

## Impact of Storage Position on Oxygen Ingress through Different Closures into Wine Bottles

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Wine bottle aging is extremely dependent on the oxygen barrier properties of closures. Kinetics of oxygen ingress through different closures into bottles was measured by a nondestructive colorimetric method from 0.25 to 2.5 mL of oxygen. After 12, 24, and 36 months of storage, only the control (glass bottle ampule) was airtight. Other closures displayed different oxygen ingress rates, which were clearly influenced by the closure type and were independent of bottle storage position (upright, laid down) for most of the closures tested, at least during the first 24 months of the experiment under controlled conditions. The oxygen ingress rates into bottles were lowest in screw caps and "technical" corks, intermediate in conventional natural cork stoppers, and highest in the synthetic closures.

**KEYWORDS:** Indigo carmine; oxygen ingress; cork stoppers; synthetic closures; screw caps; storage position

### INTRODUCTION

It has recently been reported that closures are one of the most important factors that influence wine development (1). Other factors are filling height, concentration of free sulfur dioxide at bottling, gas composition in the headspace, bottling line conditions, temperature, and humidity of storage and composition of the wine. Oxygen is an essential component for determining the aging potential of wine, and the oxygen ingress into the bottle is extremely dependent on the sealing effectiveness of the closure.

Pasteur in 1873 stated that "l'oxygène est le pire ennemi du vin" (oxygen is the greatest enemy of wine) but also "c'est l'oxygène qui fait le vin, c'est par son influence qu'il vieillit" (oxygen makes the wine, which ages under its influence) (2). Nowadays, it is recognized that wine quality is generally impaired by excessive oxygen exposure, but slow and continuous oxygenation may be beneficial for wine aging (3–6).

Jean Ribéreau-Gayon, in studies conducted in the 1930s, was the first to show the oxygen ingress through natural cork closures during horizontal bottle storage: 0.10–0.38 mL of oxygen over the first 3 weeks and between 0 and 0.07 mL in the 4 months thereafter (7). When bottles were stored in a vertical position, the oxygen permeation rates were more variable. From these results, the author concluded that oxygen entering into the bottle was not enough to influence wine development. However, since Ribéreau-Gayon, technological developments in bottling processes, bottles, corker machines, and sealing systems have progressed significantly. There are, however, few published studies about the influence of closure type and bottle storage

position on oxygen ingress during aging to confirm the Ribéreau-Gayon data.

Several methods have been developed to measure the oxygen ingress rates through closures (9–13). The Mocon method, based on the measurement of oxygen transmission rates through dry packages using a coulometric sensor, is widely used (1, 13). Recent studies based in this methodology have shown that different closures differ in their ability to act as barriers to oxygen ingress. Generally, synthetic closures exhibited high permeability, while screw caps let in relatively little oxygen. Furthermore, natural cork stoppers presented intermediate performance. However, the Mocon method only measures oxygen permeation in dry packaging, which actually does not happen during wine aging, where closures are in contact with wine (14). Furthermore, this methodology does not allow the kinetic study of oxygen ingress through closures over time. Recently, a nondestructive colorimetric method that allows a single bottle to be analyzed without compromising the closure seal was developed (8). This method measures the oxygen ingress through different closures under similar conditions of wine bottle aging.

There have been several studies of the influence of closure type on wine development after bottling (15–23). Some of these studies have shown that wine sealed with synthetic closures exhibited a high level of browning and undesirably high oxidized aroma scores in comparison with other closures (17–20, 22). On the other hand, undesirable struck flint/rubber (reduced) aroma characters were detected in wines sealed under screw caps or in glass ampoules (13, 17, 20, 22). Conversely, wine sealed under natural cork stoppers shows negligible reduced characters (22).

Storage position is one of the variables that might influence oxygen ingress rates into bottles and, consequently, wine

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**Table 1.** Mean Dimensions, Density, and Coefficient of Porosity of the Different Cylindrical Closures Prior to Bottling

	closures	length (mm)	diameter (mm)	density (g/cm <sup>3</sup> )	coefficient of porosity (%)
natural cork	"Flor" grade	44.7 (0.3) <sup>a</sup>	24.0 (0.2)	0.16 (0.01)	2.8 (0.7)
	1st grade	44.8 (0.4)	24.1 (0.1)	0.19 (0.01)	8.2 (2.1)
technical cork	Neutrocork	43.6 (0.1)	23.7 (0.0)	0.29 (0.01)	
	Twin Top	44.3 (0.1)	23.4 (0.0)	0.29 (0.01)	
synthetic	Supremecorq	44.6 (0.1)	21.4 (0.1)	0.54 (0.01)	
	Nomacorc	42.8 (0.1)	21.9 (0.1)	0.38 (0.00)	

<sup>a</sup> Parentheses indicate standard deviations.

development. Mas et al. reported that wine sealed under natural cork stoppers was better conserved when the bottles were stored horizontally rather than vertically (18). In contrast, Skouroumounis et al. have shown that bottle orientation during storage had little effect on the composition and sensory properties of white wines (22).

