Impact of stoppers on the aging of wine in bottles

Part 1 of 3 – Characterization of oxygen transfer with cork stoppers

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Introduction

Even though the partnership of cork and wine dates back to Antiquity, the use of cork stoppers became widespread mainly in the 19th century, with the expansion of transport and storage of wines in glass bottles. During the last 30 years, stricter market requirements, coupled with the emergence of new closures (screw caps, synthetic stoppers and micro-agglomerated cork stoppers), have led the scientific community to examine the factors that affect the quality of traditional cork stoppers produced by punching from a cork plank. One of the main reasons was the premature oxidative aging of dry white wines from Bordeaux and Burgundy in the early 2000s when bottled with traditional cork stoppers. It was shown that the stopper had a significant effect on the appearance of this premature oxidative aging, even though this phenomenon is also, of course, related to the quality of the raw materials and to the care that the winemaker takes in making the wine *(Godden et al., 2001).*

Research has focused on measuring oxygen transfer (OTR: Oxygen Transfer Rate) through several types of stoppers, in order to more precisely assess their impact on the organoleptic properties of wines. During the 1990s, the development of new measurement methods, whether manometric *(Rabiot et al., 1999),* polarographic *(Vidal et al., 2004),* colorimetric *(Lopes et al., 2005),* coulometric *(Godden et al., 2001)* or *via* chemiluminescence *(Diéval et al., 2011),* helped to better quantify gas transfer through closures. Screw caps, synthetic closures and variable-porosity micro-agglomerated cork stoppers have been shown to be more homogenous than traditional cork stoppers *(Lopes et al., 2007; Oliveira et al., 2013).* The increasing number of methods used to evaluate OTR has, however, caused some confusion in evaluating the performance of closures. Depending on the chosen measurement method, it can be hazardous to try to compare the OTR values of closures. OTR is highly related to the measurement protocol used, and in particular to the pressure gradient between the two sides of the closure.

However, knowledge of the oxygen contribution of each type of closure can be of great help for enologists. It can be used to guide their closure choices, depending on the type of wine being made.

The objective of this study is to acquire a better understanding of oxygen contributions from microparticle cork stoppers with various formulations as well as from traditional cork stoppers (natural corks of the Flower, Extra and Super visual grades).

Materials and Methods

In this study, oxygen transfer measurements have been conducted via chemiluminescence. The equipment used is a Fibox 3 LCD Trace V6 from PreSens Precision Sensing GmbH. The system is composed of a transceiver, which emits a blue light flow. This flow is directed towards a sensor (also called a spot) glued on the inside of a transparent bottle. These sensor spots are composed of fluorescent compounds, which absorb the light energy sent by the transceiver, and then they reconstitute it as red light. The measurement is based on the fact that the reconstitution time for this light is inversely proportional to the oxygen concentration in the bottle. The result is expressed as partial pressure of oxygen inside the bottle (pO_2). This method has several advantages: it can be used to track the oxygen input kinetics from the corking step to the end of bottle aging; it is non-destructive; and lastly, the measurement is simple to perform and can be done under various conditions (temperature, humidity, oxygen pressure gradient) reproducing those found in a winery or cellar. This method is widely used in the wine industry and has already been the subject of numerous publications aimed at better control of oxygen contributions before and during bottling *(Ugliano et al., 2015).*

The study was conducted at 23 ± 2°C and atmospheric pressure (partial oxygen pressure = 200 hPa). We chose to work with empty bottles, so that we did not have to worry about the impact of wine. Owing to its composition, wine is a major consumer of oxygen (in particular, as a function of its polyphenol or SO_2 content). Complementary analyses on full bottles are also underway, in order to quantify the role of stopper moisture more precisely. Those results will be published at a later date. The closures studied here are stoppers from the Diam Bouchage company, with dimensions of 44 mm x 24.2 mm (length x diameter), pre-stabilized in a climate-controlled chamber for 48 hours at 20°C and 50% relative humidity. The bottles are transparent with a CETIE neck, whose profile was found to be compliant prior to use.

