Supercritical fluids

An innovation for cork closures! Part 2 of 2

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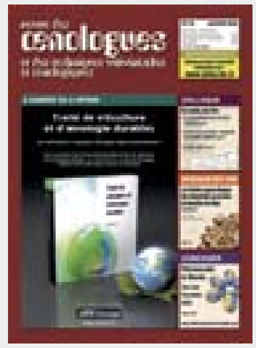

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Introduction

In our previous article, we discussed the properties and industrial applications of supercritical fluids (SCF). We saw that in the majority of cases, the applications mainly involved the use of carbon dioxide (CO_2). It is so commonly used because it is relatively inexpensive, abundant and inert with respect to other products or substrates with which it comes in contact, thus enabling its use as a food-grade fluid. Technically, its critical point (73 bar at 31 °C) makes it easily compressible in order to reach the supercritical range that is of interest to us. Its properties mean that it will behave as both a liquid, owing to its high density, and as a gas, thanks to its very low viscosity. As a function of the pressure and temperature parameters, its density and therefore its solvency will be adjusted as a function of the medium being treated (preservation of mechanical properties) and the target solute that one wants to extract (polarity and molar mass of the compound). Carbon dioxide also contributes to greenhouse warming. However, the carbon dioxide used in SCF facilities comes from the capture and storage of carbon waste from some chemical processes (ammonia, ethylene oxide, etc.). This CO_2 is captured and conditioned by firms that specialize in gas sales (Carboxyque, Messer, etc.), and is then supplied to various segments of the food industry (inert gas blanketing, carbonated soft drinks, brewing, etc.). The DIAMANT® plant, whose process is based on the extraction of 2,4,6-trichloroanisole (TCA) from cork using SCF, will ensure full recycling of the CO_2 used in order to compensate for the high costs of investment, while also preventing environmental emissions. The quantities emitted are much lower than those released from fossil fuels (natural gas, gasoline, coal, transport, etc.).

The core aim of the wine closure business is to exploit the fantastic characteristics of cork, a natural product with properties that make it particularly suitable for the preservation of wine in bottles. Furthermore, at a time when its use is starting to be disputed and replaced by plastic (polymer-based) or metal (screw cap) closures, cork is still the most sustainable solution. Its cultivation and use are endlessly renewable and do not drain resources. Cork oak forests, like any other form of agriculture, are desirable, since they help to maintain and/or increase plant biomass, which is a well-known source of carbon matter that can absorb the excess CO_2 released by the use of fossil fuels.

Some occasional issues of cork taint have compromised the natural relationship between cork and wine. Cork is not inert with respect to wine, since it provides components that can interact with wine, either positively or negatively. Many studies have been conducted around the world in order to search for the origin of the cork taint issue and to resolve it. Cork taint is most often associated with the presence of organic compounds, the most frequently cited ones being the chloroanisoles (particularly 2,4,6-TCA (trichloroanisole)) and their precursors, the chlorophenols.

The cork taint issue

When one looks at the complexity of a cork closure production line, one understands that each of the steps is likely to affect the organoleptic quality of the finished product. This is why it is preferable to set up a policy of integration in the cork industry, in order to better control the selection and inspection of raw materials from the forest all the way to delivery to the customer. Generally, production units work in accordance with the rules defined by the International Code of Cork Stopper Manufacturing Practices (ICCSMP). Compliance with this code of Good Manufacturing Practices must be verified annually, by means of a third-party audit, within the framework of Systécode.

A great number of tests, involving both tasting and chromatographic analyses, are implemented throughout the production process. The application of these different measures has decreased the frequency of cork taint issues, but has not eliminated them. Variable concentrations of chlorophenols and chloroanisoles are found in corks. The need to extract these compounds has quickly become evident. The constraints that must be taken into account have led to the compilation of the following specifications:

- **A dedicated process** for preparation and cleaning of the raw cork, with minimal impact on the treated material, on operator safety and on the environment,
- **A process which eliminates** the undesirable organic compounds selectively and with the greatest possible extraction yield: chlorophenols, chloroanisoles, etc.,
- **A process which does not affect** the other organic compounds that give cork its essential properties for its use as a closure or as a raw material for making closures.

