



Information Bureau | 2016 QUALITY





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# **QUALITY**

The Portuguese cork industry has tried to achieve the highest quality standards in its different phases and aspects of production, with special emphasis on the production of stoppers, where the effort of identifying and eradicating possible flaws has been the main priority. Investments have been reflected in modernization and new factories as well as new technologies in the different phases and processes.

# EFFORTS MADE BY THE CORK INDUSTRY

#### Quality guarantee of cork stoppers

The production of cork stoppers is a complex process, which requires quality control in the various phases of production. The following are the main aims to guarantee quality in the manufacture of cork stoppers:

- Achieving suitable functionality from the cork stopper as a closure;
- Harmlessness of the cork stopper;
- Efficiency of the productive processes.

The quality of natural cork stoppers is determined according to a seven-class scale and depends on the raw material used as well as the productive processes adopted by the manufacturer. There are also specific types of stoppers for spirits, sparkling wines or still wines (see Document about Stoppers and Technical Manual about Cork Stoppers, <a href="http://www.apcor.pt/portfolio-posts/manual-rolhas-versao-actualizada/">http://www.apcor.pt/portfolio-posts/manual-rolhas-versao-actualizada/</a>).

#### **Laboratory tests**

Finished products are subjected to laboratory tests in the following areas:

- Visual analysis;
- · Control of the moisture level;
- Dimensions (length, diameter);
- Residual oxidant control;
- Microbiological analysis;
- · Capillarity;
- Sealing ability;
- Elasticity/Size recovery;
- Extraction force of the cork stoppers;
- Sensory analysis.

These are the fundamental tests that complement the industry's internal standards and which are aimed at complying with increasingly strict technical requirements.

Manufacturing quality products with a competitive price requires careful implementation of the key factors of the Portuguese cork industry, namely:

- Compliance with the technical specifications;
- Compliance with contractual requirements;
- Reduction of production costs;
- Continuous improvement of human and technological resources.



## **The Quercus Project**

European associations representing the cork industry met at the European Cork Confederation (C.E. Liège) between 1992 and 1996 and they commissioned a study on the production phases of cork stoppers – from cork harvesting to storage – with a view to scientifically assessing the possibility of cork being responsible for organoleptic changes in wines. By using suggestions from previous studies along with the findings of this vast project, it was possible to expand knowledge of the compounds responsible for this type of anomaly, such as 2,4,6 – Trichloroanisole (TCA).

This project was organized in three phases:

- 1. Bibliographical analysis aimed at complementing existing data, essentially regarding the development of techniques and existing analytical methods;
- 2. Identification of the "musty taste" and assessment of laboratory test methods;
- 3. Industrial study on the control of the productive process by recourse to analytical methods, that were perfected following inter-laboratory experiments.

The industrial study was carried out by the Portuguese Cork Technology Centre (CTCOR). Its aim consisted in pointing out possible critical phases in the cork production process and analyzing all the agents involved with the utmost rigor.

Two main recommendations emerge from the Quercus Project:

- Prepare a Code of Good Practices for the production of stoppers and their use as a closure;
- Prepare and complete analytical methods, that meet the requirements of the directives of European laboratories (ISO, CEN, etc.) and help in standardizing work practices.

The Quercus Project found negligible or even nonexistent levels of TCA in the raw material cork samples used for laboratory testing.

The lack of rigor in some processes during the production of stoppers encouraged its development. Despite the abovementioned low levels, the project required the publication of a list of quality procedures to be applied to the cork industry in order to achieve a level of standardized production and high quality.

#### The International Code of Cork Stopper Manufacturing Practices

The International Code of Cork Stopper Manufacturing Practices (ICCSMP) was edited, promoted and implemented after the results of the Quercus Project.

This code describes and establishes the procedures to be observed by the cork industry. Furthermore, it was created with the aim of implementing quality control standards throughout the entire productive process by guaranteeing a contamination-free product with absolute quality control to producers and bottlers.

The code defines the correct practices to be adopted:

- · When stabilizing cork, after harvesting;
- During the cork stopper production process;
- In the transport of stoppers.

The SYSTECODE Accreditation system was created in association with the ICCSMP.

The accession of businesses has grown by 82.35% worldwide (from 170 to 310 companies) and by 178.16% in Portugal (from 87 to 242 companies) in the thirteen last years of the system's implementation.



Chart 1 - Nº of companies certified by Systecode - 2015 241 41

Portugal Spain France 15 Italy 5 Morocco Tunisia 2 Germany Total 308 0 50 100 150 200 250 300 350 Source: CELiège

It should be noted that of all Portuguese cork companies (670 in 2014 according to the Department of Strategy and Studies – Ministry of the Economy (2016)) about 35.97% are certified by Systecode (241 companies). Also of note is that 81.48% of these are APCOR members, i.e. 220 companies, and only 7,41% are not yet members (21 companies).