As part of ongoing studies on the oxygen barrier properties of different closures available on the market, the authors have previously reported a nondestructive colorimetric method to measure in situ oxygen ingress into bottles (8). The oxygen ingress was inferred by measurements of the changing color of indigo carmine directly scanned through commercial bottles. The aim of this study was to investigate the impact of different cylindrical closures on oxygen ingress into wine bottles during horizontal and vertical storage. The influence of screw cap closures was also assessed.

## MATERIALS AND METHODS

**Chemicals.** Deionized water was purified with a Milli-Q water system (Millipore, Bedford, MA) prior to use. Indigo carmine was purchased from Acros (Noisy-le-Grand, France). Sodium dithionite and sodium benzoate were obtained from Prolabo (Fontenay S/Bois, France).

**Closures.** Ten different closures were tested as follows: two natural cork stoppers, the best grade ("flor") and the intermediate grade (first); two "technical cork" stoppers (Twin Top and Neutrocork); two synthetic closures, Nomacorc classic and Supremecorq 45; and four different screw cap closures.

All natural and technical cork stoppers were supplied by Amorim & Irmãos, S.A. (Santa Maria de Lamas, Portugal). Nomacorc closure produced by an extrusion process and a Supremecorq closure produced by a molding process were supplied by Supremecorq, Inc. (Kent, WA) and Nomacorc S.A. (Thimister-Clermont, Belgium), respectively.

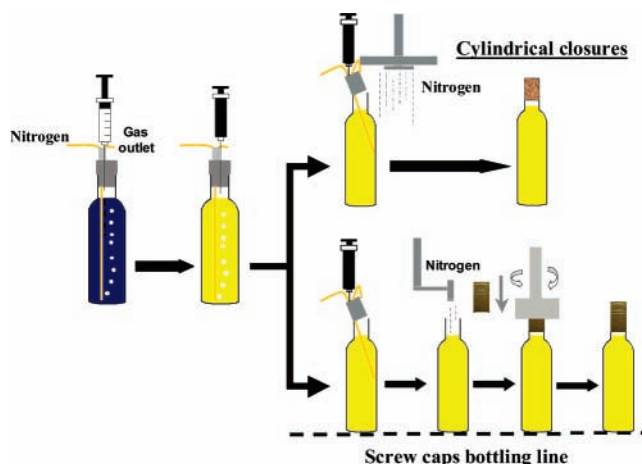
The Stelvin screw caps were supplied by Pechiney Capsules (Chalon sur Saône, France), and the other three screw cap closures (Auscap, Cospak, and CSA) were taken from a range representing commercial stocks supplied by their manufacturers. All screw cap liners were saran tin foil.

The cork stoppers and Supremecorq closures were silicone coated. The Nomacorc closures were covered with a nondescribed coating. Closures were analyzed prior to bottling for dimensions and porosity coefficient by surface analysis (Table 1).

The moisture content of the natural and technical corks ranged from 4 to 7%. The corks were hydrogen peroxide bleached; however, no peroxide residue was detected.

**Bottles.** "Extra-white" (colorless) "bordelaise" classic bottles (375 mL) were used for cylindrical closures. The bottleneck dimensions complied with the CETIE specifications. For screw cap closures, "extra-white" bottles (375 mL) with a screw thread were used. All bottles were supplied by Saint-Gobain Glass Packaging (Cognac, France).

The white glass bottles (375 mL) used for the control were supplied by Gantenbrink Corp. (Limburg, Germany). The bottle used for calibration was purchased from Atelier Jean Prémon (Bordeaux, France) (8).



**Figure 1.** Diagram of the reduction of indigo carmine in commercial bottles and bottling procedures of cylindrical and screw caps closures.

**Calibration Procedure.** The procedure for reduction and oxidation of indigo carmine solution in the calibration bottle is fully described in Lopes et al. (8). Briefly, a sodium dithionite solution (2.25 g/L) was used to reduce the indigo carmine solution (250 mg/L), which led to a color change from blue indigo to yellow.

Controlled amounts of oxygen were injected 20 different times into reduced indigo carmine bottled solution, which led to the original indigo blue color of the carmine. Color changes were measured with a colorimeter apparatus (see below). Each one of the 21 points of the calibration curve was obtained by calculating the mean of five replicates.

For each bottling trial, a new calibration curve was performed. The amounts of sodium dithionite used to reduce the 350 mL solution of indigo carmine (250 mg/L) in each trial were 2.25, 3.0, and 3.9 g/L, respectively.

