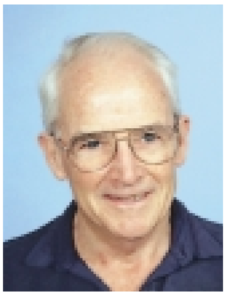
Controversies about corks



John Casey

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Traditional technologies often operate successfully without any real understanding of the precise nature of the processes involved. Winemaking and the use of cylindrical cork stoppers as closures for wine bottles are good examples. Despite the well-established techniques for the production and use of cork stoppers, there has always been some uncertainty about the reasons for their effectiveness as closures for wine bottles, and about the changes which take place in a wine after bottling.

The major controversy in the late 19th century was about the permeability of cork. Experts of the day were unable to reconcile the manifest permeability of cork with the apparent oxygen barrier properties of cork in a wine bottle. They were not aware that the permeation of gas can only take place in the direction of a declining concentration gradient. When a cork is compressed in the neck of a bottle, the pressure of the air in the cells is doubled, and the entry of atmospheric oxygen is not possible. While the inner face of the cork is covered with wine, the only permeation of oxygen that can take place is from the cork to the infinite volume of the atmosphere.

Currently, controversies about the use of cork centre mostly on three issues, and these are the main topics of this article:

- Venting or leaking?
- Post-bottling oxidation, sometimes called 'random oxidation'.
- Chloro-anisole taints.

These issues have been discussed at some length in earlier articles (Casey, 1998; 2001; 2003) and the following is intended as a synopsis.

Venting or leaking?

For a bottle to 'leak' or 'vent', the pressure inside the bottle must exceed the sealing pressure of the closure. When a 24mm diameter cork is forced into an 18.5mm bore, its volume is reduced by some 40%, and it exerts a sealing pressure in the region of 200kPa. Over a period of time, the sealing pressure declines to about 100kPa. The effectiveness of such high sealing pressures is sometimes diminished by the generation of pressure as the stopper enters the bore, and by the large increases in pressure due to a combination of temperature increases and small headspace volumes. No other liquid product in glass bottles has such small headspace volumes as bottled wine. Some wine bottlers choose 25 or 26mm corks to ensure superior sealing pressure for wines likely to be stored for an extended period. By comparison, Champagne stoppers are usually 30 or 31mm in diameter and will resist internal pressures of 800kPa or more. Because the pressure in a bottle of sparkling wine is largely due to carbon dioxide and not nitrogen, and because the headspace volumes are in the region of 25mL, the relative increase in pressure with temperature rise is not as great as with bottled still wines.

True leakage is very rare in bottled wines; that is, bottles that leak continuously when inverted. So-called 'leakage' usually involves the expulsion of a few drops of liquid, maybe just the once, or maybe on several occasions with increases in temperature. The motive force for the expulsion of liquid is excessive headspace pressure. Elevated pressures are mostly caused by malfunction during the corking operation, and they are aggravated by a number of other factors:

- Bottling at low temperatures.
- Corking without consistent application of CO_2 flush or vacuum.
- Small headspace volumes.
- Dissolved gases in the wine, ***particularly air or nitrogen***.
- Inverted or horizontal storage soon after bottling.
- Storage or transport at elevated temperatures.

Attention to these factors is often neglected because, individually, they do not always have a significant adverse effect. However, a combination of several of these factors is enough to produce disastrously high headspace pressures.

In addition to the stress imposed directly on the seal, elevated headspace pressure can cause a premature decline in the sealing ability of the cork. This occurs when the wine comes in contact with the cork shortly after corking. That is, while the headspace pressure is at its maximum. Like chronic hypertension in humans, excessive headspace pressure can cause tissue damage without there being any obvious symptoms. Elevated hydraulic pressure accelerates and increases the uptake of liquid vapour by the cork, which in turn softens the cell wall material. This is the reason for the recommendation to allow the bottles to remain upright for a certain period after corking; that is, until there is a significant reduction in any headspace pressure.