For the third year, Systecode awarded the "Systecode Premium" to the companies that meet most requirements - in terms of hygiene and food safety, sustainable development and environmental impact. 13 companies were rewarded with the certification "Systecode Excellence", that is the new level of this certification, which emphasizes the best of the sector in terms of finishing of cork stoppers production. The remaining companies obtain "Systecode Base". 75 companies worldwide have achieved the most demanding certificate, 49 of which are Portuguese.

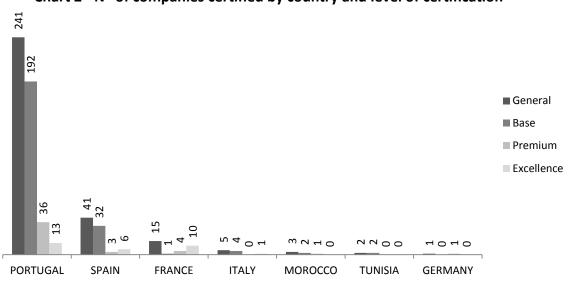


Chart 2 - Nº of companies certified by country and level of certification

Source: CELiège



APCOR is responsible for promoting the implementation of the International Code of Cork Stopper Manufacturing Practices in Portugal.

The digital version of the 6th edition of the International Code of Cork Stopper Manufacturing Practices is available at APCOR website: http://www.apcor.pt/wp-content/uploads/2015/11/ICSMP-International-Code-of-cork-stoppers-manufacturing-Practices-ENGLISH.pdf.

#### **SYSTECODE** certification

Companies that apply for the official accreditation of the International Code of Cork Stopper Manufacturing Practices are audited by Bureau Veritas. This independent organization is responsible for deciding whether a particular company complies with the established requirements and subsequently issues the SYSTECODE certificate. Companies must re-apply for the certification annually, thus guaranteeing the continuity of the practices prescribed by the International Code of Cork Stopper Manufacturing Practices.

This certification is a guarantee to clients of the supplied product's quality. The code is a fundamental element for the future success of the industry and it encourages companies to improve their productive processes continuously as well as to produce cork stoppers of increasingly better quality.

# Other certification systems

Cork companies have continued to implement other quality standards, of which we highlight:

• ISO 9001 (Quality): 28

• ISO 22000 (Food safety): 10

ISO 14001 (Environment): 4

Source: IPAC, 2016

It must be stressed that some companies of the sector also implemented the **Hazard Analysis Critical Control Points or HACCP**, the application of which has been compulsory in the production and packaging of foods since 1998. This is a preventative food safety management system, which when implemented, ensures hygiene as well as the chemical and microbiological safety of foods. Seeing as cork stoppers are in direct contact with a foodstuff (wine), the compulsory application of the HACCP system in the wine sector has greatly increased the level of hygiene during the bottling process.

With regard to forest certification and chain of custody by the Forest Stewardship Council (FSC) there are around 147.000 hectares of certified cork oak forest ("montado"), representing 20% of the total area in Portugal and 59 Chain of Custody certificates held by Portuguese companies of cork sector. Certification by the PEFC system (Programme for the Endorsement of Forest Certification) has almost 21.946 hectares of cork oak that is certified, representing 3% of the total national area and 4 Responsibility Chain certificates held by companies of the cork sector.

### **Investment in Human Resources**

The Portuguese cork industry has in recent years invested in the qualification of its human resources. This can be seen in the increase in companies' mid and upper management, as well as in the numbers of highly qualified and qualified professionals and decreasing numbers of trainees and apprentices. As a result of the investments made in recent years and innovation processes currently underway, the sector now encompasses a new set of professions, implying a need for new knowledge and skills and therefore new professionals.

As shown in the table below, there is a clear decrease in unqualified and semi-qualified workers and an increase in qualified professionals.



Table 1 – Qualification Level

Qualification Level	2005	2006	2007	2008	2009	2012	2013
Trainees and Apprentices	47	50	40	42	20	36	19
Managers, supervisors, foremen and chiefs	660	634	630	637	596	601	582
Unqualified professionals	3.234	3.155	3.153	2.992	2.331	2.004	1.838
Semi-qualified professionals	2.963	2.795	2.771	2.645	2.181	652	614
Qualified professionals	2.963	2.831	2.839	2.811	2.376	4.249	4.041
Highly qualified professionals	183	180	188	181	165	131	138
Middle management	236	210	283	269	256	255	238
Senior management	811	824	769	750	652	682	692
Not considered	185	157	187	178	146		
Total	11.050	10.629	10.633	10.285	8.557	8.610	8.162

Source: MSSS (2015)

As regards professional training, the Professional Training Centre of the Cork Industry (Cincork - www.cincork.com) offers a set of training courses to workers of the sector in the areas of quality, hygiene and safety, foreign languages, industrial management, environment, production, communication and marketing, amongst others, and as follows:

- Learning
- EFA Adult Education and Training (double certification and academic certification)
- Modular Training
- Ongoing Training
- Provision of Services
- Training for Entrepreneurs

Total training hours in 2015 were close on 283 thousand hours and the number of courses was about 200. More than 3.860 people studied at the center.