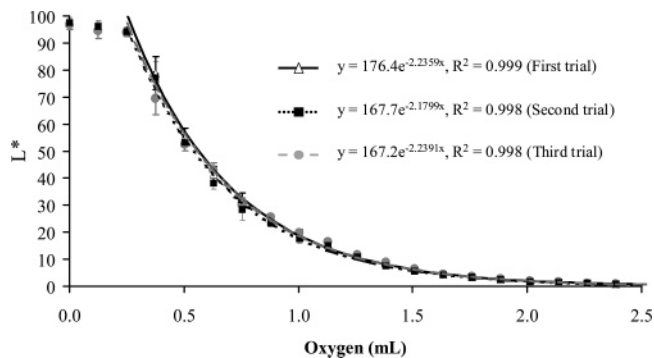
**Bottling and Storage.** For the bottling trials, 375 mL sterilized commercial bottles were used. These bottles were filled with indigo carmine solution that was reduced as described in Figure 1.

For the cylindrical closures, the bottled indigo carmine reduced solutions were placed in the corking machine (single-headed corker, La Girondine, Bordeaux; France) under a continuous flush of nitrogen (0.5 bar) (Figure 1). The cylindrical closures were compressed to a diameter of 15.8 mm before insertion. The final filling level for each bottle was  $65 \pm 3$  mm from the top of the bottle. The headspace pressure after cork insertion varied from 0 to 10 kPa. The temperature of the indigo carmine solution ranged from 18.1 to 22.4 °C during the first trial and from 20.5 to 21.1 °C during the second trial.

For the screw cap closures, the bottled indigo carmine-reduced solutions were placed in a Eagle Closys Arol (Italy) single head screw capper, with a flush of nitrogen (0.2 bar) immediately prior to the application of the screw caps (Figure 1). The final filling level for each bottle was  $45 \pm 2$  mm from the top of the bottle. The internal pressure in the headspace after screw cap insertion was close to zero. The temperature of the indigo carmine solution ranged from 17.3 to 19.7 °C during the bottling procedure. The control bottles were prepared using the same procedure describe previously, except that they were sealed with a glass stopper by flame welding at 1200 °C (Gantenbrink Corp.).

In the first trial, four replicates of six closure types and bottle control containing reduced indigo carmine solutions were sealed. All bottles were left upright for 24 h after bottling and then stored horizontally over 36 months. In the second trial, another 32 bottles were sealed using the same closure types and the bottle control. All bottles were stored vertically over 24 months. Finally, in the third trial, four bottles of each screw cap type were sealed and then stored horizontally over 12 months. All 80 bottles were stored under a constant temperature of  $20 \pm 1$  °C and a constant relative humidity of  $65 \pm 1$  % over this period.

**Bottle Colorimetric Measurements.** The CIELAB measurements of the parameters  $L^*$ ,  $a^*$ ,  $b^*$  were performed by directly scanning bottled solutions with a Minolta series CM-508i spectrophotometer equipped with a transmittance accessory CM-A76 (Osaka, Japan). These



**Figure 2.** Calibration curves for each bottling trial relating  $L^*$  parameters and amounts of oxygen injected. Error bars represent the standard deviation of five replicates.

measurements were obtained using illuminant D65 and a  $10^\circ$  observer according to the CIELAB76 (24).

A clean Pyrex bottle filled with water was used to carry out auto-zero calibration (blank). All bottles were cleaned with ethanol and dried before CIELAB measurements. These measurements were carried out in the upright position at 5 cm from the base of the bottle. Four body measurements were collected by rotating each bottle  $90^\circ$  on its vertical axis. All positions were marked on the bottleneck to allow consistent measurement over time. All measurements were made in the dark at room temperature ( $22 \pm 2^\circ\text{C}$ ).

**Data Analysis.** Microsoft Excel 2000 software was used for data analysis. Analysis of variance, Tukey's procedure, Fisher's least significant difference, and correlation and regression analyses were carried out with STATISTICA 6 (StatSoft Inc., Tulsa, OK).

## RESULTS AND DISCUSSION

**Calibration Curves.** According to our calibration procedure, an aqueous solution of reduced indigo carmine was oxidized by injecting 20 controlled oxygen volumes. Each oxygen injection led to a color change, which was submitted to CIELAB measurements. Thus, an exponential relationship between the oxygen content of the bottle and the  $L^*$  values between 0.25 and 2.5 mL (Figure 2) was established. A calibration curve was performed for each bottling trial. The curves were made in an identical way, only differing in the amount of sodium dithionite needed for the reduction of indigo carmine. The analytical data obtained revealed that the  $L^*$  measurements showed identical patterns in each curve. There was no statistically significant effect of the concentration of sodium dithionite on  $L^*$  values ( $p = 0.05$ ). The oxygen ingress into the bottle during each trial was calculated according to the following equations:

