The Path to TCA-free Cork, Part 2:
Production and Testing

Richard Carey
Amorim’s ROSA procedure is part of the process used for removing TCA from granules and cork discs. This photo shows the engineering complexity that the industry has developed to provide high quality stoppers.
PART 1 OF THIS SERIES on cork discussed changes the industry has undertaken to protect its place in serving the wine industry, from growing the cork oaks, *Quercus suber*, to delivering cork planks to the processing plant. This article will review changes in cork production methods from that point until the corks produced are shipped to wineries or suppliers. Changes in the cork manufacturing technology began about 30 years ago, and today production equipment and techniques for testing corks have been improved so that the cork industry can now assure quality control, clean cork and an improved distribution system.

Every year improvements are made to bring the main problem, 2, 4, 6 Trichloroanisole (TCA), under control. This compound has bedeviled cork suppliers and wine consumers alike. The good news is that the presence of TCA in corks in the distribution system is, on average, trending lower as new systems are introduced. Wineries can have fewer worries that a given bottle will have the aroma and taste of TCA in that wine.

First Steps in Cork Plank Processing

Much of the cork bark arrives at the processing plant loaded on trucks, and some has been stacked on pallets. Each load is tagged and identified with its original location for traceability and problem solving in the forest. Planks are then stored on concrete surfaces and on pallets, either outside or under roof. Many acres of ground are devoted to storing planks of cork bark. Most suppliers indicated that they process their cork within the growing year from harvest. For example, Cork Supply seasons their cork for six months and then produces corks over the next six months.

In the early days of cork preparation, it was common practice to dump the cork planks into a boiling water bath. The primary purpose of this was to soften the cork for processing. It also removed gross contaminants, such as dirt and other materials, and made the cork easier to process. In the late 1980s, cork producers found that this system released TCA into the water. Too often batches failed to remove TCA because one severely contaminated plank affected the entire batch. Just boiling did not reduce TCA to a concentration level below threshold, so a new system was needed.
WHEN TWO INNOVATIVE COMPANIES COME TOGETHER, EXTRAORDINARY THINGS HAPPEN.

“Because of their forward-thinking and innovative nature, Cork Supply was a perfect fit as a scientific partner when we first theorized how to eliminate TCA from large format bottles of wine. Together, we developed what is now widely known as the ‘Dry Soak Method,’ which was first published in the Journal of Agricultural and Food Chemistry and is today an open source technology available to the entire global wine and cork industry. Our work together has changed the game for the cork closure industry collectively, and at Silver Oak specifically.”

Christiane Schleussner
Silver Oak Alexander Valley Winemaker

www.corksupply.com
TCA Removal from Cork Bark

Ganau Cork was one of the first companies to use an autoclave to remove more TCA. That autoclave was installed in 1995 by the father and uncle of Mariella Ganau, current president of Ganau USA. Amorim installed an autoclave in 1999. These commercial-sized autoclaves perform the same function as laboratory autoclaves: both autoclaves have a pressurized container where water boils above 100°C. The initial success in removing TCA resulted in M.A. Silva developing and installing their Dynavox system in 2003. Cork Supply added a similar system in the same time frame. These various boiling methods minimized the previous fixed-volume bath method.

The newer systems recycled water and degassed volatile compounds through a variety of methods and filtration to minimize the possibility of TCA carry-over from one batch to the next. Some volatiles are extracted during the boiling process, and the bark plank actually increases in volume by about 20 percent. This step removes waste and also ensures and expands a good cell structure to help seal the cork to the bottle.

The autoclave operates at 1 atmosphere pressure, and the increased temperature helps extract the cork volatile compounds that can either co-distill with water vapor or vaporize compounds according to their boiling point.

In some facilities the steam from the autoclave is recirculated through a tower, and TCA or related compounds are scrubbed out of the vapor so the water can be reused. In other places, the water is not reclaimed. While the processing of water for reclaiming or for one time use was an important advance, it had some drawbacks. This process reduced the amount of TCA by 85 percent or more, but that was not enough to handle a severely contaminated plank in a given batch. It was common knowledge that the physical mass of the plank would not allow sufficient TCA to be removed in a reasonable length of time for it not to be a continuing problem.