Table 2 – Cincork total training hours in 2015

Year	Nº training courses	Nº Trainees	Training Hours	Nº Adults in RVCC courses	Total number of people studying at the center
2011	91	1.851	172.745	2.662	4.513
2012	206	3.839	195.393	1.488	5.327
2013	181	3.403	217.663		3.403
2014	195	3.906	248.710		3.906
2015	200	3.867	283.765		3.867
TOTAL	873	16.866	1.118.276	4.150	21.016

Source: Cincork (2015)



#### **Patents**

According to the Portuguese National Institute for Engineering and Industrial Technology (INETI), there are 169 national invention patents with the word "cork" in the title (February 2016). If we search for brands related to the product "cork" you can find 2000 records. We can also do a search for products related with design and this generates 21 registered products that use cork as an application (www.marcasepatentes.pt).

## **APCOR** research projects

APCOR conducts a number of studies with a view to contributing towards a better understanding of the sector and its products. Projects of note in recent years include:

# 1. Sequencing the cork oak genome, create a DNA chip

In 2009, the world discovered that research was under way to sequence the genome of the cork oak and create a DNA chip of the Portuguese economy's most important tree. Gather the largest number of genes expressed in the cork oak brings together genetic information to condense into a chip. This research will allow us to draw conclusions about the behaviour of the cork oak in certain conditions, to predict disease, understand the sudden death syndrome and eventually accelerate its growth. It is a kind of newborn's test for the cork oak. This research is in charge of Centro de Biotecnologia Agrícola e Agro-Alimentar do Alentejo (CEBAL) (Center for Agricultural Biotechnology and Agro-Food of Alentejo). Further information can be found in www.genosuber.com.

#### 2. Increase the volume of cork

A team of Portuguese researchers created a new method that allows the volume of cork to be increased by about 85%, without changing the characteristics of this material and making its use more sustainable. The process consists of inserting water into the cork and using microwaves to increase the volume of cork granules. The idea was one of three finalists for the European Patent Office's 2013 European Inventor Award, in the Industry category. It was the first nomination of Portuguese inventors for this award.

Cork moistened with water and exposed to microwave radiation can expand by 40% to 85% of its original size. The characteristics of this 100% natural material are thus reinforced in a process that just expands the cork cells, without changing the structure and without any chemical degradation, and maintaining the properties that give it interesting behaviour in several areas. This patented method makes it possible to expand cork in a short space of time and with the least amount of energy, which of course has an impact on the industry.

Portuguese investigators have unearthed another impressive ability of cork, i.e. its "growth" when the cells are subject to a certain humidity and temperature increase by radiation. Helena Pereira, professor and researcher at Instituto Superior de Agronomia (ISA) of the Lisbon Technical University, and António Velez Marques, professor and researcher of Instituto Superior de Engenharia de Lisboa, of Lisbon Polytechnic Institute, coordinated this research which will certainly lead to new applications for cork. The uniformisation of the raw material improves the performance and reliability of the material's performance in very demanding industries such as the manufacture of insulators for space purposes.

# 3. Cork Carbon Footprint: from trees to products

"Cork Carbon Footprint: from trees to products" is the name of the project developed by University of Aveiro – Environment and Planning Department/Environment and Sea Studies Center (CESAM) – and by High Institute of Agronomy – Natural Resources, Environment and Territory Department/Forestry Studies Centre (CEF) and it has as the main goal the evaluation of carbon footprint of cork sector in Portugal, i.e., the emissions and removals of greenhouse effect in all sector, from the forest to the final product, including its industrial process.



Which is concerned to carbon footprint of the Montado, the study concludes that the Montado of Herdade da Machuqueira do Grou (Coruche) represented a carbon sink of 250 g C/m2/year (average value from 2009 to 2014), having been a sink even in the dry years of 2009 e 2012. This result confirms the stability of this montado in terms of carbon sink and contrasts with the results obtained in a holmoak forest with lower density in Evora region with a balance close to zero in dry years. The preliminaries results still show that stripping doesn't have substantial impacts in the balance of carbon at the level of the tree and the ecosystem even in the dry year of 2015.

At the point of the project related to carbon accumulation in cork products, the same study concludes that cork products produced from national cork constitutes growing reservoirs of carbon, either during use or when they are disposed in landfill, having accumulated between 40 and 70 thousand t C/year in the last 15 years. So the usage of cork products contributes to the mitigation of the climatic changes, not only by its ability of accumulating carbon, but also by the fact of replacing the alternative products that are more energetically intensive. The calculation model developed to the project allows cork products of being included in the national inventories of greenhouses effect, such as is already happens with wood products.