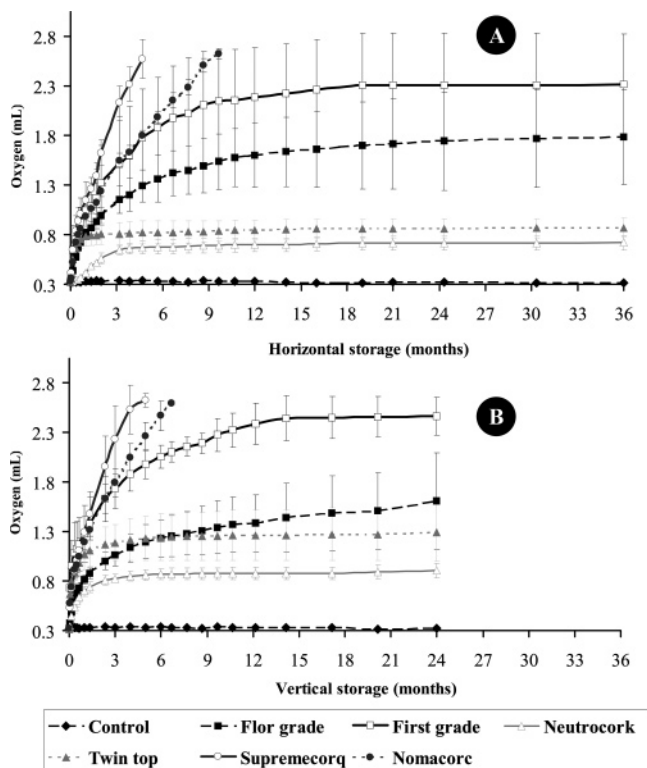
$$\text{first trial } O_2 = \ln(L^*/176.4)/-2.2359$$

$$\text{second trial } O_2 = \ln(L^*/167.7)/-2.1799$$

$$\text{third trial } O_2 = \ln(L^*/167.2)/-2.2391$$

**Oxygen Ingress through Different Cylindrical Closures during Horizontal Storage.** The analytical data obtained for the oxygen ingress during 36 months of horizontal storage showed significant differences between all sealing systems ( $p = 0.05$ ). The control bottle showed no oxygen ingress over this period. This indicated that the control bottle was essentially airtight, while the other closures allowed oxygen ingress into bottles (Figure 3A).

Technical cork stoppers (Twin Top and Neutrocork) allowed ingress of 0.7–0.8 mL of oxygen over this period. Furthermore, 55–90% of this oxygen intake took place over the first month

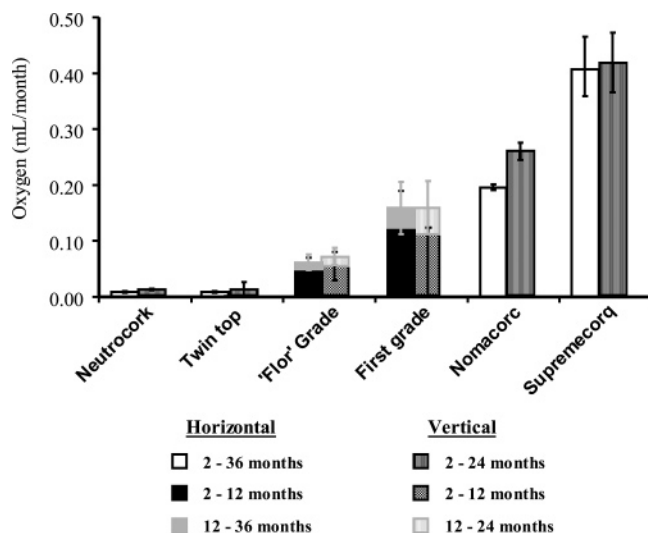


**Figure 3.** Kinetics of oxygen ingress through different closures into commercial bottles stored horizontally over 36 months (A) and vertically over 24 months (B). Error bars represent the standard deviation of four replicates.

of storage. These closures formed a statistically homogeneous group, which exhibited consistent low rates of oxygen ingress, with a range from 0.002 to 0.0011 mL of oxygen per month (2–36 months). These findings confirm those of the previous study, where we have shown the same oxygen ingress patterns over 12 months of storage.

The synthetic closures, Nomacorc and Supremecorq, had high oxygen permeation, reaching 2.5 mL of oxygen (limit of quantification for our method) within 140 and 290 days. Respectively, 35 and 45% of this oxygen ingress was observed during the first month. After this period, Nomacorc and Supremecorq allowed ingress of 0.2 and 0.4 mL oxygen per month, respectively. These data agree with previous studies, reporting that synthetic closures produced by a molding process had high permeability, when compared with those produced by coextrusion (25).