The solution was to create a process that was both preventative and curative to target individual punched corks for TCA removal. The processed planks are stored and then positioned for reduction into punched cork or micro-agglomerated stoppers, including champagne stoppers.

Punched Cork Process

No one process or step is sufficient to remove any carry-over TCA from plank to stopper. It is all the steps taken together that get the individual cork to the point where it can seal a bottle and ensure that it does not contaminate the wine.

Bark planks are sliced into widths to produce the proper length of cork. These slices are then fed manually or automatically into a puncher that produces each cork. The thickness of cork bark orients the direction a stopper takes to punch a cork. A stopper is punched parallel to the trunk, and each cork then goes to bins for quality selection. The excess bark is sent to the agglomerated cork system for conversion into other products; what is not used there (dust <0.5 mm) is turned into energy to help run the plant.
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*Releasable TCA content at or below the 0.5 ng/L quantification limit; analysis performed in accordance to ISO 20752.
Punched corks travel through a maze of selection processes. At every opportunity, the defects found refine the selection process to the quality standard for that process. For example, immediately after punching, grossly misshaped corks are eliminated and sent to the granule side while the rest are collected in bins. Here, machine inspection speeds increase the selection process exponentially. At the outset of this visual quality categorization process, it is important to understand that, other than the oxygen transport rate (OTR), there is no structural difference in corks’ ability to seal wine bottles between the lowest commercial quality cork and the highest.

Despite research efforts to identify internal structural elements, specific elements in a given cork’s internal structure have not been found that reliably determine whether a cork will fail on extraction. Visual elements only provide a higher visual uniformity of each cork.

The visual examination of what the cork surface should look like is developed by each company. That exam considers the number of lenticles, their size and their arrangement. Other deformities on the surface of the punched cork are taken into account. The result is a digital image of what constitutes one quality level from another.

There are several devices that help with this sorting so that the manufacturer can produce their quantities of cork. In fractions of a second, a cork flies off into a bin, based on its visual representation compared to a standard image made by the producer for each level of quality. When the cork reaches a trigger point on the cork track, it shoots the cork into the proper grade hopper. This happens at a rate of three or more corks per second per machine. Collectively, all cork producers must have many machines working simultaneously to produce 5 to 6 billion punched corks a year.

After the cork bark has been reduced to individual punched corks in the first quality selection, the next phase varies from producer to producer. After using their proprietary autoclave, which has been in use since 1995 on cork bark, Ganau started using it on punched corks in 2016 when vacuum steam was added as part of the process. They adopted an ozone washing system in 2019.

Amorim introduced their ROSA process in 2002/2003 for cork bark treatment that was also modified to treat punched corks. They have a patented process known as therma desorption that is based on vacuum steam to further reduce TCA in their punched corks.

In both of these processes the goal is to reach a higher effective pressure differential to drive TCA out of the cork.

Other companies have different variations on this processing method. M.A. Silva’s Maszone process released in 2003 uses peroxide and ozone to neutralize aromas in punched cork, and in 2018 they introduced a dry steam treatment. Cork Supply has a two-step process for their punched corks. In 2019 they added PureCork, a process where corks undergo steam distillation for 24 hours as the first part of TCA removal. This is followed by Innocork, a process started in 2007 that combines high temperature steam and ethanol extraction for one hour to remove TCA.

The final steps in punched cork processing are sanding and washing. The degree to which corks need sanding depends on the end product. Some corks are chamfered, meaning the edges are tapered.
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After punched corks are treated for TCA removal, they are collected into bins of similar quality and readied for several packaging options. There are two primary paths for packaging from the supplier’s viewpoint: local consumption or export. For the local market, various coatings are applied to the corks that allow them to be inserted easily into the bottle. Corks for export are packaged dry into larger bales. In both markets, many corks are branded and coated locally. Many hand-selection options are available for higher-end customers.

1+1 Cork Creation

In the early 1980s, the cork industry was looking for ways to add value to their business. TCA was a real problem, and its removal from cork became more difficult as the mass of cork that needed treatment increased. 1+1 corks were designed so that a thin punched disk of cork was the wine contact point.