This project was developed between July 2013 and November 2015, wherein the several stages of the process and the information set produced during its execution is available at http://corkcarbon.web.ua.pt.

The Foundation for Science and Technology (FCT) was the promoter of the project within the Tender of Scientific Research Projects and Technological Development of 2012. The project was funding by national funds through FCT and by funds of European Funding for the Regional Development through Compete – Operational Program for Competitiveness factors.

# Symbios - CTCOR

Symbios – The Knowledge of Nature is the name of the new innovative process developed by the Cork Technology Centre (CTCOR), which prevents the formation of chloroanisoles in cork, of which we highlight 2, 4, 6 Trichloroanisole (TCA). This is a biological process of a preventative nature, which encourages the development of "benign" microorganisms occurring naturally in cork to the detriment of microbiological species with the potential to produce undesirable metabolites and promotes the inhibition of the biosynthesis of chloroanisoles during the cork transforming stages.

As an additional advantage, this process encourages greater extraction of water-soluble materials from cork during the boiling stage, such as, for example, earth and polyphenols (with potential negative impact on the beverage in contact).

# **CHANGES IN WINE CHARACTERISTICS**

Various factors may affect the characteristics of wines, which can arise during various moments during the bottling or storage of the actual wine itself. Some of the factors here may be associated with the closures as well as with the place and manner in which the wines are stored.

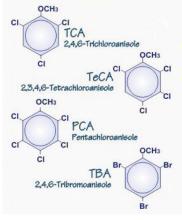


#### **Contamination by Haloanisoles**

Haloanisoles may be transferred to wine by cellar conditions or through contact with materials that are contaminated such as, protection of the reservoirs, hoses, barrels, oak wood fragments, filters, closures and additives such as bentonite.

Haloanisoles may transmit a mouldy or musty taste to wine, to other drinks or to foods. The haloanisoles most commonly found in wine are:

- 2,4,6 Trichloroanisole (TCA) wines contaminated with TCA present a wet cardboard taste the 'musty taste';
- 2,4,6 -Tribromoanisole (TBA) this compound essentially appears because of the use of bromine-based fire-resistant compounds in the treatment of woods found in cellars. Fungi grow with humidity and produce this compound with a very similar aroma and detection limit to TCA;



Source: ETS

- 2,3,4,6 Tetrachloroanisole (TeCA);
- Pentachloroanisole (PCA).

#### Oxidation/Reduction

This evolution occurs in the components of a wine because of oxygenation (oxidation) and the absence of oxygen (reduction). The bottled wine undergoes an oxidation-reduction process. If the absorbance/lack of oxygen in wine occurs to an excessive degree, then it can cause the deterioration of its structure and quality by producing a characteristic caramel aroma and sometimes brownish tones<sup>1</sup>, in the case of oxidation, and a "rotten egg" taste in the case of reduction<sup>2</sup>. The sketch below explains the process.

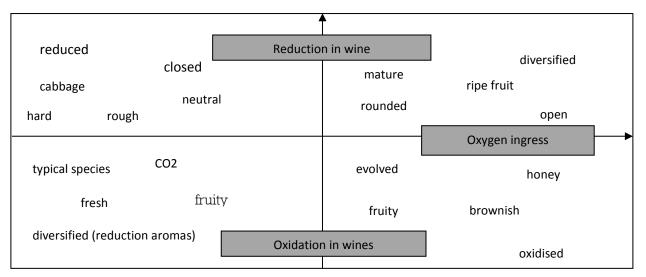


Table 3 – Oxidation/Reduction Evolution

Source: 2006 Wine, Oxygen & Closures; OTR and Consistency; Laurent Dulau

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<sup>&</sup>lt;sup>1</sup> Lopes, Paulo - Study of Oxidation phenomena during wine bottle aging. Closures' role - Faculté d'Oenologie de Bordeaux, Université Victor Segalen Bordeaux (2005).

 $<sup>^{4}</sup>$  Limmer, Alan – Do corks breathe? Or the origin of SLO – The Australian and New Zealand Grapegrower and WineMaker (2005).



### Sulphites in wines

The volatile sulphur compounds that can be found in wines may contribute towards reduction or "rotten egg" aromas. These aromas are nearly always caused by sulphites or mercaptans. About 100 compounds may be found. Nevertheless, only about 10 are normally associated with undesirable aromas. The table below lists the main ones.