Before corking, the bottles are equipped with Pst6 sensor spots, enabling oxygen pressure measurements up to 41 hPa (= 41 mbar) with a limit of detection of 0.02 hPa. The bottles corked with natural cork stoppers were also equipped with Pst3 spots, enabling us to measure much higher quantities of oxygen (up to 500 hPa). All the bottles were blanketed with nitrogen prior to vacuum corking with a GAI corker, model 4040, which enabled us to reach residual oxygen contents of less than 0.1 mg/bottle (value subtracted hereafter from the results).

Results and Discussion

The partial pressure of oxygen (pO_2) was measured at regular intervals inside each bottle for periods of up to two years, and the resulting curve, $pO_2 = f(t)$, was plotted.

With the exception of a few specific cases found with natural cork stoppers (illustrated at the end of this section), all the curves have the same shape ***(Figure 1 A)***.

Firstly, we can observe a very quick increase in pO_2 during the first few days. Then the rate slows down until a stationary phase is reached after 12 months.

We can distinguish between two phases

The first phase, which occurs between zero and six months, corresponds to a dominant phenomenon of release of oxygen contained in the stopper. During corking, the diameter of the stopper goes from 24.2 to 18.5 mm, or a decrease in stopper volume of nearly 40%. Automatically, oxygen pressure in the cork pores or cells increases significantly. This generates a high pressure gradient between the inside of the stopper and the inside of the bottle. To re-establish balance between the pressures (equilibrium law, or Le Chatelier's principle), overpressurized oxygen is expulsed into the bottle, and the rate of this expulsion increases as the pressure gradient becomes higher. The overpressure in the stopper is at its maximum when it is compressed during bottling, and the kinetics of oxygen release are thus very fast during the first few days in bottle. Then, as oxygen leaves the stopper, the overpressure decreases, thus automatically decreasing the oxygen release rate.

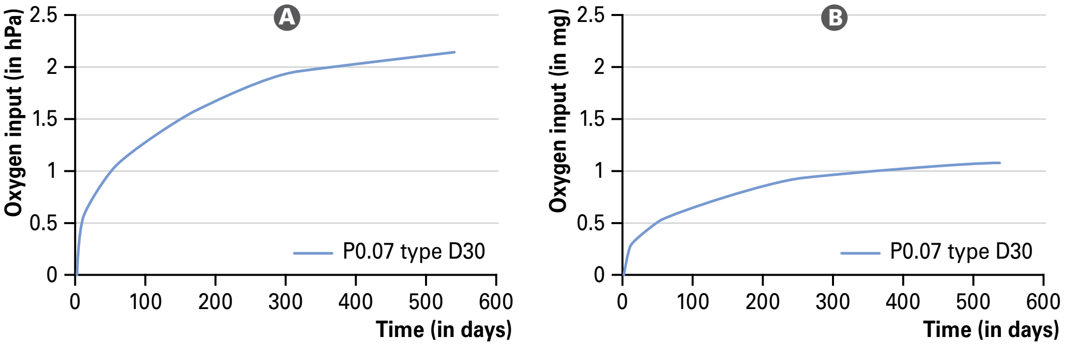
The second phase corresponds to a stationary period. The pressure inside the stopper has stabilized, the pressure gradient between the outside and inside of the bottle is constant and imposes transfer kinetics.

To make it easier to read the curves and use units more commonly found in the wine industry, the unit on the y-axis, hPa (hectopascal), was converted to "mg oxygen". The latter unit is more explicit for winemakers and bottlers ***(Figure 1 B)***. Conversion was done using the perfect gas equation: $PV = nRT$, where P is partial pressure of oxygen, n is the number of moles of oxygen, V is the volume of the bottle after corking, T is temperature, and R is the universal perfect gas constant.