Cork producers had been using the large amounts of waste from punched corks to create products with additional value. Grinding seemed a good alternative. At first, agglomerated cork was composed of ground cork granules bound with a binder into one cork. This process created a problem as TCA is not uniformly distributed within cork. It can vary widely in concentration level. If one area has a high concentration and is then ground into small parts and mixed with a larger batch, that larger batch now has an elevated average concentration at a possibly organoleptically significant amount for the batch as a whole. This was the problem with the first agglomerated corks.

To reduce the chance of TCA transferring to the wine, thin strips of cork were prepared from specially selected lots that tested low for TCA. These disks were then glued onto the ends of the agglomerated stopper, and the chance of TCA reaching the wine was reduced.

Unfortunately, this process also has had several problems. In the past, 1+1 corks used larger chunks of cork, many of which had incomplete removal of TCA because the larger the chunk, the more difficult it was to remove TCA. A second problem occurred frequently during cork removal. In older bottles with 1+1 corks, the removal process strained the cork, which then lost stopper integrity, either at the disk or in the body during removal. The use of 1+1 corks has fallen significantly with the advent of new technology. While the use of micro-agglomerated corks has taken over much of the market share of 1+1 corks, producers have used the technologies outlined here to improve the quality of 1+1 corks.

Micro-agglomerated Corks

Just as the 1+1 cork structure has changed, the agglomerated cork class changed in a parallel manner as the removal of TCA became more efficient. The smaller the cork particle, the easier and more complete was the removal of TCA. Now micro-agglomerated corks are more consistently lower in TCA presence than many punched corks. While the basic process of producing micro-agglomerated corks follows a similar sequence of steps, these steps can vary between processors.

DIAM², the second largest producer of cork stoppers, has pushed the envelope for processing granular cork. Both Amorim Cork and DIAM Bouchage use different super-critical CO₂ technologies to remove TCA from cork granules. All manufacturers that produce agglomerated cork have investigated their sourcing material and understand their supply chain. There is a growing bulk market for cork granules from which many take advantage. Both M.A. Silva and Cork Supply state they do not buy cork granules on the open market, which then defines the maximum number of stoppers they can produce from their own raw material. However, this does provide them with a finer degree of knowledge on the potential for defects that need to be addressed during production. They use a mixture of different cork bark materials, including cork bark plank remnants and thin wood.

There is great competition among the various producers to provide an ideal TCA-free cork stopper. Amorim, which uses their Xpur process for their Neutrocork Premium and Qork cork, and DIAM, with their Diamant process as the basis for all their corks, both claim they reached the TCA-free level a few years ago with their use of super-critical CO₂. Amorim uses a patented fluid bed version of extraction, whereas DIAM is using its patented full-immersion style of super-critical CO₂ extraction.

M.A. Silva states that they have reached a similar goal by using a fluidized bed process, which involves a wet-steam washing of the granules. Cork Supply uses Vapex, which is an alternating process of hot air water vapor followed by a disinfection process. Both companies determined that time and temperature reduce TCA in the microgranules to their process specifications. Ganau has adapted their thermal desorption process for TCA removal from granules.
The Vocus Cork Analyzer is the world’s most sensitive detector of volatile compounds in natural cork stoppers. The validated method uses advanced mass spectrometry to quantify trace levels of TCA and other off flavors in individual stoppers. The finest wines deserve only the purest cork stoppers.

VERIFIED PURITY

A NEW STANDARD OF EXCELLENCE FOR PREMIUM NATURAL CORK STOPPERS
DIAM has a unique feature that is part of cork granule preparation. Cork bark has two layers: the outer bark and the inner bark. The outer cell layer is primarily lignin, whereas the inner layer is higher in suberin encapsulated in a very thin layer of lignin. DIAM takes advantage of this difference by using a slightly sloped vibrating table to separate the mostly lignin part of the cork bark from the suberin-containing cells. As expected, the lignin particles are somewhat more dense than the mostly suberin cells. When the mixed ground bark enters the table, the heavier particles move faster than the lighter suberin. The lignin-separated part falls off the end in greater quantity, and the suberin-containing granules are removed in higher concentrations at a different level. The separated part then goes to DIAM’s biomass power generator to provide power and heat for processing.