This approach has made it possible to evaluate a large number of processes, but none have met all of the requirements. This evaluation has led to the choice of an extraction technique for these compounds by steam entrainment. This technique is now applied to the treatment of granulated cork used to make standard technological cork closures. However, it is only a partial solution, since the extraction yields are not at a maximum.

Cork treatment: From the laboratory to industry

The studies started in 1996 consisted in observing the yield of the extraction technique, which involved measuring the residual contents of chlorophenols and trichloroanisole, and also in verifying that the process did not alter cork's mechanical properties. Initially, **in the laboratory,** the study consisted in varying several parameters:

- The pressure/temperature pair (choice of solvency),
- The solvent rate (quantity of supercritical fluid per kilogram of treated material),
- The addition of a co-solvent (to enable selective extraction).

We chose a specific co-solvent to increase the polarity of the supercritical fluid and thus decrease the solubility of non-polar compounds such as waxes. Different types of materials were tested in the laboratory (on extractors with capacity of a few liters), as shown in ***photos 1a and 1b.***

The results obtained in the laboratory on samples whose PCP (PentaChloroPhenol) and TCA contents were known, were quite encouraging. We can see that the yield on boiled cork is 96% for PCP and 100% for TCA, as indicated in ***figure 1.***

We have also observed that there is a synergistic effect, provided by the chosen co-solvent, on the destruction of micro-organisms. This unexpected effect was verified on different populations of micro-organisms. This effect is very significant, since it drastically minimizes the risks of later recontamination, via these micro-organisms, on the treated materials. In parallel, a great number of studies have helped to confirm that the process does not negatively affect the internal structure of the cork, which retains its dimensions and its mechanical performance, as ***photo 2*** and ***figure 2*** illustrate.

All of these studies have been the subject of an international patent application. The supercritical fluids & membranes laboratory at CEA in Pierrelatte (Drôme) possesses a semi-industrial unit (600 liters) dedicated to tests that estimate the yields of the processes developed in the laboratory, when the size of the treated batches is increased. As such, this tool has enabled us to implement an increase in scale by a factor of 100 with respect to the laboratory. ***Photos 3 and 4*** show, first, a pilot unit, and secondly, tests conducted on cork powder.

Figure 1: Effectiveness of treatment of different samples.

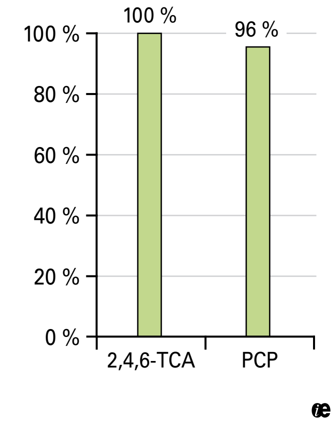
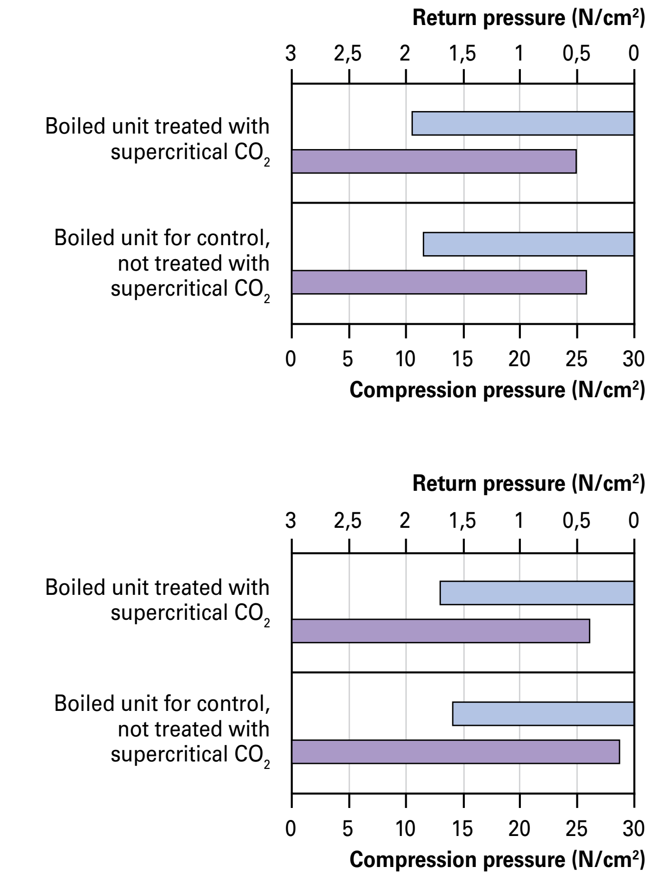


Photo 1a: Loading of a cork plank.

