and Caloghiris *et al.* (1997) are highly misleading to the wine industry. Further, the claim by Godden *et al.* (2001) that closure effectiveness can be predicted from the extent of Free SO₂ decline in the six months after bottling is incorrect and likely to mislead anyone testing closures for wine bottles.

But why?

Effective, large-scale and high speed application of wine corks can be quite a challenge for Production and Quality Control personnel. When there are problems, cork suppliers and their corks can often become targets for antipathy. Thus many winemakers were enthusiastic about the suggestion that post-bottling oxidation could be attributed to the corks. There was little or no scrutiny of the evidence or the proposed hypothetical mechanisms because it all seemed so plausible and convenient. Such is the appeal of the proposition, that considerable resources were invested in unsuccessful attempts to *prove* that corks are somehow responsible for post-bottling oxidation.

There have also been numerous pointless instrumental measurements of Oxygen Transmission Rates which have absolutely no relevance at all to the oxygen barrier of corks in wine bottles.

The simplistic notion of 'random oxidation' was given wider currency when it was passed on to the wine media. As Fred Hoyle once remarked, "*Words are like barbs, once they go in they're very hard to pull out.*" It may be some time before the term 'random oxidation' is abandoned.

Conclusions

The evidence for the notion of 'random oxidation' and its attribution to corks via unproven mechanisms was and is largely wishful thinking. It can be shown that sporadic post-bottling oxidation is caused by one or more malfunctions in the bottling operations, and that the physical and chemical properties of corks play no part at all in the problem.

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Describes the many different ways in which wines can pick up oxygen during handling, filling, sealing and storage.

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Includes a brief refutation of the misapprehensions about the sealing ability of corks and their ability to exclude atmospheric oxygen.

John Casey is a former Chief Chemist for McWilliam's Wines Pty Ltd. He completed the Associate Diploma in Applied Chemistry at The Melbourne Technical College (now RMIT) and worked for a number of research and industrial organisations, including 32 years at McWilliam's Wines where he was involved in the control of finishing and packaging operations. After leaving the wine industry, he worked for four years in the 'residue chemistry' of foodstuffs, soil, water and air. He has written 30 or so technical articles about the chemistry of wine, wine-tasting, quality control, wine packaging, aseptic filling techniques, corks and other closures, and the physical chemistry of sparkling wines. He has also given presentations on closures for wine bottles at seminars in Australia, USA, South Africa and UK.