The entire cork industry is conducting research to develop techniques that will provide economically versatile products to meet the various needs of the growing wine industry. For example, micro-agglomerate stoppers used to be extruded, but this method has been supplanted by the molded production of micro-agglomerates. Molded corks have a more uniform structural integrity, and the final product can be constructed with different capabilities. Amorim is now producing an agglomerated cork where 80 percent of its mass is cork and 98 percent of its volume.

DIAM uses a construction technique for micro-agglomerated corks that is designed to offer a predictable response in the bottle and additional consistency. First, they add the cleaned granules into the mold mix and then add plastic micro-spheres and a heat-sensitive binder. The heat (about 50°C) in the mold expands the micro-spheres and causes the binder to seal everything together. This construction process allows DIAM to create corks that have defined aging and OTR for different winery aging profiles, from two to 30 years. Their goal is to provide a more predictable life expectancy for a given stopper that meets winemakers’ expectations for the stoppers. DIAM has developed a plant-based binder for their corks under their Origine brand. The cork is manufactured with this plant-based binder and beeswax.

### Super-critical Box

Super-critical box technology takes advantage of an important aspect of compound removal from an insoluble matrix. CO₂ has the property of converting from a solid phase to a gaseous phase directly, a property known as sublimation. However, if the right temperature and pressure are applied to the gas, CO₂ forms a liquid with the diffusivity of a gas and the solubility of a liquid. That allows compounds in an insoluble material to be solubilized into a super-critical fluid. The solubilized compounds can then be extracted from the super-critical fluid by simply letting the fluid return to its vapor state. All of this can occur at more moderate temperatures. The beauty of this process is its efficiency and the ability to recover essentially all the CO₂ used for extraction, which can then be cleaned for reuse. The only problem is that this process system is a plumber’s nightmare of tubes, pumps, tanks and more.

The complexity of the processing equipment for super-critical CO₂ is shown in the photo on the left. The diagram on the right shows the path of the CO₂ in a closed loop system where the CO₂ is reused.
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The greatest task that faces the cork industry is how to manage TCA responsibly and effectively to preserve the market share for cork. Every step taken by a company to prevent TCA is a molecule that doesn’t have to be found and removed later. As outlined above, there are now numerous preventative steps, and more discoveries are made each year. Detection is the subject of robust debate, one that needs to proceed so that there are clear milestones for detection, with quantification limits and variances of results between tests on the same sample. For winemakers, a non-destructive test on individual cork is the best method of assurance for their high-end products.

Many labs and cork stopper companies have used the human nose as their gold standard for non-destructive detection. Unfortunately, research has shown the human nose of any one person is notoriously bad at prolonged exposure to a single compound and is subject to fatigue. Think of baking bread: great when you first smell it but after awhile, your brain becomes accustomed to the odor and no longer triggers the same response. While the human nose is better at differential perception, fatigue is still the primary limitation. With all that, the human nose is a valuable tool but not on a large-scale. It should be reserved for high-end corks where cost is less of an issue as it takes many teams rotating in and out of the testing protocol to keep pace. The only way to extend the volume of cork subjected to the sensitivity of the human nose is by batch testing and then only use human noses to test individual corks in failed batches. From the producers’ perspective, it’s all about their team and how accurate they are at making the discriminations.

The best way to provide neutral analytical information is non-destructive instrumental analysis. Until now, the only reliable instrument for TCA analysis has been gas chromatography mass spectroscopy, which requires equipment that costs hundreds of thousands of dollars and takes incredibly long periods of time to produce results. Therefore, this type of analysis has been reduced to grouping corks into batches where a subsample is soaked, then extracted from the solution and tested. This method slows the detection process so much that detection is delayed until the very end, which is too late. All the cost of conversion into the final product has been spent. If detection of that and all similar contaminations happened earlier, everyone could save money. The industry needs to reach essentially zero TCA, where a statistical chance of a contaminated sample being found is one in thousands, not one in hundreds.

