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Influence of Steam Cleaning Processes on the Geometry of Finished Cork Stoppers

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Abstract

Over the centuries, cork stoppers have become the most widely used closure for still and sparkling wines. The cork presents great advantages among which stand out its lightness, flexibility and capacity to allow the passage of gases, but it also presents problems derived from its heterogeneity and its capacity to absorb and transmit the cork transmits harmful aromas to the bottled wine. These aromas include 2,4,6-trichloroanisole (TCA) and 2,4,6-tribromoanisole (TBA) associated with wet cardboard and mould aromas. Numerous treatments have been developed to reduce and eliminate trichloroanisole content in corks, many of which are associated with the combined effect of steam, time, temperature and pressure. In the present study, different treatments were tested on cork stoppers in order to determine the influence of these treatments on the geometry of the stopper, as well as the limits of application of each of these parameters in the finished stoppers.

Keywords: cork; stoppers; steam; pressure; deformation

1. Introduction

The use of cork as a closure for wines has been known since classical antiquity (Alegoët et al. 1990).

Nowadays, the cork is still one of the preferred closures by the winemakers for the conservation of wines and sparkling wines. Due to the shortage of raw material and the cost of the stoppers, in the last years alternatives to the natural cork stoppers have arisen like the synthetic stoppers or the agglomerated and microgranulated ones. Anyway, any closure must comply with a series of common characteristics:

- Elasticity. The diameter of the cork stopper is, in general, much larger than the internal diameter of the bottle neck. The cork must fit perfectly to the bottle neck of the bottle
- Must allow for gentle removal of the stopper
- Must not be broken during the extraction of the above-mentioned cap.
- Must be chemically and biologically inert.
- Must allow the exchange of gases with the atmosphere outside the bottle so that the aging and evolution of the wines can be achieved (Silva et al. 2003).

Cork has characteristic properties and that make it especially interesting. Among these, we can highlight the compressibility and elastic recovery (Barker n.d.). These characteristics allow it to reduce its diameter in the process of closing the bottle while maintaining sufficient pressure on the glass to prevent the leakage of the wine from the interior.

However, the use of corks implies the appearance of several problems. The first of these lies in their heterogeneity. (Karbowiak et al. 2010) that makes difficult the possibility of obtaining identical stoppers from a different raw material because of its own vegetal origin. Also, the cork stoppers present other problems such as the presence of trichloroanisoles (TCA) (Chatonnet et al. 2003) that provide negative aromas to the wine that come in contact with the contaminated stopper or the permeability to gases that, although necessary for the aging of the wine, in excess can cause the oxidation of the wine (Brajkovich et al. 2005).

Consecuence to this situation, although the natural cork is still used in a recurrent way for the closing of wine and sparkling wine bottles, new technologies have appeared (microgranulated cork closures, plastic closures,...). There are currently different possibilities (Silva et al. 2003) however, natural cork is still used in large quantities.

1.1. Cork physical characteristics

Cork is a material of natural origin in which Suberin predominates with a percentage of between 33 and 50%, followed by lignin with a percentage of between 13 and 29%, polysaccharides with a percentage of between 5 and 25% and other components in lower quantities among which we highlight extractable compounds with a percentage of between 8 and 28%, tannins with a percentage of between 6 and 7%, waxes with between 2 and 8% or the presence of ash with a percentage of between 2 and 3% (Silva et al. 2005). The variability of its properties can be due to several factors such as the age of the tree, the distance of the lamina used from the base, the climatic characteristics in which the tree has grown, (Conde et al. 1997; Mazzoleni et al. 1988).

Mechanical capacities and especially the compression capacity of the cork are fundamental for its correct performance, given that during bottling, the cork can suffer a reduction in diameter of more than 25%, going from an initial diameter of between 26 and 24 mm. (depending on the type of stopper) to a final diameter of 18.5 mm. for a Bordeaux bottle (slats used in the marking of still wines today). The maximum compression should be between 15.5 and 16 mm to avoid excessive mechanical damage to the lenticels (Karbowiak et al. 2010).

Once the bottling process is completed, the cork expands at a cellular level, so that the bottle neck is pressed diametrically, providing a seal without risk of leakage (Silva et al. 2003). Obviously, the compression will vary depending on the diameter of the cork as well as the inner diameter of the bottle neck. The capacity of recovery will depend on several additional factors, among which the humidity of the cork stands out, being able to arrive at a total recovery of the initial form of the cork for relative humidities of 100% (Lagorce-tachon et al. 2015).