Table 4 – Sensory descriptors for sulphur compounds

Compound	Stucture	Sensorial Description
Hydrogen sulphide	H2S	Rotten eggs, rubbish
Ethyl mercaptan	CH3CH2SH	Phosphorus, sulphides, earth
Methyl mercaptan	CH3SH	Rotten cabbage, burnt rubber
Diethly sulphides	CH3CH2SCH2CH3	rubber
Dimethly sulphides	СНЗЅСНЗ	Canned corn, cooked cabbage, asparagus
Diethyl disulphides	CH3CH2SSCH2CH3	Garlic, burnt rubber
Dimethyl disulphides	CH3SSCH3	Vegetable, cabbage, onion
Carbon disulphide	CS2	Sweet, light, green, sulphides

Source: ETS

# Other changes

- Volatile acidity a characteristic vinegar smell, which may be associated with bacterial contamination.
- Volatile phenols the presence of volatile phenols is associated with the growth of yeasts (of the Brettanomyces and Dekkera genus), which are able to grow in wines in low residual sugar concentrations as well as have the ability to transform phenol acids into volatile phenols. The presence of one group of components called volatile phenols (4-ethylguaiacol and 4-ethylphenol) in wine is responsible for this flaw. These chemical components have the following descriptors: condiments, vanilla, carnation, but also smoke and burnt wood (when 4-ethylguaiacol predominates); and the smell of leather, stables and horse sweat (when there is a higher concentration of 4-ethylphenol).

#### TCA and the natural cork stoppers

It is common to associate the cork stopper to contamination with TCA – hence the reason for the expression "cork taint". This expression is applied erroneously, seeing as contamination with TCA may have various origins. TCA has been detected in various products since the '80s: bottled mineral water, beer, wine bottles sealed with screw caps, soft drink cans, packed food products and even raisins. "Presently, it is widely accepted that a 'musty taste' can be originated from many sources and not only from cork stoppers..." - Wine & Spirit Association (United Kingdom), www.wsta.co.uk. Another article published in the Australian Journal of Grape and Wine Research (2005), by Mark Sefton and Robert Simpson describes the "Compounds causing cork taint and the factors affecting their transfer from natural cork closures to wine", www.asvo.com.au.

It is currently known that TCA results from the activity of microorganisms, namely, fungi, in the presence of organochloride compounds. There is a risk of TCA occurring whenever phenols, chlorine and fungi are present.



Being aware that TCA can occur in cork stoppers, the cork industry invested heavily in research and it has already acquired enough knowledge to control the appearance of this compound.

#### **TCA detection studies**

#### a. SPME-GC/MS analysis

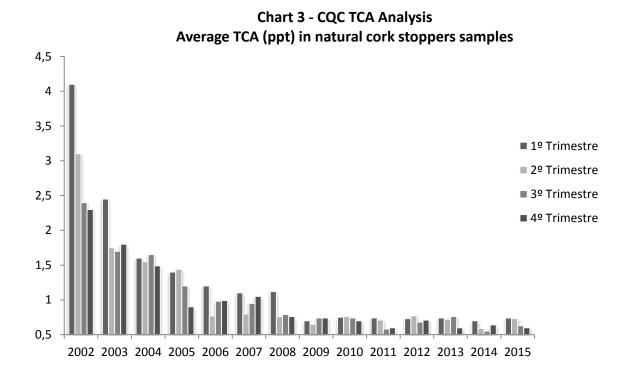
This applied research project, which is an initiative of the Cork Quality Council, that allowed technologically complex and highly sensitive equipment to be used in the quantification of TCA in cork lots.

This concerns the combination of the Solid Phase Micro Extraction (SPME) technique with Gas Phase Chromatography (GC), preferably adopting the Mass Spectrometric Detection (MS). The use of other highly sensitive detecting systems, such as Electron Capture Detection (ECD) is also feasible. During the first phase of the research, new analytical tools were identified in order to replace the sensory method with a chemical testing procedure. According to researchers, "The aim was to develop a non-destructive qualitative test by simultaneously allowing an improvement with regard to sensitivity and reliability".

The second and third phase of the research ended with the definition of releasable TCA by laboratory analysis of the level of TCA of cork stoppers and the correlation with their performance in wine bottles. Information on the dynamics of TCA transfer was necessary to understand what conditions are required for a representative analysis.

The fourth phase, which is currently in progress, is aimed at applying the laboratory methodology to a commercially viable quality control tool, giving rise to the current ISO 20752.

In 2015, CQC ran over 30.000 tests based on this methodology. The results of the last thirteen years show a sharp reduction in TCA levels, of around 95%. In the last test, 91% of samples of natural cork stopper shipments showed values of under 1.0 ng/l and only 7% had results between 1.0-2.0 ng/l.



Source: Cork Quality Council USA



Visit the website of the Cork Quality Council (<a href="www.corkqc.com/currentresearch/CorkTaint/ETS%20CQC-SPME.pdf">www.corkqc.com/newsandpress/cnews2.htm</a>) for more detailed information on SPME-GC/MS analysis of TCA.

