

LEADING THE FIGHT AGAINST TCA

The cork industry is applying considerable resources to eliminating TCA (2,4,6-trichloroanisole) contamination in cork and wine. At Amorim, the strategy is to attack TCA at every point in the cork production process.

The issue of TCA is one of the wine industry's biggest concerns.

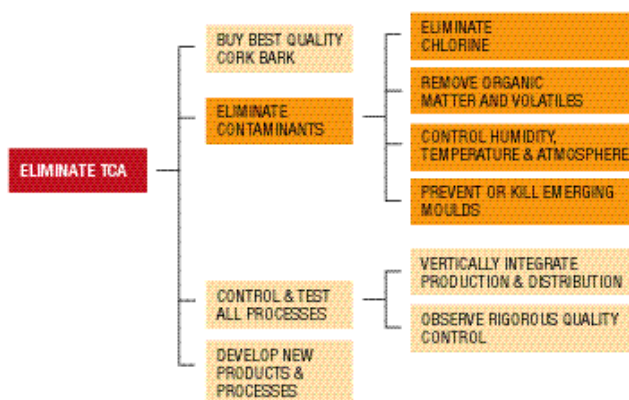
A great deal of research has been done around the world in recent years to isolate the causes of TCA (2,4,6-trichloroanisole) contamination in cork and wine. However, while the picture of TCA sources has become more defined, we still do not have a clear idea of how to defeat them totally.

It is established that TCA is most commonly formed when microorganisms such as moulds come into contact with chlorine compounds, usually chlorophenols (see following article).

There is considerable effort on the part of the cork industry to reduce and finally eliminate this problem using a range of different ideas and approaches. Microwave technology, for example, which is intended to rid the corks of contaminants at the end of the manufacturing process, is one such approach.

Amorim's strategy is to attack TCA at every point of the cork production process—by eliminating the use of chlorine entirely and minimising the opportunities for mould growth at each stage of processing. The aim is to start with the best quality bark available, remove all contaminants at the outset, and avoid conditions in which problematic moulds are known to develop—by controlling moisture,

FIGURE 1 – AMORIM'S ANTI-TCA STRATEGY



Eliminating contaminants is Amorim's main R&D focus at present.

temperature and atmosphere. Punched corks are then sterilised to prevent or kill any emerging moulds (see Figure 1).

This approach applies to the entire production and distribution process, from initial boiling through to final dispatch.

Amorim has also moved to assert control over every stage in the supply chain through 'vertical integration' and enforces stringent quality assurance procedures to ensure its products are monitored and controlled at all times.

An extensive research and development program pursues continuous improvement in products and processes. The program's main

priority is the elimination of TCA taint from wine cork stoppers.

Figure 2 (next page) summarises the main strategic initiatives under Amorim's current program to eliminate TCA and produce corks of the highest possible quality. The remainder of this article describes those elements in greater detail.

Buy the best quality bark

Scientific research conducted for the Quercus Project¹ identified TCA in raw material from cork forests, albeit at very low levels, and found it could be transmitted through to the final cork product. The researchers also found that the concentration of TCA in bark taken from the base of affected trees was higher than that taken from further up the trunk. The research suggested that this difference could be due to leaching of rainwater or contamination from the soil or atmosphere. TCA was also found to be more prevalent in bark that was 'green' or suffering from 'yellow stain'.

Portuguese law bans the use of all pesticides in cork forest agriculture. To minimise the risk of TCA, the European Cork Federation's 1996 Code of Good Practice² recommends that cork from the base of trees, green wood and that affected by yellow stain should not be used for wine closures. It has also proposed that cork planks be kept from direct contact with the ground during the six-month seasoning period after harvest. Its new accreditation system, introduced in 1999, will publish the names of suppliers complying with these guidelines.

Amorim does not rely solely on this accreditation system. The company uses its own purchasing records (spanning 40 years) to track the yield and quality of each of the properties it buys from. At present, Amorim is compiling a more comprehensive database and implementing systematic tracking that will eventually provide a more detailed profile of each property — annual yield, quality, climate, soil, the age of the trees and so forth.

At Amorim's newly opened primary processing facility at Ponte de Sôr (in the south of Portugal), cork from each property is stacked separately, away from direct contact with the soil, and is allocated a unique code that it retains throughout production and distribution. In future Amorim will be able to track an individual cork from the forest to the bottle.

These initiatives will allow Amorim to build a complete profile of cork quality and yield from each forest, identify differences and choose the best raw material. They could also provide data to enhance the understanding of TCA incidence attributable to raw material, pinpoint possible causes and develop targeted solutions.

Eliminate chlorine from water and processing

Since 1994 Amorim has banned the use of chlorine throughout its cork stopper processing.