The natural cork stoppers displayed mean oxygen ingresses of 1.7 and 2.3 mL for flor and first grade, respectively, over 36 months of horizontal storage. As presented in Figure 3A, natural cork stoppers flor display less oxygen ingress than first grade; however, there were no significant differences between the two visual grades ( $p = 0.05$ ). This could be explained by the variability among the four replicates of each natural cork type (15, 21). The kinetics of oxygen ingress differed from the other closures (technical and synthetic). The ingress of oxygen was greater in the first month of storage, ranging from 0.7 to 1.3 mL of oxygen, which represented 28–53% of the overall ingress of oxygen during the 36 months of storage. Between the second and the 12th month, the amount of oxygen that entered into the bottle varied from 0.03 to 0.17 mL of oxygen per month. Finally, after the first 12 months in bottle, oxygen ingress per month ranged from 0.002 to 0.07 mL, until the completion of the study at 36 months.



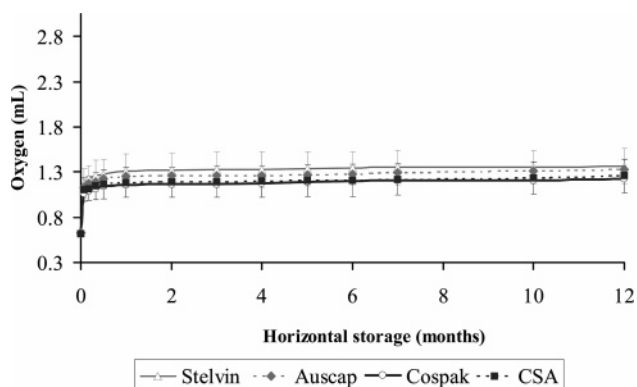
**Figure 4.** Mean rate of oxygen ingress through different closures into commercial bottles between 2 and 36 months (horizontal storage) and between 2 and 24 months (vertical storage). For the natural cork stoppers, the mean rate of oxygen ingress is divided in two periods: 2–12 months and 12–36 and 12–24 months (horizontal and vertical storage, respectively). Error bars represent the standard deviation of four replicates.

**Oxygen Ingress through Different Cylindrical Closures during Vertical Storage.** After 24 months of vertical storage, only the control was airtight, whereas other closures exhibited oxygen permeation (**Figure 3B**).

Technical cork stoppers (Neutrocork and Twin Top) allowed ingress of 0.8–1.2 mL of oxygen over this period. In the first month, Neutrocork and Twin Top allowed ingress of 0.6 and 1 mL of oxygen, respectively. Moreover, the oxygen ingress during the first month of vertical storage was statistically higher than those observed in the same period in horizontal storage. After the first month, similar oxygen ingress rates were found for these closures, respectively, 0.010 and 0.011 mL of oxygen per month with no significant differences between closures and closures vs storage position (**Figure 4**).

The synthetic closures, Supremecorc and Nomacorc, exhibited high levels of oxygen permeation and reached 2.5 mL of oxygen within 150 and 200 days of vertical storage. The oxygen ingress rate through Supremecorc was similar in horizontal and vertical storage while the analytical data for the Nomacorc indicated that the oxygen ingress was slightly (statistically significant,  $p = 0.01$ ) higher in vertical storage (**Figure 4**).

The natural cork stoppers allowed a mean ingress of 1.5 and 2.4 mL of oxygen, for flor and first grade, respectively, over 24 months of vertical storage. The mean ingress of oxygen for the two cork stoppers was significantly different ( $p = 0.05$ ). The flor natural corks exhibited lower oxygen ingress than the first grade corks during the first month of storage (0.8 and 1.3 mL of oxygen). It is possible that the first grade natural corks (higher coefficient of porosity; see **Table 1**) contained more air within their structure, which diffuses out of the cork into the bottle during the first month. After this period, no significant differences were found between both natural cork stoppers tested. The mean ingress of oxygen from 2 to 12 months was 0.05 and 0.10 mL for flor and first grade, respectively, and 0.02 and 0.04 mL between 12 and 24 months. The ingress of oxygen through the different natural corks was little affected by storage position; there were no significant differences between horizontal and vertical bottle storage (**Figure 4**). Ribéreau-Gayon has already reported that oxygen ingress through natural corks



**Figure 5.** Kinetics of oxygen ingress through each screw cap closure into commercial bottles stored horizontally over 12 months. Error bars represent the standard deviation of four replicates.

during vertical and horizontal bottle storage was not significantly different although more variable in the vertical position (6).

The oxygen ingress kinetics through natural cork stoppers differ from those obtained with others closures (technical corks and synthetic closures). The oxygen ingress through natural corks occurs in three phases: the first during the first month where high oxygen diffusion was observed; a second period (between 2 and 12 month of storage) of decrease of oxygen ingress into bottles. After 12 months, cork closures exhibited relatively low and stable oxygen ingress until the completion of the study at 24 and 36 months of vertical and horizontal storage, respectively. On other hand, the oxygen ingress through technical corks and synthetic closures was high during the first month. After this period, the ingress of oxygen was consistently low in technical corks and high in synthetic closures.