Photo 1b: Loading of cork powder.

Photo 2: Dimensional variation measurements on cork closures.

■ **Figure 2: Comparative measurements of mechanical characteristics.**



■ **Photo 3: SCF pilot unit (3 x 200 L) at CEA.**

■ **Photo 4: Unloading of cork powder.**

The results obtained from the naturally contaminated cork batches have confirmed the yield, the good homogeneity and the repeatability of the extraction process and have enabled us to refine and validate the process parameters. The quantities produced have enabled the manufacture of a significant number of technological cork closures and verification that performance levels are maintained.

An external validation process was conducted on different wines from different countries. The panels selected the test wines as a function of their sensitivity to this type of organoleptic defect as well as the laboratories in charge of chromatographic testing.

In the United Kingdom, the tasting panel was composed of respected professionals and opinion leaders from the trade press and retail trade. The varietals were Colombard and Cabernet/Merlot, and the analytical laboratory was Campden & Chorleywood Food Research Association (CC-FRA). In the United States, the tasting panel was composed of professional tasters and winemakers. The varietals were Semillon and Dolcetto, and the analytical laboratory was ETS (Expertises, Technologies & Services). In Australia, the tasting panel was composed of professional wine tasters from the Australian Wine Research Institute (AWRI), the varietal was Semillon and the analytical laboratory was AWRI. In all cases, the results produced by these three panels were found to be very positive after more than 18 months since bottling. The analysis of the wines was done by SPME (solid phase micro-extraction), gas chromatography (GC) and mass spectrometry (MS).

Analytical results

United Kingdom

Out of a total of 1440 wine samples that were tasted and then analyzed by GC-MS (CC-FRA data):

- **97.8%** were found to have a 2,4,6-TCA content lower than the limit of detection of the analytical method (LOD: **0.2 ppt)** (ppt: parts per trillion: 10-9 g/g),
- **99.3%** were found to have a 2,4,6-TCA content lower than the limit of quantification of the analytical method (LOQ: **0.5 ppt),**
- **99.9%** had a 2,4,6-TCA content < **1.0 ppt.**

USA/Australia

Out of a representative sample of 300 wines that were bottled, tasted and then analyzed by GC-MS:

- **100.0%** were found to have a 2,4,6-TCA content lower than the limit of detection of the analytical method (LOD: 1.**0 ppt)** (ETS data),
- **100.0%** were found to have a 2,4,6-TCA content lower than the limit of detection of the analytical method (LOD: **0.5 ppt)** (AWRI data).

Sensory analyses

Figure 3 displays the results of the sensory analysis performed by AWRI after 18 months. The samples, including the natural cork closures and the screw caps, were evaluated under blind tasting conditions, using standardized procedures, in a random order with a constant volume of wine in each glass. The tasters first evaluated each wine by olfaction and then by taste. The participants scored each attribute on a scale of 0 to 9, where 1 corresponds to barely detectable, 5 to moderate intensity and 9 to very high intensity.

An analysis of variance was performed in order to assess the closure effect, taking into account replicates, using a mixed model that treated the judges as a random effect.

Owing to a highly significant TCA effect, a new analysis of variance, taking into account the TCA perceptions, i.e. dealing with the TCA perceptions as co-variables, was conducted. The DIAM® technological closure performs very well. We can note a significant difference in reduction aromas between DIAM® and the control screw cap. The result obtained for the oxidized descriptor confirms that the internal structure of the cork material is not negatively affected by the extraction process. The enological analyses for free and total sulfur dioxide in the wine, which are critical parameters as concerns wine stability and protection against oxidation, have shown that losses are similar between DIAM® and the screw cap, with the same performance homogeneity.