1.2. “Cork taste" problem

One of the most notable defects present in some wines corresponds to the presence of smells with a mildewed character. These are unpleasant aromas classified as serious defects by tasters and consumers. Although there are several molecules that transmit these unpleasant aromas, the influence of chloroanisoles, and especially that of 2,4,6-trichloroanisole (TCA) and 2,3,4,6-tetrachloroanisole (TeCA), stands out.

These compounds are frequently identified in those wines with defects derived from the presence of "moldy" or "corky" aromas in tasting.

Regarding the origin of TCA, we must first specify that the cork, as material coming from the cork oak bark (Quercus suber) is a potential transmitter agent of TCA to wines in case the raw material is contaminated or its quality is deficient (Tanner et al., 1981, Buser et al., 1982, Tanner et Zannier, 1983). This effect has been aggravated for years by the use of chlorine to wash the stoppers in an attempt to sanitize them. However, although this practice is not recommended, it is not a source of TCA either, as is evident from the fact that the abandonment of these practices has not eradicated the present problem. Anyway, the cork is an excellent material support for the proliferation and accumulation of substances considered from the gustatory and olfactory point of view like negative reason why, even considering the mentioned risk of contamination after its manufacture, all the necessary measures will have to be taken so that the process of production avoids contamination of these corks.

1.3. Cork treatment

There are different types of technology aimed at reducing or eliminating TCA contamination On the one hand, since there are certain micro-organisms present on cork which, through a biomethylation reaction of trichlorophenols to trichloroanisoles, are responsible for the appearance of metabolites that are the origin of compounds such as TCA, the elimination and/or reduction of these micro-organisms will contribute to reducing the contamination defect. But if the compound has already been formed they will not be effective, so the techniques aimed at this effect, although they may be appropriate at a preventive level, are inefficient as a corrective measure.

There are also a group of techniques aimed at eliminating or reducing the presence of TCA itself. For these technologies, the geometry of the cork to be sanitised is fundamental, given that as a general rule these are processes in which the aim is to penetrate the whole volume of the cork. This is the reason why most processes have been designed for granulated cork from which agglomerate or microgranulated corks will be made.

Within these techniques, we can identify the application of treatments by irradiation for the sterilization of natural cork stoppers (Pereira et al. 2007). This technology allows reductions of the order of 70-95% in the total concentration of TCA present in the sample (not as transferred TCA) by applying radiation doses of 15-400 kG, with the possibility of reaching eliminations of more than 90% under certain circumstances and obtaining acceptable results from radiation doses of 52 kGy (concentrations < 4-10 ppt/l corresponding to the perception threshold).

There are, however, certain aspects to be considered in this technology, such as the difficulty of implementing it or the heterogeneity of the results obtained without a clear trend regarding application dose.

Another reference to be considered would be the plate and cap treatment system designed on a laboratory scale and using steam and ozone as well as other sterilising gases through their application in pulsed pressure-vacuum cycles (Vlachos, et al. 2007).

From the studies carried out, it appears that the unique application of ozone treatment is a promising system, although its combination with pulsed treatments (pressure-steam) can achieve TCA elminations of more than 90% and reductions in the population of bacteria and fungi of more than 99%. The need to extrapolate the technology to the industrial sector and to study the costs of applying the process should be considered in this respect.

Another technology applied for the extraction of trichlo-roanisoles from granular products is the application of carbon dioxide in the supercritical state (Rowe, 2003; Taylor et al., 2000).

An example of this technology is the DIAMANT process, developed by SABATÉ DIOSOS S.A. (OENEO S.A.) in which the sample is placed in an autoclave at a pressure of 100 bar and a temperature of 40ºC with the presence of CO2 and a co-solvent for between 30 minutes and 120 minutes.

In its application to microgranules, one of the main advantages of this process is the non-generation of negative changes in the internal structure of the cork (Rowe, 2003) as well as the capacity of supercritical CO2 to solubilize organic molecules of molecular weight lower than 1500 g/mol (Banister, 2005).

Finally, most extended treatments are dedicated to granulated sanitation because particle geometry is smaller, so the application of steam is more effective.