**Oxygen Ingress through Screw Cap Closures during Horizontal Storage.** Screw cap closures allowed ingress of a mean of 1.1 mL of oxygen over 12 months of storage, with a range from 0.9 to 1.3 mL (**Figure 5**). The kinetics of oxygen permeation differed from the cylindrical closures. The apparent ingress of oxygen into bottles was substantially higher over the first 2 days of storage (85–90% of overall ingress of oxygen) than in the following months. However, there was oxygen ingress into bottles prior to the application of the screw cap closures. During the bottling procedure, bottles were exposed for a few moments to atmospheric oxygen before screw cap application, which does not happen with the cylindrical closures that were sealed individually under a continuous nitrogen flush (see **Figure 1**). To determine the amounts of oxygen due to the air exposure and those within the screw caps, 15 bottles containing reduced indigo carmine solutions were sealed with silicone closures under similar operating conditions used in screw caps bottling. We estimate that 0.7 mL of oxygen was linked to the air exposure (data not shown) and the other 0.4 mL was certainly related to some oxygen within the screw cap. After the second day of storage, the screw caps allowed ingress of 0.01–0.02 mL of oxygen per month. There were no significant differences in the oxygen permeation between the different screw cap closures tested ( $p = 0.05$ ).

**Rates of Oxygen Ingress through Different Sealing Systems.** The research reported in this paper was done in order to investigate the influence of closure type and bottle orientation on the ingress of oxygen during the postbottling period. **Table 2** shows the full ranges of oxygen ingress rates and compares values obtained with literature. The control bottles exhibited constant oxygen ingress rates of 0.02  $\mu\text{L}$  per day. These indicate that our method was not accurate enough to measure oxygen ingress rates lower than that value.

**Table 2.** Full Range Oxygen Ingress Rates ( $\mu\text{L}/\text{Day}$ ) of Screw Caps, "Technical" and Natural Cork Stoppers, and Synthetic Closures As Compared to Those Obtained from Other Studies

closures	our study		Mocon method	
	first period <sup>a</sup>	horizontal <sup>b</sup>	vertical <sup>b</sup>	ref 1 ref 13
control		0.02	0.02	
screw caps	<250	0.2–0.7		0.2–0.8 <1
technical cork	15–40	0.1–0.4	0.1–0.9	0.7–1.3
natural cork	25–45	1.7–6.1 <sup>c</sup> 0.1–2.3 <sup>d</sup>	0.5–4.4 <sup>c</sup> 0.1–2.7 <sup>d</sup>	0.1–122.7
Nomacorq	30–40	6.2–6.5	7.8–9.0	
Supremecorq	35–45	11.4–14.7	11.4–12.2	~10

<sup>a</sup> Data from both vertical and horizontal storage: 2 days (screw cap closures) and 1 month (cylindrical closures). <sup>b</sup> Between 2 and 36 months and from 2 to 24 months in horizontal and vertical storage, respectively. <sup>c</sup> Between 2 and 12 months of storage. <sup>d</sup> Between 12 and 36 months and from 12 to 24 months in horizontal and vertical storage, respectively.

It is clear from **Table 2** that oxygen ingress rates are low in screw cap closures and technical cork stoppers, intermediate in natural cork stoppers, and high in synthetic closures. The storage position had little effect on the oxygen ingress rates for most of the sealing systems tested, with the exception of Nomacorq closures, which are more permeable during vertical bottle storage.

It is likely that the different abilities of closures to act as a barrier to oxygen ingress are linked to wine development during bottle aging (15, 25). Given their high oxygen permeation rates, the use of synthetic closures results in wines with high levels of browning and undesirably high oxidized aroma scores (18–20, 22).

Recent studies, using the Mocon method, found that screw caps allowed ingress of 0.2–0.8  $\mu\text{L}$  of oxygen per day. A particular technical cork closure exhibited a slightly high oxygen ingress rate, ranging from 0.7 to 1.3  $\mu\text{L}$  of oxygen per day (1). Hart and Kleinig reported oxygen ingress rates through screw caps of less than 1  $\mu\text{L}$  of oxygen per day (13). In our study, we found that screw caps and technical corks allowed ingress of 0.2–0.7 and 0.1–0.9  $\mu\text{L}$  of oxygen per day, respectively, which is in agreement with those obtained by previous authors. The overall amount of oxygen was slightly higher in technical corks due to the oxygen ingress during the first month (15–40  $\mu\text{L}$  per day) as compared to <250  $\mu\text{L}$  per day (over 2 days) in the screw caps. These findings may partially explain those reported by Godden et al., who showed that the loss of  $\text{SO}_2$  in white wine was lower with screw caps and slightly more evident for technical cork closures (17). Brajkovich et al. have shown that the loss of  $\text{SO}_2$  over the first 3 months was always higher under cork than under screw caps with different fill heights (23). The low oxygen ingress through the screw caps resulted in wines with lower scores of oxidation but with the highest scores for undesirable struck flint/rubber aroma attribute (reduced) (18, 22).