The effects of headspace pressure are often underestimated. This is because the expulsion of liquid and the dissolution of the headspace gases in the wine lead to a lowering of the pressure. An examination of a bottle which has lost some wine may show only low to moderate headspace pressure and a prematurely softened cork. This gives a superficial impression that the problem lies with the 'soft' cork rather than with the initial excessive headspace pressure. Because not all bottles 'leak' [sic], and because the incidence of so-called 'leakage' varies from batch to batch, it appears *obvious* that the problem is caused by

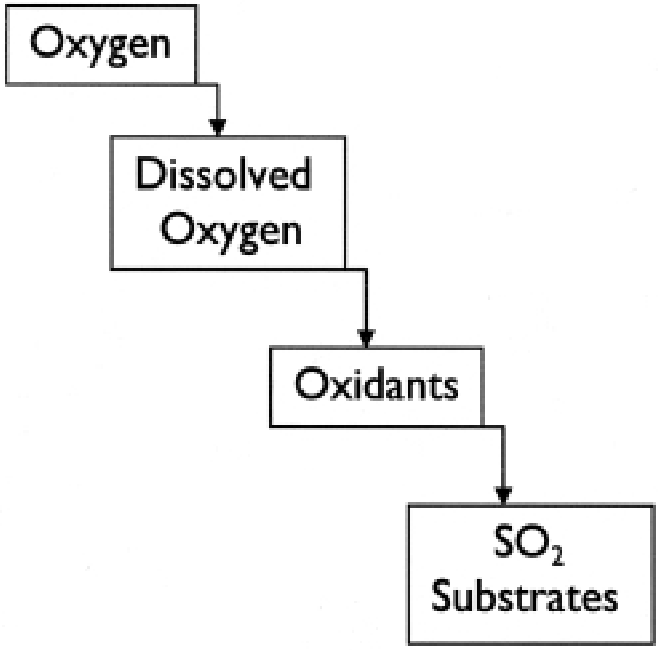

Fig.1. Oxidation of wine is a stepwise process.

differences in the sealing ability of the individual corks. In fact, the major variable is bottle-to-bottle differences in headspace pressures. These differences are sometimes observed at the time of corking or in retail bottles taken from the same carton.

Although cork is a 'natural material', minor differences between individual corks are suppressed when the cork is compressed in the neck of a bottle to 60% of its normal volume.

Post-bottling oxidation

The oxidation state of white wine is inextricably linked to the concentration of sulfur dioxide. There must always be sufficient sulfur dioxide in bottled white wines to suppress the adverse sensory effects of certain carbonyl compounds, particularly acetaldehyde and chromophoric carbonyl groupings. Complete suppression usually occurs when the Free SO_2 is in the region of 10- 15mg/L If the Free SO_2 falls below this 'critical' level, symptoms of oxidation, visual and gustatory, begin to appear, (Godden *et al.*, 2001). By the time the Free SO_2 approaches zero, the wine is well and truly 'oxidised' from the sensory point of view.

Thus, sulfur dioxide has a dual role in bottled white wines:

- It suppresses the undesirable sensory effects of carbonyl compounds by forming bisulfite addition compounds with them.
- The sulfur dioxide surplus to this minimum requirement acts as an anti-oxidant by reacting with oxidants derived from oxygen contact.

If all the surplus sulfur dioxide is oxidised, any further oxidation gradually releases the carbonyls and their adverse sensory effects. Therefore, when the wine is bottled, the SO_2 concentration must be raised above the 'critical' level by an amount sufficient to compensate for the expected ***maximum*** post-bottling decline. This decline results mainly from the incorporation of oxidants and air at the time of bottling, and to a much lesser extent from the entry of any atmospheric oxygen during prolonged storage (Figure 2). Because there are several steps in this process (Figure 1), it can take some time for the symptoms of oxidation to appear in a bottled wine.

The progress of oxidation can be followed by measuring the changes in concentration of SO_2. This can be seen in the results of DeRosa & Moret, (1978), Leske *et al.* (1998) and Godden *et al.* (2001). These show that the initial decline in SO_2 is greater and

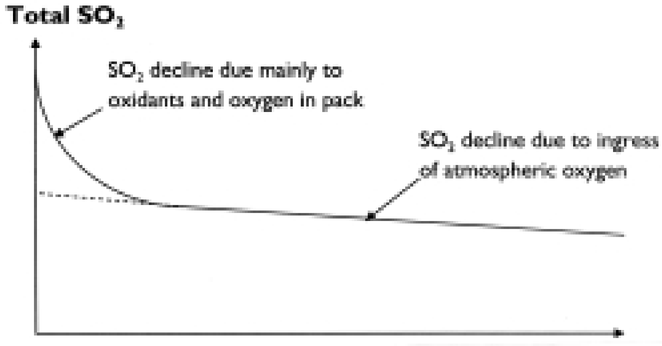

Fig. 2. Schematic diagram of SO_2 decline in packaged wine.

Table 1. Results from a survey of 13,780 retail wines by UK Wine & Spirit Association.