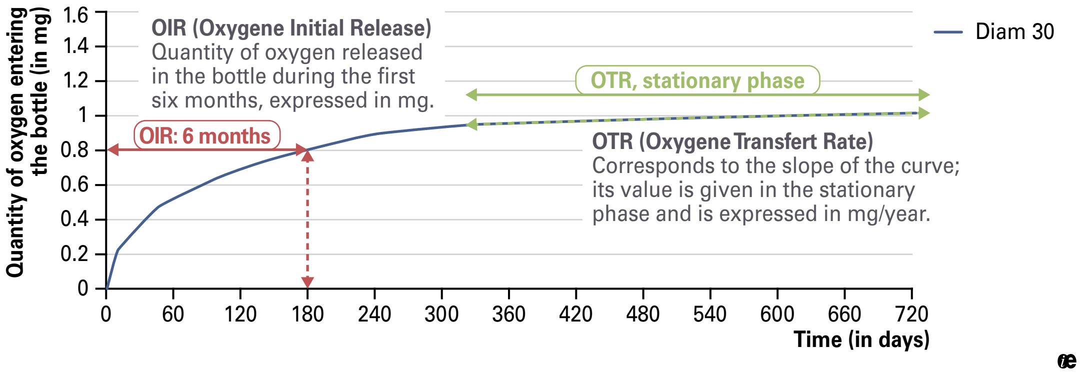
The number of moles is directly related to mass, via the relationship $n = m/M$, where m is the mass of oxygen, and M is the molar mass of oxygen.

On the basis of these observations, we decided it was important to introduce two values that define the oxygen contribution added to the wine by the stopper:

■ Figures 1: Example of evolution of the quantity of oxygen, respectively Ⓐ in hPa and Ⓑ in mg, measured in a bottle closed with a Diam 30 stopper.



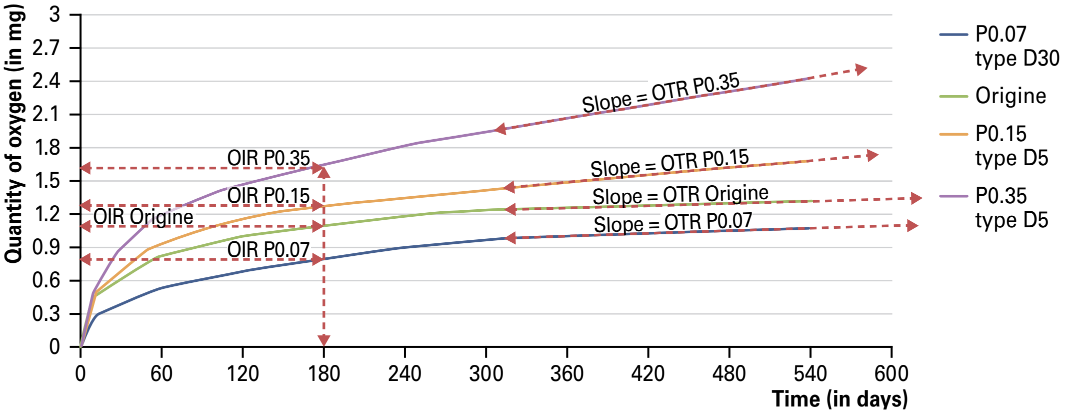
■ Figure 2: OIR and OTR – Example of a batch of Diam 30 stoppers.



OIR (Oxygene Initial Release)
Quantity of oxygen released in the bottle during the first six months, expressed in mg.

OTR (Oxygene Transfert Rate)
Corresponds to the slope of the curve; its value is given in the stationary phase and is expressed in mg/year.

■ Figure 3: Four levels of permeability of Diam stoppers.