Amorim factories in Portugal use non-chlorinated groundwater and

FIGURE 2 – KEY INITIATIVES IN AMORIM'S ANTI-TCA PROGRAM

STRATEGIC ELEMENT	IN PLACE (APRIL 2000)	IN DEVELOPMENT
BUY BEST QUALITY CORK BARK	<ul style="list-style-type: none"> Collecting & analysing data from each property 'Tagging' cork from forest to winemaker 	
ELIMINATE CHLORINE	<ul style="list-style-type: none"> Dechlorination of processing water Washing in H₂O₂ 	<ul style="list-style-type: none"> Washing in H₂O₂ and O₃
REMOVE ORGANIC MATTER AND VOLATILES	<ul style="list-style-type: none"> New boiling process with continuous volatile extraction INOS II (Twin Top & SPARK) 	<ul style="list-style-type: none"> INOS II (natural & granulated)
CONTROL MOISTURE, TEMPERATURE & ATMOSPHERE	<ul style="list-style-type: none"> Good ventilation, clean air, dust extraction Oven-drying 	<ul style="list-style-type: none"> Controlled rehumidification to replace second boiling
PREVENT OR KILL EMERGING MOULDS	<ul style="list-style-type: none"> Ozone treatment of processing waters Washing in H₂O₂ and O₃ solution 	<ul style="list-style-type: none"> Stabilisation in ozone atmosphere

in 1999 began ozone treatment of the processing water to eliminate organic contaminants.

At the new factory in Melbourne, Australia, Amorim first de-chlorinates the processing water using activated carbon filtration and then sterilises it using UV radiation.

Hydrogen peroxide has replaced hypochlorite as the disinfectant for washing finished corks since 1988.

These measures have significantly reduced the incidence of TCA in Amorim corks, to an average of less than half a percent over the past seven years. Current efforts focus on minimising the opportunities for contamination due to mould growth during processing.

Eliminate contaminants at the outset

Cork planks have always been boiled at the start of processing to remove organic matter and contaminants and to make the bark more malleable. Boiling has also been found to have the greatest impact in reducing any TCA in cork.³ Traditional processes do not, however, guarantee thorough decontamination. Amorim has developed a new boiling process for all corkwood intended for wine stoppers. Introduced at Amorim's new Ponte de Sôr factory in November 1999, it is being used for the 1999 and subsequent harvests.

The process uses stainless steel autoclaves or closed-system boilers (similar to a pressure cooker), fitted with a unique device that continuously extracts TCA and other volatile compounds. Heat, pressure and water flush out any organic matter and volatile compounds, which are then continuously extracted from the process. In addition, the processing water is filtered, and changed after each boiling cycle. This means that Amorim is using mechanical and chemical means, as well as heat, to decontaminate the cork.

Tests have shown that the process significantly reduces the tannins and microbial load in the corkwood and slows the rate of mould growth. Whereas previously, moulds could develop in three to four days after boiling, now the period is at least 15 days in an uncontrolled environment. Even so, the new post boiling stabilisation chambers are environmentally controlled to further restrict growth and prevent contamination.

Amorim's exclusive INOS II process, developed specifically for the discs used in Twin Top® and SPARK® corks, has been another revolution in cork cleaning. These 'technical' corks have solid discs of high quality natural cork at each end and a granulated body made from the material left over after natural cork punching.

The INOS II washing process uses 'hydrodynamic extraction' to clean deep within the disc lenticels. Hot water is pumped under pressure

into an autoclave containing the discs – the pressure forces the hot water up into the cork structure. The water is then removed from the autoclave, creating a vacuum, which extracts moisture and contaminants.

The process utilises the unique honeycomb structure of the cork, in effect turning the cork cells into mini pumping stations that expand and contract to force out contaminants deep within the lenticels. The process is performed three times on each batch of cork discs, with clean water used for each cycle.

Amorim is presently conducting trials using INOS II on natural and granulated corks.

Control moisture, temperature and atmosphere

Moulds need moisture and warmth to grow and can be transferred through the atmosphere. An important part of Amorim's anti-TCA strategy is to control the environmental conditions throughout cork processing to avoid such occurrences.

Good ventilation of the cork planks before and after boiling is a necessity, and Amorim has observed this practice for many years.

Amorim factories constructed in the last three years — Amorim II and Twin Top® in Portugal and Australia — all contain powerful ventilation systems to extract cork dust and other possible contaminants from the atmosphere.

Research has established that a moisture content for corks of between six and eight percent is ideal. Less than eight percent moisture content at 20°C inhibits indigenous mould growth⁴ without impairing the technical performance of the cork. To achieve this, corks are oven-dried immediately after washing.

However, the stabilisation period after boiling is known to present some risks.⁵ Traditionally, cork planks selected for wine corks are boiled twice and then left to rest until their moisture content stabilises at around 10 to 12 percent, the most suitable for working the cork. The presence of moisture and warmth during this time creates an ideal climate for mould growth.