- Mean detection threshold of assessors 1.5ng/L
- Verified level of mustiness 0.7%.
  - For various reasons, true level may have been 0.7-1.2%
- Significantly higher in still white wines.
- Significant differences between tasters and verifiers, particularly at low intensity
  - Verification rate was higher in white wines than in red wines.
- Reported occurrence of oxidation, (0.9%) was higher than the verified mustiness, and was higher in white wines.
- Reported oxidation with synthetic closures was similar (1.1%) to cork closures.
- Reported levels of other wine defects, 0.6%.

faster than any subsequent decline in SO_2. Some of the data of DeRosa and Moret show the effect oxygen exclusion on the initial decline in SO_2. They are tabulated below:

Treatment	SO_2 decline 12 months after bottling
Plain bottling and corking	28 mg/L
" " & vacuum corking	16
N_2 flush of MT bottles & vacuum corking	5

When cause and effect are separated by more than six months or so, the link is not always perceived. Thus, the onset of symptoms of oxidation six or twelve months after bottling is not necessarily attributable to the closure, and more often than not, it is caused mainly by the presence of oxidants and oxygen at the time of bottling. When the amounts of oxidising substances are variable, and the wine has only a marginally adequate concentration of SO_2, a certain proportion of the bottled wines become 'oxidised'. It is misleading to say that post-bottling oxidation is "random", because its causes and the reasons for its sporadic occurrence are known, although perhaps not widely known. The persistent invocation of this pseudo-phenomenon is because of the delay between the cause and the onset of oxidation, and because of an instinctive but mistaken belief that the only variable operating factor in bottled wine is a difference between the individual corks. Just like the misconception about so-called 'leakage', the major variable factor in post-bottling oxidation has nothing to do with the cork. It is the presence of oxidants and oxygen incorporated in the bottle at sealing which is responsible for almost all the subsequent oxidation.

Under certain circumstances, the amount of SO_2 that a wine can oxidise far exceeds that expected from the solubility of oxygen in wine. Air contact, or repeated air contact, in the days before filling, will cause the accumulation of oxidants in the wine, and turbulent filling emulsifies air in the wine even though the wine may already be saturated. These are unusual occurrences in the majority of wine companies, but they can and do occur, especially when there is no awareness of the mechanisms involved.

Factors that predispose a wine to post-bottling oxidation:

- The presence of exogenous 'auto-oxidisable' substances, such as ascorbic acid, ellagi-tannins from oak and polyvalent metallic ions.

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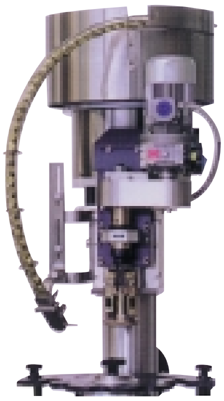

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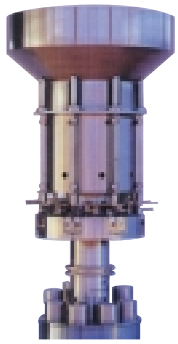

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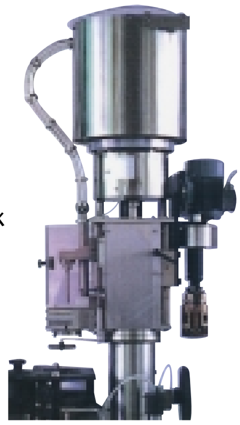

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- Scheduled or unscheduled stoppages of the filler.
- Inadequate or inconsistent application of vacuum or gas flushing at the corking machine.
- Running the corking machine at slow speed.

Some wine companies do not experience post-bottling oxidation, and it seems that they have been reticent about their achievements. There has been some needless speculation that the presence of 'residual oxidants' [sic] in the cork, or that oxygen permeability of the cork, might be responsible for post-bottling oxidation. However, there has been no direct evidence of any significant effects by these processes, and post-bottling oxidation is readily accounted for by the oxidants and oxygen in the sealed product. Post-bottling oxidation appears to be more prevalent with synthetic stoppers.