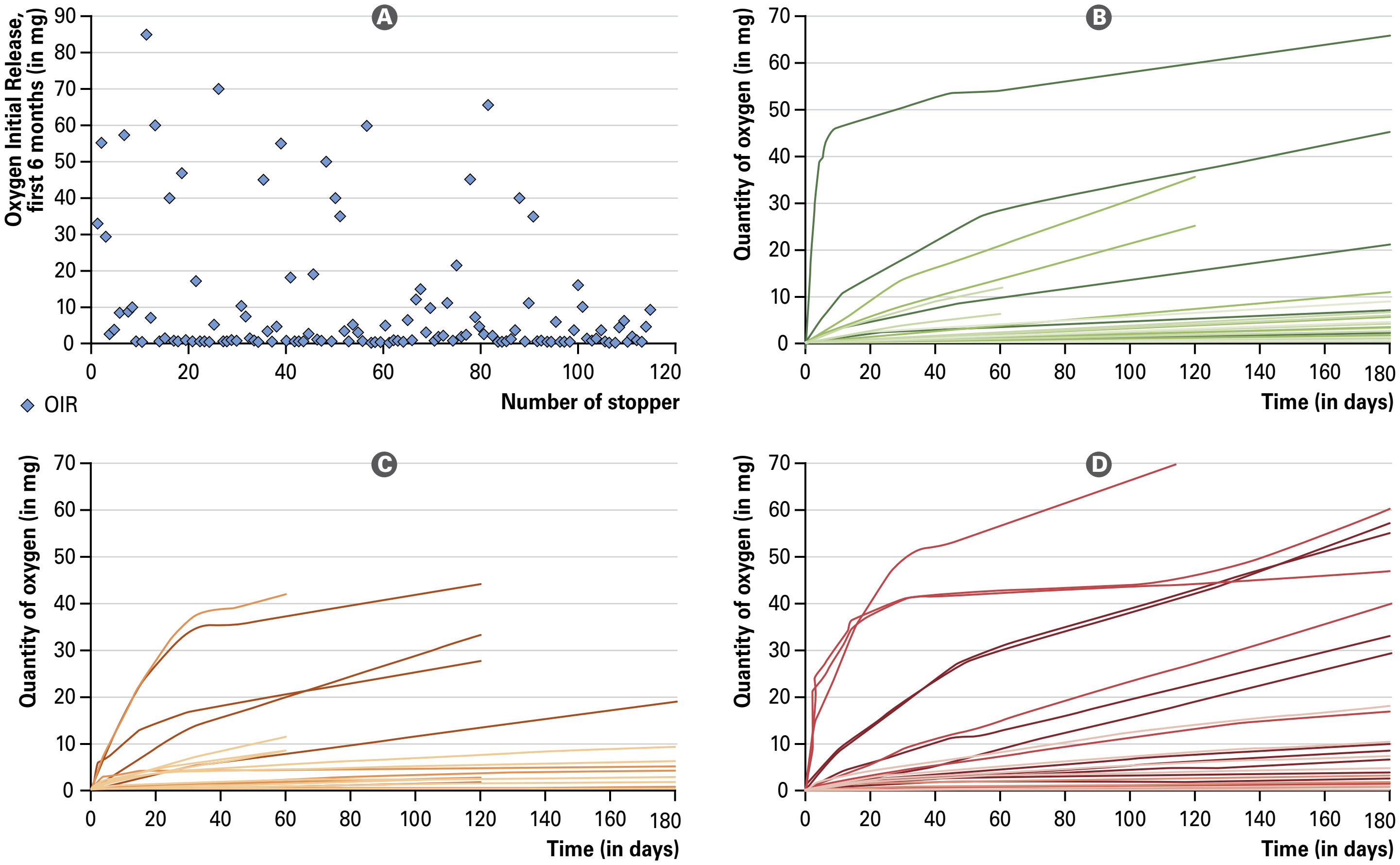


■Table 1: Values for dry Diam and natural cork stoppers.

	Diam P0.07	Diam Origine	Diam P0.15	Diam P0.35	Natural Flower Extra Super
OIR in mg	0.8 mg	1.1 mg	1.3 mg	1.6 mg	From 0.2 mg to > 60 mg
OTR mg/yr	0.3 mg/yr	0.3 mg/yr	0.4 mg/yr	0.6 mg/yr	From 0.2 mg/ yr to > 500 mg/yr ***(*)***

(*) *Values obtained on leaking natural cork stoppers prior to oxygen saturation in the bottle.*

Figures 4: Ⓐ **OIR for about 100 natural stoppers, Flower, Extra and Super categories. Oxygen input curves for each of the natural stopper categories:** Ⓑ **Flower,** Ⓒ **Extra,** Ⓓ **Super.**



– **OIR:** Oxygen Initial Release, quantity of oxygen entering the bottle during the first six months: this mainly corresponds to the release of oxygen contained in the stopper. OIR is expressed in mg;

– **OTR:** Oxygen Transfer Rate, corresponds to oxygen transfer kinetics via the stopper in the stationary phase. As opposed to OIR, which is a quantity in mg, OTR is a flow expressed in mg/year. Its value is stable until the stopper reaches mechanical fatigue.