Amorim plans a radical departure from this practice, doing away with the second boiling altogether. Over a period of two weeks, just before they are ready to be punched, the planks will be gradually brought up to the correct humidity using water vapour in an environmentally-controlled chamber. Ozone will be used in the chamber to maintain a sterile atmosphere. The company expects to introduce this new system of rehumidification by June 2000.

Prevent or kill emerging moulds

Hydrogen peroxide washing and adding sulphur dioxide to sealed bags of corks have proved effective in protecting corks against microbiological activity. However, Amorim believes an even higher level of protection can be achieved using ozone, one of the most effective sterilising agents known.

Already Amorim uses ozone to treat groundwater used during processing in Portugal.

Two other uses of ozone are being tested. The first is the introduction of ozone to the cork washing process, in combination with hydrogen peroxide. On its own, ozone is a more effective disinfectant than hydrogen peroxide, but breaks down readily in water. The combination of hydrogen peroxide and ozone produces a powerful hydroxyl radical with a potentially higher oxidising effect than either ozone or hydrogen peroxide and is thus a very effective sterilising agent.⁴

The second looks at using ozone to sterilise the atmosphere in which the corks rest after washing. This is being trialled at the new Amorim Twin Top® plant in Melbourne, Australia.

Control and test all processes

Traditionally, cork manufacturers buy and sell their product through agents or representatives who may service several companies. This means that the manufacturer has no control over important parts of the supply chain and is not necessarily receiving full and timely feedback from the end user. To overcome this, Amorim has undertaken a process of vertical integration so that it controls every stage of cork production and distribution, from the forest through the factory to the end user.

As mentioned, Amorim has extended its presence in the forest and will increasingly deal directly with cork growers rather than through intermediaries. The new factory at Ponte de Sôr, which is responsible for cork purchasing, is an important part of this strategy, as is the purchase of two cork trading and primary processing companies in Spain.

Similarly, Amorim now has a controlling interest in distribution companies in each of the major wine-producing regions of the world — some 17 in all — which customise products to the winemaker's specifications. Amorim's goal is to strengthen its relationships with individual winemakers, get a better understanding of the requirements of the wine industry, identify any problems and resolve them promptly.

Amorim has also established rigorous and comprehensive quality control procedures, recognised by the ISO 9002 accreditation of all of its factories in Portugal. Its distribution companies undertake additional



Laboratory testing is a major part of Amorim's quality control procedures.

quality control and laboratory testing.

Altogether, Amorim corks are subjected to a wide range of tests before they reach the winemaker. These include visual and sensory assessments and tests for compression and recovery, insertion and extraction forces, dimensions, humidity levels, residual solids and oxidants, capillarity and sealing ability. Microbiological analyses test for the presence of harmful bacteria, yeasts and moulds. Packaging materials are also tested to ensure maximum protection for the corks during transit.

Develop new products and processes

Finally, Amorim maintains a very large-scale research and development program, in which it currently invests \$US 6 million a year. This R&D program pursues continuous improvement in Amorim's products and processes. Products such as Twin Top® and processes like INOS II, ozone treatment and continuous volatile extraction during boiling, are some of the results of this ongoing investment.

¹ Campden & Chorleywood Food Research Association, 'Quercus – Qualitative Experiments to Determine the Components Responsible and Eliminate the Causes of Undesirable Sensory Characteristics in Drinks Stopped with Cork. Final Synthesis Report', June 1996, 11-12

² European Cork Federation, 'Code of Good Manufacturing Practice', 1st edition, December 1996

³ Campden & Chorleywood Food Research Association, op cit., 13

⁴ Daly, NM, TH Lee and GH Fleet (1984), 'Growth of fungi on wine corks and its contribution to corky taints in wine', Food Technology in Australia, V 36(1), 22-24

⁵ Campden & Chorleywood Food Research Association, op cit., 14

⁶ Southland Environmental Hydrogen Peroxide Water Treatment Applications, H₂O₂ Update Online, Volume 2

A BACKGROUND TO TCA — ITS SOURCES, FORMATION AND PREVENTION

Since its identification in 1981, TCA (2,4,6-trichloroanisole) has been the subject of research aimed at pinpointing its sources, identifying the processes that lead to its formation and determining the measures that will result in its eradication.

Wine spoilage is a commercially significant quality control issue for the wine industry historically, with an estimated two to five per cent of wines affected by some form of taint.

Wine may be spoiled or tainted in several ways: the incorrect use of preservatives, a poorly managed fermentation, erroneous acidification, and exposure to oxygen, bacteria or fungi. The sources of contamination include oak barrels, storage tanks, mouldy fruit, chemical leaks and spills, faulty processing equipment and closures.