#### Main developments by the industry in combating TCA

In addition to the recommendations made in the ICCSMP, companies of the sector implemented other processes to eradicate TCA, including:

#### a. Methods to extract/neutralise TCA

# i. Boiling systems

These processes are dynamic systems where water is circulating continuously and it is treated before it re-enters the boiling system. These systems allow all the cork planks to be uniformly boiled at high temperatures. Furthermore, these systems do not only allow an increase in the extraction of soluble compounds, but also the extraction of volatile organic compounds such as TCA, while also preventing the possibility of cross-contamination.

#### ii. Distillation under controlled steam

The steam distillation of cork products, particularly granular products to be used in champagne and specialized stoppers, is a highly effective process for the extraction of TCA. The volatility of TCA allows its entrainment in the vapour stream. This process is patented by a company of the sector.

# iii. Volatilization by entrainment at controlled temperature and humidity

This process takes advantage of the fact that TCA has a volatilization temperature of 60°C. In a constantly renewed atmosphere of high relative humidity and temperatures above 60°C a significant extraction of TCA from cork stoppers is achieved. This process is patented by one company in the industry. It is used on natural cork stoppers since, besides being highly effective in reducing TCA, it does not deform the stoppers.

iv. Volatilization by entrainment in gas phase with polarity adjusted, under controlled temperature and humidity

This process patented by a company of the sector relies on principles of distillation and steam entrainment and seeking a polarity adjusted to the extraction of molecules such as TCA, it adds the use of ethanol in the entrainment phase.

The process allows the effective treatment of natural cork stoppers, preserving all of the physical and mechanical properties, through the optimal combination of temperatures - close to 60°C - ethanol concentration in the vapour phase and continuous introduction of hot air.

The process simulates the transfer of molecules from the cork to the wine in the bottle, through the solvent effect of ethanol. Thus, it promotes the early migration of undesirable aromas that are entrained by a stream of continuous extraction during the treatment cycle.

The technology developed is inspired in the concept of migrating TCA that emerged in the late 1990's. It also opened doors to new practices of quality control for stoppers.

# v. Extraction with CO2 in the supercritical state

This process subjects granulated cork to a stream of CO2 in supercritical state to remove TCA and possibly other volatile compounds from cork products. This process was patented by a company of the sector.



## b. Methods for prevention of TCA formation

#### i. Ionisation

The substantial reduction of the microbial load contributed significantly to the prevention of TCA forming. Ionisation is a sterilizing process of different materials, which can be used in cork products, contributing to its microbial decontamination.

#### ii. Microwaves

The system operates by vibrating the intramolecular bonds using electromagnetic waves, which cause internal heat generation. This increase of internal temperature promotes the phenomena of evaporation, namely water present in matter, allowing co-volatilisation of metabolites by the action of steam.

#### iii. Symbios

Symbios is the process developed by Cork Technology Centre (CTCOR) that prevents the formation of chloroanisoles in cork, which include TCA. It is a biological process of a preventive nature that promotes the development of "benign" microorganisms naturally occurring in cork, to the detriment of microbial species that may potentially form unwanted metabolites and it promotes the inhibition of chloroanisoles biosynthesis during the cork processing stages.

An additional advantage is that during the cork boiling stage this process promotes greater removal of water soluble materials from the cork, for example earth and polyphenols (which could have a potential negative impact on the beverage in contact with the cork).

#### iv. Enzymatic actions

Trichlorophenol is the main precursor of TCA by fungal methoxylation of the OH group. Some enzymes are capable of polymerizing phenolic compounds, including chlorophenols, making them unavailable for the above-referred methoxylation.

# c. TCA control methods

i. Gas phase chromatography (SPME-GC/MS, SPME-GC/ECD); (ISO 20752).

# ii. Sensory analysis (ISO/PRF 22308)

Sensory analysis has contributed for many years to the quality control of cork stoppers. The analytical procedure is stated in ISO/PRF 22308 standard and it has the advantage of not only describing methods to identify musty smells, but also other aromas that may possibly be present in the cork stoppers. Recently high technology has been developed and implemented, which allows a revolution in quality control, introducing for the first time an individual sorting in the production lines of cork stoppers, based on gas chromatography, one of the most sophisticated chemical analysis of the world. As a result it is possible to provide to the market natural cork stoppers with the guarantee of undetectable TCA, ensuring an irreproachable sensory control. It means that this technology enables to detect in any cork that presents more than 0.5 nanograms per liter (ppt – part per trillion) of TCA, removing it from production line.

The TCA curative, preventive and control processes in cork products have significantly contributed to the qualitative improvement of those products and their improved image among users, consumers and wine critics.