There are several patents among which we must highlight the ROSA process developed by AMORIM where a steam cleaning treatment is applied (WO 2004/014436) to the granulated cork, achieving reductions of close to 80% in the concentration of TCA (Cabral, 2006).

Other procedures, such as the one described in the patent ES 2247180 (WO 03/041927) consists of a treatment with water steam and ethanol in corks or cork sheets submitted to temperatures ranging from 25 to 100 ºC and pressures ranging from 0.01 to 2 bar by means of a semi-continuous system.

Other processes, such as the one proposed in the ES patent, propose a treatment with water vapour at temperatures between 100 and 130ºC and pressures between 1 and 2.7 bar for a period of between 30 and 90 min. For the treatment of agglomerated corks.

However, in all cases, these treatments are applied to cork sheets, granulated in mass or corks formed from granulates due to the lesser influence of these processes on the final geometry of the product.

2. Materials and methods

The objective of this study is to evaluate the effect of saturated steam treatments applied to natural corks on their geometry, determining the possibility of practical application of these treatments on finished corks. To this end, work will be done by applying different combinations of the variables pressure, temperature and time.

2.1. Objective

The objective of this study is to evaluate the effect of saturated steam treatments applied to natural corks on their geometry, determining the possibility of practical application of these treatments on finished corks. To this end, work will be done by applying different combinations of the variables pressure, temperature and time.

2.2. Matherials

In order to carry out this study, a preliminary study has been made to determine the range of times, pressures and temperatures to be used. To this end, 12 tests were carried out on 10 plugs/test pieces subjected to pressures of 2 bar, 1 bar and 0.5 bar and times of 60 minutes, 90 minutes and 120 minutes. Based on the data obtained in this test, the range of the final test was established by making 12 samples of 50 corks each, with pressures of between 0.1 and 0.8 bar and times of between 60 and 180 minutes. The initial geometry of the corks studied is 44 millimetres in length and 24 millimetres in diameter. A 10-litre autoclave was used to test the stoppers, with a maximum working temperature of 134 ºC and a maximum working pressure of 210 KPa (2.1 bars).

2.3. Methods

The cork stoppers have been previously stabilized in a controlled humidity chamber, achieving a humidity of between 6 and 8%. The stoppers are introduced in the autoclave tank, establishing the time and pressure corresponding to the proposed sample. Once the test is finished, the stoppers are taken to the stabilisation chamber at 25 ºC for 24 hours, after which they are measured. In order to analyse the evaluation of the effect of the proposed process, taking into account the two independent variables (pressure and treatment time) and considering the response variable to control the deformation, a sequential experimental design has been considered, so that the intervals of these operational variables were progressively limited.

The experiment was carried out in two stages. The first of these stages is aimed at determining the maximum pressure range to which the stoppers can be subjected without critical deformation preventing the use of the stoppers. Once the applicable pressure range has been determined, a new battery of tests suitable for the determined pressures and for a battery of times will be determined to determine the deformation suffered by the stopper for each of these tests.

3. Results and Discussion

An analysis has been made of the effect of different steam treatments for different values of pressure and time applied to 44 mm. long and 24 mm. diameter corks. Initially, a battery of tests was carried out to determine the range of pressures at which the cork stoppers suffer a deformation that makes them impossible to use. Table 1 shows the battery of 12 initial tests carried out to limit the maximum pressures at which they can be operated.

Table 1. Description of the initial tests carried out.

Test	Pressure (bar)	Time (min)
1	0,5	45
2	0,5	60
3	0,5	90
4	0,5	120
5	1	45
6	1	60
7	1	90
8	1	120
9	2	45
10	2	60
11	2	90
12	2	120

Figure 1. 24x44 mm control cork.

As a result of these tests, it can be seen how the deformations suffered by stoppers subjected to treatments with pressures equal to or greater than 1 bar of pressure, even for short treatment times, make the stoppers unusable for industrial use. Figure 1 shows the 44 mm long and 24 mm diameter corks used as controls.

Figures 2 to 5 show the results obtained for some of the tests set out in Table 1.

Figure 2. 24x44 mm cork stoppers subjected to a treatment of 110 ºC - 0.5 bar for 45 min.

Figure 3. 24x44 mm cork stoppers subjected to a treatment of 120 ºC - 1 bar for 45 min.