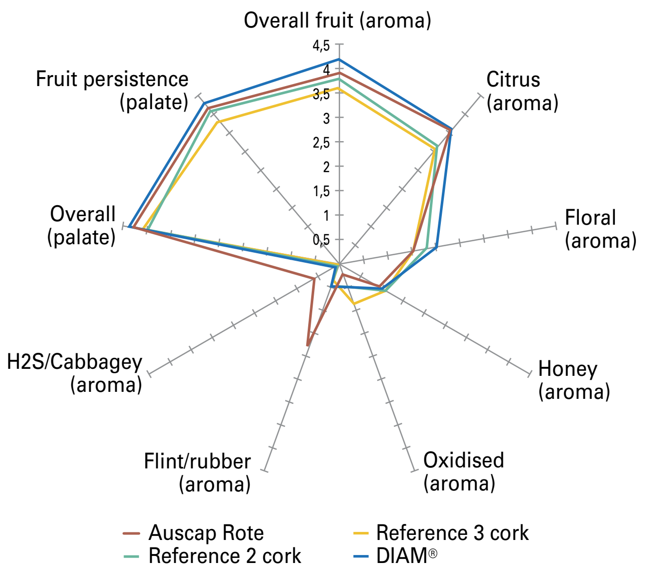
On the industrial scale, a subcontractor with an industrial-scale supercritical fluid extraction unit (capacity: about 20 m³) was selected. The scale factor is 30 with respect to the CEA pilot unit. The parameters were, once again, optimized and validated, such as contact time and solvent rate...

On this scale, in continuous operation, the extraction yield was then evaluated thanks to the results of releasable TCA measurements conducted on each of the treated batches, as presented in ***figure 4.*** The results for residual releasable 2,4,6-TCA on granulated cork are systematically below the limit of quantification of the analytical method (< 0.5 ng/L).

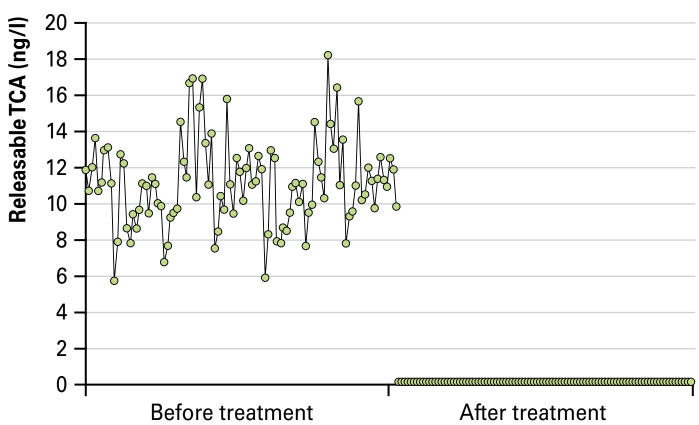
Conclusion

The investment decision (€ 15 million) was made by the industrial firm at the end of 2003, for a facility using SCF as the cork treatment solution. It is located in San Vicente de Alcantara (Extremadura, Spain). This highly original initiative is a world's first in the cork industry, and this facility will be one of the largest of its kind in the world. To meet current demand, cork treatment is conducted by an industrial partner, which enables the cork producer to produce and distribute DIAM® closures at a rate of ten million units per month. In the second semester of 2005, the start-up of the treatment unit (approx. 2500 metric tons/year) will bring this monthly production capacity up to 40 million DIAM® units. As it has been shown that even low TCA concentrations lead to a loss of quality in certain bottled wines, thus decreasing their aroma cleanness and intensity, the use of these closures thus eliminates this very high risk factor for winemakers. In effect, when taint issues arise, the final consumer has a tendency to consider this defect as being related to the wine, and not to the closure. Furthermore, this performance is homogenous for all closures. Lastly, this helps to offer consumers bottles with a homogenous taste that does not vary from one to the other and to propose a solution whose process is based on sustainable chemistry and whose raw material is natural and perfectly in line with the principles of sustainability. In terms of future outlook, studies are now underway to validate the results for natural cork closures on the industrial scale. ■

■ **Figure 3: Sensory analysis results 18 months after corking (AWRI data).**



■ **Figure 4: Unloading of cork powder.**



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