Some examples of what we have just mentioned are expressed in the following references: Christian Butzke, Ph.D., Associate Professor Food Science, Purdue University said: "TCA is no longer a problem..." His analyses at the Indy Wine Competition recorded TCA levels below 1%. (May/June 2009 edition of Vineyard & Winery Management);



Robert Parker, at the end of The Grand Garnacha Tasting at the Winefuture Conference in November 2009, said: "A great success and triumph for Spain .... my tasting had over 650 people and about 200 on the waiting list ... 600 bottles of wine opened and less than 1 percent had "cork taint". Jancis Robinson, following a tasting with more than 200 bottles of Bordeaux 2006 vintage, said:

"Perhaps the best news is that we had virtually no bottles contaminated with TCA, which means that the cork industry took the problem of TCA seriously." The article is titled 'A mean, green streak in the crimson', and was published on 30 January 2010.

# Oxygen permeability of stoppers

Understanding the impact of oxygen in the various stages of preparation and storage of wine is crucial to ensure the quality standards set by the producers. Oxygen is a factor involved in the ageing of wine in the bottle. Its transmission is closely related with the closure.

The management of oxygen in the wine starts during vinification, continues in bottling, extends to the storage in the bottle through factors such as: the head space between wine and cork, volume, pressure and gas composition of the head space, and lastly, the ingress of oxygen through the closure. The closures play a significant role with regard to the transmission rates of oxygen during the storage of wine. In a three year study developed by the University of Bordeaux (France), and using a non-destructive colorimetric method, the inflow of oxygen was quantified in natural cork stoppers, technical cork stoppers, synthetic stoppers and different aluminium caps. The results showed that the different types of closures have significantly different permeability to oxygen. The screw caps (Liner Saran-tin) are hermetic and do not allow the entry of oxygen into the bottle over time. In contrast, the synthetic closures permit a substantial and constant flow of oxygen from when placed on the bottle. Between these two extremes of behaviour for oxygen are cork stoppers that have, however, different kinetics, depending on the type: technical cork stoppers allow a small flow of oxygen during the first month after bottling, which is then negligible thereafter; natural cork stoppers allow a significant increase of oxygen

In the same study it was concluded that vertical or horizontal storage has little impact on the inflow of oxygen through the various closures. These results are in line with data published in 2003 by Skouroumounis et al. which showed that there is no effect on the composition and sensory properties of white wines for a period of five years when left in storage.

in the bottle in the first months, followed by a period of dwindling inflow until about one year, after

#### **Oxidation and Reduction**

which the inflow of oxygen becomes negligible.

The ability of a closure to contribute to oxidation and/or reduction of bottled wine is very heavily linked to its oxygen transmission rate (OTR). Most winemakers acknowledge that some oxygen transmission through the closure is favourable for the evolution of the wine.

In a study, the performance of different closures on the evolution of a Sauvignon Blanc for two years in bottle showed that the sensory evolution of the wine was balanced with cork stoppers. The wine proved to be more evolved using synthetic closures and presented notes of reduction with the screw cap Sarantin, showing a better evolution with Saranex.

The results of the chemical analysis (ascorbic acid, sulphurous, colour, 4MMP, 3MH, H2S) correlated with the sensory evolution observed for different closures.