As an example, ***Figure 2*** illustrates the OIR and OTR values for a Diam 30 stopper. We observe that its OIR is 0.8 mg and its OTR is 0.3 mg/year (slope of the curve). This OIR value may seem low in regard to the other oxygen sources during bottling, but it should be noted that it is far from negligible. In this case, it corresponds approximately to the same quantity of oxygen which will be provided by the stopper during the first three years of bottle aging (OTR = 0.3 mg/year). This expulsion of oxygen for a short period of time may be responsible for a greater or lesser change in the wine's redox potential just after bottling, and it should be compared with the work conducted by researchers from the University of Zaragoza on the evolution of the redox potential of wines *(Vicente Ferreira, 2014; Franco-Luesma, 2014).*

Our measurement campaign was extended to all other stoppers of the range. ***Figure 3*** illustrates the average curves obtained for the four permeability levels of Diam stoppers: P0.07; P0.07 Origine; P0.15; and P0.35. ***Table 1*** gives a recap of the OIR and OTR values obtained. The characterization protocol put in place for this study enables us to clearly distinguish between them based on increasing OIR and OTR values. The most permeable stoppers have the highest OIR and OTR values, and vice-versa.

The Origine by Diam 30 stoppers can be distinguished from the Diam 30 stoppers because the former have a slightly higher OIR value, but a similar OTR level. This phenomenon comes from the replacement of microspheres by beeswax, leading to a structure that has more oxygen in the pores, while maintaining identical gas permeability in the stationary phase.

For comparison purposes, a measurement campaign that was identical to the previous one was conducted on 180 natural stoppers (60 Flower, 60 Extra, 60 Super). The oxygen accumulation kinetics as well as the OIR and OTR values of these stoppers are shown in ***Figures 4 A, B, C, D*** and in ***Table 1.***

We can observe a very high level of heterogeneity of oxygen contributions, regardless of stopper grade. The OIR values are extremely variable, from 0.2 mg to more than 60 mg, or a factor of 300 between two stoppers, independently of the selected visual grade. Similarly, the OTR values show the same scatter, with values ranging from 0.2 mg/year to more than 500 mg/year (OTR measured before bottle saturation).

The significant heterogeneity of these natural cork stoppers has led us to search for a structural effect that would enable us to predict this erratic type of behavior. All of the stoppers were examined by X-ray, in order to detect any internal structural defects. However, this approach did not enable us to clearly establish a precise link between their morphology and the OIR and OTR values obtained (results not presented in this article), it proves that oxygen transfers *via* natural cork stoppers are still far from being fully under control.

Conclusion

Many publications deal with the need to control oxygen transfer through the stopper during the aging of wine in bottles. This study highlights the importance of distinguishing between two oxygen enrichment phenomena in bottle-aged wines. To do this, we have defined the concept of OIR, in addition to the OTR value, which is already widely used in the wine industry. These two values are used to predict the quality of bottle aging. It is known in enology that the kinetics of oxygen contribution affect final wine quality (for example, micro-oxygenation). We can therefore imagine that with a high OIR, some wines could be protected for a certain amount of time from the development of reduced odors (cabbage, rotten eggs).

In contrast, for other wine types that are made with an eye to longer bottle aging, this rapid contribution will have less of an impact, and only the OTR will affect the quality of the wine aged in bottle. Thus, a slow, controlled addition of oxygen over several years can lead to a wine with aroma complexity, which is also called "Reduction bouquet". Other work aimed at better defining the oxygen needs of wines in bottle, as a function of varietal, grape ripeness, winemaking and aging techniques, will be the subject of future publications. ■

■ Bibliography

J.-B. Diéval, S. Vidal, O. Aagaard (2011). *Measurement of the oxygen transmission rate of co-extruded wine bottle closures using a luminescence-based technique.* Packaging Technology and Science 24, 375-385.

P. Godden, F. Leigh, J. Field, M. Gishen, A. Coulter, P. Valente, P. Hoj, E. Robinson (2001). *Wine bottle closures: physical characteristics and effect on composition and sensory properties of a Semillon wine. 1. Performance up to 20 months post-bottling.* Aust. J. Grape Wine Res 7, 64-105.

P. Lopes, C. Saucier, Y. Glories (2005). *Nondestructive colorimetric method to determine the oxygen diffusion rate through closures used in winemaking.* Journal of Agricultural and Food Chemistry 53, 6967-6973.

P. Lopes, C. Saucier, P.-L. Teissedre, Y. Glories (2007). *Main Routes of Oxygen Ingress through Different Closures into Wine Bottles.* J. Agric. Food Chem 55, 5167-5170.