Cork and 2,4,6, Trichloroanisole (TCA)

Chloroanisole taints have been a problem for the food, beverage and packaging industries for the last several decades, and their identification in the 1970s was a major analytical achievement. It is generally accepted that chloro-anisoles derive from the profligate use of chlorinating compounds, chlorophenols and possibly other chlorine compounds in industry and rural areas as bleaching agents, preservatives and biocides in a whole range of items such as, paper products, adhesives, timber, power poles, end-posts in vineyards, cooling towers. The first identification of TCA in a 'corky' wine was in 1981. The announcement was greeted with some scepticism by a number of researchers investigating the problem of 'corkiness' in wine. This was because of their very strong conviction that the problem was a direct result of microbial activity on or in the individual stoppers, and because of the then difficulty of detecting TCA at concentrations less than several hundred nanograms per litre. It was to take more than a decade for complete acceptance of the view that the presence of chloro-anisoles was the major cause of 'musty/mouldy' odours in wine, and that because of its affinity for cork and its extraordinarily low sensory threshold, TCA was the dominant, if not the only ingredient of 'cork taint'.

TCA has a moderate affinity for cork, and it can not only be acquired by corks from their surroundings, but can be displaced

Tasters	Thresholds			
	Detection		Recognition	
	Paired	Single	Paired	Single
Elite The winemaker Professional tasters	1 -2 ng/L			
Discerning A range of abilities and experience.				
Ordinary A range of abilities and experience.				50 -100 ng/L

Fig. 3. There are different types of thresholds and a wide range of abilities to detect low levels of 'foreign' odours in a wine.

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from the cork by the entry of liquid vapour. Like a worm in an apple, its presence in the cork is not detectable by cursory examination. When the cork is compressed in the neck of a bottle, and liquid vapour penetrates into the cork, some but not all of the TCA migrates into the wine. Detection of TCA in cork requires a formal test which can displace and detect any significant amounts of TCA. Quantifying the magnitude of the TCA problem is made extremely difficult by the time and cost of analytical detection, the enormous numbers of corks, and the lack of solid data on the incidence and circumstances of taints in bottled wine.

The presence of a TCA *taint* in wine may be detected in one of two ways. As a recognisable musty/mouldy character at levels above the 'recognition threshold' of the taster, or at lower levels as a 'flavour modification', where the character of the wine is altered in some way without there being any distinct mustiness or recognisable taint as such. Although the latter seems to be of greater concern to winemakers, evidence of the effect is necessarily subjective and tenuous, like 'figures in the mist', and the affected wines are disappointing rather than objectionable. Taints at very low levels of TCA are usually detected only by experienced, sensitive tasters in a sequestered environment with a pristine sample for comparison. Thus, concerns need not extend to a possible commercial impact, because the presence of TCA at levels below the *detection* threshold of ordinary consumers cannot have any effect on their enjoyment of the wine. That is, if the consumer is unable to detect any difference between the wine and a pristine sample, his/her enjoyment of the wine is not affected.

'Sensory threshold' can be a slippery concept. There is no universal, absolute threshold, because the measurement of a sensory threshold is a subjective assessment of the individual taster's response to a given stimulus. In addition, the magnitude of different types of sensory threshold depends on the circumstances and the sensitivity of the taster (Figure 3). Unfortunately, reports of 'tainted wines' usually make no distinction between types of thresholds. A taint that rated as "barely detectable" by an expert panel under ideal tasting conditions may later be reported as being musty, mouldy, unpleasant or even disgusting, despite the fact that it would be undetectable to the vast majority of consumers. Wines containing very low levels of TCA are disappointing rather than objectionable, and even this disappointment is limited to those consumers with a low detection threshold.

Reliable information on the occurrence of TCA taints is a crucial element in identifying and locating the sources of contamination. Just as there can be no consensus on low level taints, there is considerable disagreement about the incidence of TCA taints in bottled wine. This is due in part to the sporadic nature of its occurrence, and to the greater probability of 'random clustering' in smaller samples. The idea of there being a single overall rate of occurrence is not valid, in much the same way that average rainfall figures are only applicable to limited areas. In addition, the perception of a taint in a wine depends on the wine type, the taster and the circumstances in which the wine is tasted. The most comprehensive survey of TCA taints in bottled wine was carried out in the UK for the Wine and Spirit Association (Table 1). Despite some disagreement about the precise validity of the results, it is clear that the sensory and commercial impacts of taint in these retail wines were much lower than many of the estimates which are widely publicised.

Sophisticated analytical techniques have made it possible for TCA to be recognised as a 'tangible' problem, and over the last decade or so, it has been possible to take certain measures to reduce or restrict both the incidence and intensity. Considerable resources have been put into identifying, locating, restricting and removing chloroanisole taints from cork, and to automating analytical procedures. There is a strong economic incentive to maintain and expand these efforts. Like the pursuit of any problem to vanishing point, success makes the task more difficult and paradoxically, it tends to increase rather than reduce customer concerns.

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