# **Technical bibliography for consultation**

- Lopes, Paulo Study of Oxidation phenomena during wine bottle aging. Closures' role Faculté d'Oenologie de Bordeaux, Université Victor Segalen Bordeaux (2005)
- Limmer, Alan Do corks breathe? Or the origin of SLO The Australian and New Zealand Grapegrower and WineMaker (2005)
- Lopes, Paulo et alli Impact of different closures on intrinsic sensory wine quality and consumer preferences; Wine & Viticulture Journal March/April (2012)
- Godden, P. W. AWRI trial of the technical performance of various types of wine closure. Australian Grapegrower Winemaker (425): 59–64; (1999)
- Godden, P. W.; Francis, I. L.; Field, J.B.; Gishen, M.; Coulter, A.D.; Valente, P.; Høj, P.B.; Robinson, E.M.C. Wine bottle closures: physical characteristics and effect on composition and sensory properties of a Semillon wine. Australian Journal Grape Wine Res. 7: 64–105; (2001)
- Herve, Eri; Price, Steven; Burn, Gordon Evaluation of a Quality Control Tool for Predicting the Distribution of 2,4,6-Trichloroanisole in Bottled Wines (2006)
- Chatonnet, Pascal Identification and Responsibility of 2,4,6-Tribromoanisole in Musty, Corked Odors in Wine, Journal of Agricultural and Food Chemistry (2003)
- Coque, Juan José Rubio Wine Contamination by Haloanisoles: Towards the development of biotechnological strategies to remove chloroanisoles from cork stoppers, Inbiotec (2006)
- Limmer, A., "Winemaking: Suggestions for dealing with post-bottling sulphides", The Australian and New Zealand Grapegrower and Winemaker, December 2005, pp 67-75
- Skouroumounis, G., Kwiatkowski, M., Francis, I., Oakey, H., Capone, D., Duncan, B., Sefton, M., Waters, E., "The impact of the closure type and storage conditions on the composition, colour and flavour properties of a Riesling and a wooded Chardonnay wine during five years' storage", Australian Journal of Grape and Wine Research 11.3, 369-384
- Brajkovich, M., Tibbits, N., Peron, G., Lund, C., Dykes, S., Kilmartin, P., Nicolau, L., "Effect of screwcap and cork closures on SO2 levels and aromas in a Sauvignon Blanc wine', Journal of Agricultural and Food Chemistry, October 2005, 10006–10011, (http://pubs.acs.org/cgibin/abstract.cgi/jafcau/2005/53/i26/abs/jf0512813.html)
- Lopes, Paulo, Saucier, C., & Glories, Y., "Non-destructive colorimetric method to determine the oxygen diffusion rate through closures used in winemaking", Journal of Agricultural Food Chemistry, 2005, 53, 6967-6963.
- Limmer, Alan, "The Chemistry of Post-bottling Sulphides in Wine", Chemistry in New Zealand, September 2005
- Gibson, Richard, "Variability in permeability of corks and closures", presentation at the American Society of Enology and Viticulture Science of Closures Seminar, June 2005.www.scorpex.net/ASEVClosures2005RGibson.pdf.
- Limmer, Alan, "The chemistry and possible ways of mitigation of post-bottling sulphides", New Zealand WineGrower, Winter of 2005, pp 34-37
- Limmer, Alan, "Redox, reactions, sulphides and general misconceptions", New Zealand WineGrower, Summer of 2004-05, pp 44-46
- Casey, John, "Sealing wine bottles with cylindrical stoppers", Australian & New Zealand Grapegrower and Winemaker, Annual Technical Issue 2001, pp 64-70
- Casey, John, "The cork paradox", Australian & NZ Grapegrower and Winemaker, Annual Technical Issue 1998, pp 15-20
- Sefton, M. & Simpson, R., "Compounds causing cork taint and the factors affecting their transfer from natural cork closures to wine a review", Australian Journal of Grape and Wine Research 11.2, 226-240
- Almeida, J., "Bouchons liege: le contrôle chromatographique du TCA comme premiere mesure de prévention", Revue des Oenologues, November 2005



- Prescott, J., Norris, L., Kunst, M., Kim, S., "Estimating a «consumer rejection threshold» for cork taint in white wine", Food Quality and Preference 16, 2005, 99 345-349.
- Chatonnet, Pascal, "Etude de la réduction de la teneur en 2,4,6-trichloroanisole présent dans le liège par un système d'entraînement continue à la vapeur", Revue Française d'OEnologie 209, November-December 2004, pp 22-26
- Godden, Peter, Francis, L., Lattey, K., Eichinger, P., Buick, D., "Results obtained from the testing of the «reference closures» included in the AWRI's «Commercial closure trial»", Technical Review 151, August 2004
- Chatonnet, Pascal, Boutou, S., & Labadie, M., "Identification et responsabilité du 2,4,6-tribromoanisole (TBA) dans l'odeur « moisie, bouchonnée » des vins", Revue des Œnologues 111, March 2004, pp19-24
- Capone, D., Skouroumounis, G., Sefton, M., "Permeation of 2,4,6-trichloroanisole through cork closures in wine bottles", Australian Journal of Grape Wine Research, 2002, 8, pp196-199
- McGarrity, M., Roberts, C., Fitzpatrick, M. "Identification, cause and prevention of musty off-flavours in beer", Master Brewers Association of the Americas TQ, vol. 40, n.º1, 2003, pp 44-47
- Capone, D., Sefton, M., Pretorius, I., & Hoj, P., "Flavour Scalping by Wine Closures", Australian and New Zealand Wine Industry Journal, Vol. 18, 5, September-October 2003
- Chatonnet Pascal, & Labadie, M., "Des clés pour choisir ses bouchons", Revue Française d'OEnologie 198, January/February 2003
- Barker, D., Capone, D., Pollnitz, A., McLean, H., Francis, L., Oakey, H., Sefton, H. & M. "Absorption of 2,4,6-trichloroanisole by wine corks via the vapour phase in an enclosed environment", Australian Journal of Grape and Wine Research 2001, 7, pp 40-46
- Casey, John, "Tain't necessarily so', Australian & New Zealand Wine Industry Journal, November-December 1999, Vol. 14 N.º 6, 49-56
- Hervé, E. Price, S. Burns, G. Weber P., "Chemical analysis of TCA as a quality control tool for cork", extended paper based on the presentation at the American Society of Enology and Viticulture Annual Meeting, Reno NV, February 1999, available at the Cork Quality Council website http://www.corkqc.com/asev/asev2-2.htm#PAGE1