With regard to natural cork stoppers, the oxygen ingress rates reported by other studies are controversial. Hart and Kleinig reported oxygen ingress rates through natural corks stoppers ranging from less than 1 to more than 1000  $\mu\text{L}$  of oxygen per day. On the other hand, Godden et al. reported for the same cork type oxygen ingresses of 0.1–122.7  $\mu\text{L}$  of per day (1). The Mocon method was developed to measure oxygen permeability in dry packages (14). In our study, we found that natural cork stoppers allowed ingress of 0.5–4.4  $\mu\text{L}$  of oxygen per day between the second and the 12th month and 0.1–2.7  $\mu\text{L}$  of

oxygen per day between the 12th and the 24th month, respectively, in vertical storage. In horizontal storage, oxygen ingress rates varied from 1.7 to 6.1  $\mu\text{L}$  (2–12 months) and from 0.1 to 2.3  $\mu\text{L}$  (12–36 month) of oxygen per day. The full range of natural cork closures (irrespective of the grade and storage position) varied in oxygen ingress by a factor of 3.5–8.8 between 2 and 12 months and 23–27 in the following months. The variability observed in our data is substantially lower than the 1000-fold or more reported by others studies (1, 13). Our kinetics profiles and analytical data are similar to those obtained by Squarzone et al., who indicated that after an initial phase of high permeation, the oxygen ingress rates through natural corks varied from 2 to 8  $\mu\text{L}$  of oxygen per day (12). The intermediary oxygen barrier properties of the natural cork stoppers, generally, resulted in "balanced" wines with lower scores of oxidation and reduction (22).

Storage position had little effect on the ingress of oxygen into bottles for most of the closures tested, at least during the first 24 months of the experiment under the conditions of this study. These findings agree with those recently reported recently by Skouroumounis et al. who showed that the bottle orientation during 5 years storage under controlled conditions had little effect on the composition and sensory properties of white wines (22). However, they are in contrast to Mas et al., who reported that wine was better preserved when the bottles were kept horizontally (18).

In conclusion, this study confirms that the closure type used to seal bottled wine is an essential factor in wine development during aging. Wine receives oxygen through closures available on the wine market, with differing oxygen barrier properties. The oxygen ingress into the bottles was consistently lowest for screw caps and technical corks, intermediate in conventional natural cork stoppers, and highest in synthetic closures. The bottle orientation during storage had little impact on oxygen ingress for most of the closures tested.

Mechanisms of oxygen ingress into bottles remain unknown, and further research will be necessary to fully elucidate these phenomena, which can occur by diffusion, permeation, or both. Moreover, further research will be necessary to understand the impact of these sealing systems on chemical and sensorial properties of red and white wines during bottle aging.

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## LITERATURE CITED

- Godden, P.; Lattey, K.; Francis, L.; Gishen, M.; Cowey, G.; Holdstock, M.; Robinson, E.; Waters, E.; Skouroumounis, G.; Sefton, M.; Capone, D.; Kwiatkowski, M.; Field, J.; Coulter, A.; D'Costa, N.; Bramley, B. Towards offering wine to the consumer in optimal condition—The wine, the closures and other packaging variables. A review of AWRI research examining the changes that occur in wine after bottling. *Wine Ind. J.* **2005**, *20* (4), 20–30.
- Pasteur, L. *Etudes Sur le Vin: Ses Maladies, Causes Qui les Provoquent, Procédés Nouveaux Pour les Conserver et Pour les Vieillir*; Imprimerie Royale: Paris, France, 1873; 264 pp.
- Singleton, V. L.; Trousdale, E.; Zaya, J. Oxidation of wines. I. Young white wines periodically exposed to air. *Am. J. Enol. Vitic.* **1979**, *30*, 49–53.