V. Oliveira, P. Lopes, M. Cabral, H. Pereira (2013). *Kinetics of oxygen ingress into wine bottles closed with natural cork stoppers of different qualities.* American Journal of Enology and Viticulture 64, 395-399.

D. Rabiot, J. Sanchez, J.-M. Aracil (1999). *Study of the oxygen transfert through synthetic corks for wine conservation.* Second European Congress of Chemical Engineering, Montpellier.

M. Ugliano, S. Bégrand, J.-B. Diéval, S. Vidal (2015). *Critical oxygen levels affecting wine aroma: Relevant sensory attributes, related aroma compounds, and possible mechanisms.* ACS Symposium Series, p. 205-216.

J.-C. Vidal, C. Toitot, J.-C.Boulet, M. Moutounet (2004). *Comparison of methods for measuring oxygen in the headspace of a bottle of wine.* Journal international des Sciences de la Vigne et du Vin 38, 191-200.

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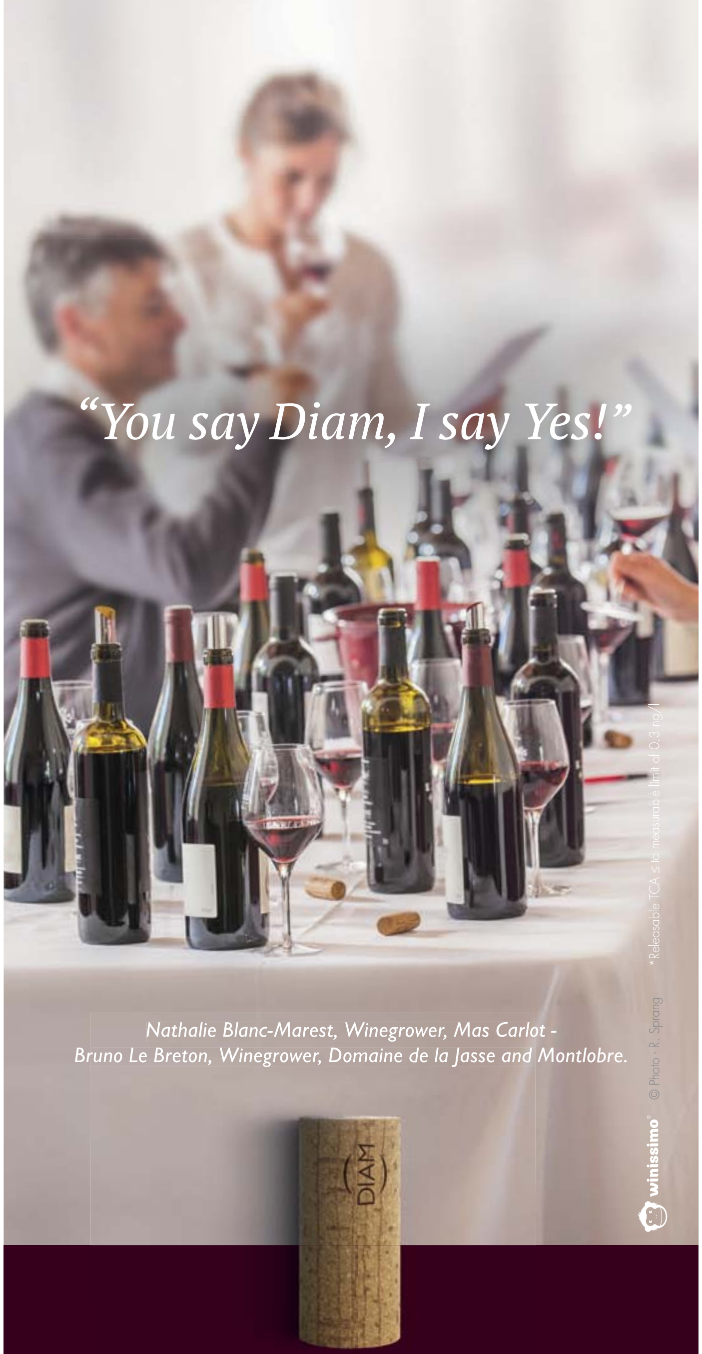

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