Figure 4. 24x44 mm cork stoppers subjected to a treatment of 127 ºC - 1.5 bar for 45 min.

Figure 5. 24x44 mm cork stoppers subjected to a treatment of 133 ºC - 2 bar for 45 min.

As we have already mentioned, for pressures equal to or greater than 1 bar, the deformation of the stoppers is so high that they cannot be used in bottle capping applications.

From this initial test, it was determined that the pressure ranges to be applied to the second stage of the deformation study should be less than 1 bar.

A battery of X tests was proposed as described in table 2.

Table 2. Description of the tests carried out in the second stage.

Test	Pressure (bar)	Time (min)
A	0,1	60
B	0,1	120
C	0,1	180
D	0,2	60
E	0,2	120
F	0,2	180
G	0,5	60
H	0,5	120
I	0,5	180
J	0,8	60
K	0,8	120
L	0,8	180

Different length and diameter data have been obtained from these tests.

For each of the 50 stoppers forming part of a test and for all the tests, both length and diameter have been measured, establishing the average values of diameter increase (X) and (D) length as well as the standard deviation () as a measure of the dispersion of these values. In tables 3 and 4, we can see the results obtained for each of these parameters.

Table 3. Results of the second stage tests for steam pressures of 0.1 and 0.2 bar.

	Test	A	B	C	D	E	F
	Pressure (bar)	0,1	0,1	0,1	0,2	0,2	0,2
	Time (min)	60	120	180	60	120	180
Lenght							
	DL (mm)	4,13	4,19	4,25	4,23	4,27	4,33
	Time (min)	0,098	0,126	0,104	0,066	0,128	0,082
Diameter							
	DD (mm)	2,03	2,04	2,09	2,10	2,13	2,19
	Time (min)	0,101	0,072	0,112	0,082	0,106	0,110

4. Conclusions

A study of the influence of the saturated steam treatments applied to finished natural cork stoppers on their geometry has been carried out. Initially, some initial tests have been carried out to determine the parameters from which the deformation of the stoppers prevents their use for the closing of wine bottles. Since saturated steam, pressure and temperature are related, they should only be treated as a single independent variable. From the initial tests carried out, it can be deduced that both the increase in vapour pressure and the increase in treatment time are factors that positively affect the deformation of the stoppers.

Table 4. Results of the second stage tests for steam pressures of 0.5 and 0.8 bar.

	Test	G	H	I	J	K	L
	Pressure (bar)	0,5	0,5	0,5	0,8	0,8	0,8
	Time (min)	60	120	180	60	120	180
Lenght							
	DL (mm)	5,50	5,51	5,52	4,49	4,52	4,54
	Time (min)	0,062	0,086	0,082	0,078	0,098	0,072
Diameter							
	DD (mm)	2,28	2,33	2,35	2,36	2,39	2,39
	Time (min)	0,043	0,054	0,048	0,045	0,055	0,052

However, from the graphic information shown, it can be seen how the increase in pressure is much more decisive, given that deformations at high pressures, equal to or greater than 2 bars with short treatment times equal to or less than 45 minutes, produce much greater deformations than those derived from exposure to lower pressures for longer periods of time. It is also noteworthy that, from 1 bar of pressure, the deformations make the stoppers unusable for closing bottles while, from 1.5 bar of pressure, the deformations are extremely high.

Based on the above, it has been determined that treatments with saturated steam on finished caps must be carried out with steam pressures below 1 bar. Based on this initial determination, the second test was proposed for steam pressures of 0.1, 0.2, 0.5 and 0.8 bar and times ranging from 60 to 180 minutes. From these tests, it can be seen how the deformations, both in length and diameter, increase with the increase in time and with the steam pressure. According to the generated deformation, the most determining factor regarding the longitudinal and diametrical deformation is the pressure.

Both dimensional values grow as the pressure increases, although it should be noted that, from 0.5 bars of pressure, the length does not change in a representative manner when the pressure or time increases, as it does when the evolution of these parameters is analysed for lower values. However, the diameter continues to vary considerably as the pressure increases.

Taking into account the influence of time, it can be determined that for any of the pressure values selected in the treatment, the increase in time implies a variation in length and diameter that grows as the treatment time increases. It is also noteworthy that, for both lengths and diameters, the standard deviation is reduced as the pressure of the steam treatment increases, especially from 0.5 bars of pressure.

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