- (4) Ribéreau-Gayon, P.; Pontallier, P.; Glories, Y. Some interpretations of color changes in young red wines during their conservation. *J. Sci. Food Agric.* **1983**, *34*, 505–516.
- (5) Castellari, M.; Matricardi, L.; Arfelli, G.; Galassi, S.; Amati, A. Level of single bioactive phenolic in red wine as a function of the oxygen supplied during storage. *Food Chem.* **2000**, *69*, 61–67.
- (6) Atanasova, V.; Fulcrand, H.; Cheynier, V.; Moutounet, M. Effect of oxygenation on polyphenol changes occurring in the course of wine-making. *Anal. Chim. Acta* **2002**, *21793*, 1–13.
- (7) Ribéreau-Gayon, J. Dissolution d'oxygène dans les vins. In *Contribution à l'étude des Oxydations et Réductions Dans les Vins. Application à l'étude de Vieillissement et des Casses*, 2nd ed.; Delmas: Bordeaux, France, 1933; 35 pp.
- (8) Lopes, P.; Saucier, C.; Glories, Y. Nondestructive colorimetric method to determine the oxygen diffusion rate through closures used in winemaking. *J. Agric. Food Chem.* **2005**, *53*, 6967–6973.
- (9) Cook, J. M.; Karelitz, R. L.; Dalsis, D. E. Measurement of oxygen, nitrogen and carbon dioxide in beverage headspace. *J. Chromatogr. Sci.* **1985**, *23*, 57–63.
- (10) Sanchez, J.; Aracil, J. M. Perméabilité gazeuse de différents obturateurs. *Bull. O.I.V.* **1998**, *805–806*, 280–283.
- (11) Vidal, J. C.; Toitot, C.; Boulet, J. C.; Moutounet, M. Comparaison of methods for measuring oxygen in the headspace of a bottle of wine. *J. Int. Sci. Vigne Vin.* **2004**, *38*, 191–200.
- (12) Squarizoni, M.; Limbo, S.; Piergiovanni, L. Proprietà barriera all'ossigeno di differenti tipologie di tappi per vino. *Ind. Bevande* **2004**, *XXXIII*, 113–116.
- (13) Hart, A.; Kleinig, A. The role of oxygen in the aging of bottled wine. *Wine Press Club New South Wales Inc.* **2005**, 1–14; www.winepressclub.com.au.
- (14) Gibson, R. Variability in permeability of corks and closures. American Society of Enology and Viticulture Science of Closures Seminar, Seattle, June 24, 2005; www.scorpex.net/ASEVclosures2005RGibson.pdf.
- (15) Waters, E. J.; Peng, Z.; Pocock, K. F.; Williams, P. J. The role of corks in oxidative spoilage of white wines. *Aust. J. Grape Wine Res.* **1996**, *2*, 191–197.
- (16) Caloghiris, M.; Waters, E. J.; Williams, P. J. An industrial trial provides further evidence for the role of corks in oxidative spoilage of bottled wines. *Aust. J. Grape Wine Res.* **1997**, *3*, 9–17.
- (17) Godden, P.; Francis, L.; Field, J.; Gishen, M.; Coulter, A.; Valente, P.; Hoj, P.; Robinson, E. Wine bottle closures: Physical characteristics and effect on composition and sensory properties of a Semillon wine. Performance up to 20 months post-bottling. *Aust. J. Grape Wine Res.* **2001**, *7*, 62–105.
- (18) Mas, A.; Puig, J.; Llado, N.; Zamora, F. Sealing and storage position effects on wine evolution. *J. Food Sci.* **2002**, *67*, 1374–1378.
- (19) Chatonnet, P.; Labadie, D. Caractéristiques physiques et comportement vis-à-vis de l'oxydation du vin de différents types de bouchons chevilles. *Rev. Oenologues* **2003**, *106*, 13–20.
- (20) Francis, L.; Field, J.; Gishen, M.; Coulter, A.; Valente, P.; Lattey, K.; Hoj, P.; Robinson, E.; Godden, P. The AWRI closure trial: sensory evaluation data 36 months after bottling. *Aust. N. Z. Grapegrower Winemaker* **2003**, *475*, 59–64.
- (21) Silva, A.; Lambri, M.; De Faveri, M. D. Evaluation of the performances of synthetic and cork stoppers up to 24 months post-bottling. *Eur. Food Res. Technol.* **2003**, *216*, 529–534.
- (22) Skouroumounis, G. K.; Kwiatkowski, M. J.; Francis, I. L.; Oakey, H.; Capone, D.; Duncan, B.; Sefton, M. A.; Waters, E. J. The impact of closure type and storage conditions on the composition, colour and flavour properties of a Riesling and a wooded Chardonnay wine during five years' storage. *Aust. J. Grape Wine Res.* **2005**, *11*, 369–384.
- (23) Brajkovich, M.; Tibbits, N.; Peron, G.; Lund, C. M.; Dykes, S. I.; Kilmartin, P. A.; Nicolau, L. Effect of screwcap and cork closures on SO<sub>2</sub> levels and aromas in a Sauvignon blanc wine. *J. Agric. Food Chem.* **2005**, *53*, 10006–10011.
- (24) McLaren, K. Food colorimetry. In *Developments in Food Colors*; Walford, J., Ed.; Applied Science Publishers Ltd.: Oxford, 1980; pp 27–45.
- (25) Jung, R.; Zürn, F. Nouveautés dans les bouchons en plastique. *Rev. Fr. Oenol.* **2000**, *183*, 29–32.

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