ToFwerk has developed a headspace ionization technique that instrumentally tests each cork. This technique provides discrimination more quickly and accurately than virtually all other analytical systems for cork. The ionized charge gives a unique signature that discriminates one compound from other...
The Tofwerk Vocus wine analyzer (above) is loaded with corks where they incubate for 2 hours. The corks then are moved into the instrument analyzer and each one is individually screened for volatile TCA. The stoppers that pass this test are returned to the production system.

On the chart below, the type of analyses that the Tofwerk Vocus instrument can analyze in 2 seconds are listed at the bottom. On the top are two spectra are the standard analyses for TCP and TCA. The lower two spectra show the same analyses in cork, where all of these analytes are analyzed at once.

**Table 1.** Eight off-flavor compounds that were determined to have significant concentrations in the 4,060 cork stoppers screened with the Vocus CI-TOF

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Acronym</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloranisole</td>
<td>TCA</td>
<td>C₆H₅ClO</td>
</tr>
<tr>
<td>Dichloranisole</td>
<td>DCA</td>
<td>C₆H₅ClO</td>
</tr>
<tr>
<td>Tetrachloroanisole</td>
<td>TeCA</td>
<td>C₆H₅ClO</td>
</tr>
<tr>
<td>Pentachloranisol</td>
<td>PCA</td>
<td>C₆H₅ClO</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>PCP</td>
<td>C₆H₅ClO</td>
</tr>
<tr>
<td>Trichlorophenol</td>
<td>TCP</td>
<td>C₆H₅ClO</td>
</tr>
<tr>
<td>Chloroanisole</td>
<td>CA</td>
<td>C₆H₅ClO</td>
</tr>
<tr>
<td>Tribromoanisole</td>
<td>TBA</td>
<td>C₆H₅BrO</td>
</tr>
</tbody>
</table>

Similar compounds and can make accurate separations between very similar compounds. For haloanisoles, this instrument is calibrated to test for eight related compounds in two seconds per sample, plus one second for sample transfer. The limit of detection is down to 0.2 ng/L. [Author’s note: An in-depth analysis of headspace ionization technology will be the topic of a future article in WBM.]

The on-demand, stand-alone Tofwerk system at the end of the production line provides results as rapidly as one cork every three seconds and assures that each cork that passes will be free of TCA. At this rate, the machine can analyze slightly less than 30,000 corks per day, which is too few corks for this machine to be the final gatekeeper for some companies. Those rejected slightly increase the per unit cost because these stoppers are selected at the end of production. The system sells for about $1.2M. Ganau and Parramon Exportap are two companies that have purchased this instrument and use it in their warranty for TCA-free corks.

Tofwerk has decided to not offer their analytical technique exclusively to any one company. Several of the larger production companies are using their technique in proprietary ways at earlier stages of production. This assures the highest conversion of cork into their most valuable product for the high-end user.

**Product Distribution by Category**

Ganau has reported that in Europe, their sales are 40 percent sparkling wine corks, followed by 20 percent for punched cork, 35 percent for micro-agglomerated and 5 percent for 1+1 corks. In the U.S., the change is not as drastic a realignment: 35 percent are punched cork, 50 percent micro-agglomerated, 10 percent sparkling and 5 percent 1+1 cork stoppers. M.A. Silva reported current ratios of sales in the U.S. as 65 to 70 percent punched cork and 30 to 35 percent for the balance of sales. Cork Supply split their production capacity into 350M punched cork and 650M technical cork. Scott Labs defined their market as 70 percent punched cork and 30 percent technical, whereas Gültig has sales of 30 percent punched cork and 70 percent technical. Portocork, like Scott Labs, caters to ultra-premium wine producers. In a survey reported by Scott Labs, U.S. customers will pay $1 more per bottle when a wine is packaged in cork as opposed to other materials. Parramon USA, as another ultra-premium cork company, until recently sold 100 percent punched cork but is now entering the micro-agglomerate market.

**Sustainability**

Space does not adequately allow a reasonable discussion about the importance of cork in wine packaging. The cork is a very sustainable part of the wine package. All the other elements of packaging have sustainability problems and there are projects in the works to address the issue. To get you started, see Amorim’s sample of their sustainability measures.[10, 11] WBM

**Acknowledgements**

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