Taint in wine due to cork closures may be the result of any one of the following: the presence of by-products from microbial growth within cork; environmental contamination by low levels of volatile industrial or agricultural chemicals; or a fault during the processing of the corkwood.

Poor processing of cork rarely gives rise to taint but instances of microbiological and environmental contamination have been well documented.

Most cork taints due to TCA

The majority of cork related taints are the so-called 'musty' taints, principally due to volatile organic compounds such as geosmin and the extremely potent chloroanisoles, of which 2,4,6-trichloroanisole (or TCA) is the best known.

TCA is a recognised problem in the packaged food and beverage industries, contaminating processed foods, soft drinks, spirits and water as well as wine. According to current literature, TCA is responsible for an estimated 70 to 80 per cent of the recorded cases of cork taint in wine.

Our noses are remarkably sensitive to TCA. The compound imparts a musty, mouldy 'wet hessian' aroma to wine which can be identified in concentrations of less than five parts per trillion (i.e. five billionths of a gram in a litre of wine). However, its detection at these concentrations is highly dependent on the sensory sensitivity and experience of the individual wine taster, and 'sensory thresholds' vary enormously.

This was confirmed by a 1996 study of TCA aroma in wine at the University of California, Davis. Of 38 sensory judges, two experienced judges were able to reliably identify a TCA-contaminated wine at concentrations as low as one part per trillion, while most of the others recorded TCA thresholds of between 10 and 50 parts per trillion.

Moulds and chlorine the main sources

Since its identification in 1981 as a significant cork taint, TCA has been the subject of research aimed at pinpointing its sources and identifying the processes leading to its formation.

International research (Australia, Germany and France) has established that the chemical precursors of TCA and the factors contributing to its formation are varied. However, it is clear that, in most instances, the presence of chlorine compounds and the growth of common microorganisms such as *Penicillium* and *Trichoderma* moulds are implicated. Figure 3 (opposite) describes some of the known pathways to the formation of TCA.

Scientists believe that the most common path is the interaction of certain moulds with trichlorophenol (TCP) in a process known as biomethylation. In a moist environment, the microorganism can modify the hydroxyl (OH) group on the chlorophenol molecule by adding a methyl (CH₃) group, thereby converting the toxic chlorophenol to a non-toxic chloroanisole.

TCP, in turn, can be formed by the interaction of naturally-occurring phenols with chlorine³. (Phenols are aromatic compounds such as tannins, and are found in many organic substances, including the suberin and lignin or intercellular matter in corkwood.) TCP may also be formed as a breakdown residue of chlorinated pesticides and wood preservatives (such as pentachlorophenols). Certain microorganisms are able to convert glucose and other common carbohydrates first into shikimic acid and then, in the presence of chlorine, into TCP⁴.

The contributory sources of chlorine include chlorinated drinking water, saline water and hypochlorites found in commercial cleaning and bleaching products. Along with many others, the offending moulds are able to develop from organic matter in the cork, particularly within its lenticels — small pores or 'breathing holes' in the corkwood. In addition, the processing of raw cork can release large numbers of mould spores into the factory environs, creating increased opportunities for microbial contamination of the cork.

Prevention required on several fronts

Current research into chloroanisole formation suggests that the eradication of TCA from cork products requires a range of preventative measures. These measures include eliminating the use of chlorine and chlorinated products in and around cork processing and storage; limiting the opportunities for microbial growth, especially within the cork lenticels; and protecting the cork from environmental contamination.

• Elimination of chlorine

Eliminating hypochlorite and chlorine-based products in all aspects of cork processing has largely been achieved. Most cork producers today have switched to non-chlorinated water for boiling and washing, and hydrogen peroxide for bleaching and deodorising corks.

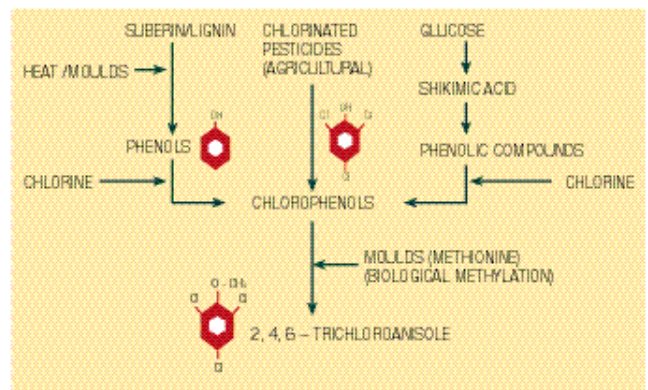
• Decontamination and protection of bark

Microbial decontamination of cork during processing is also necessary, as are protective measures in storage and handling, to prevent contamination of corks prior to bottling. This is because chlorophenols are ubiquitous — found, for example, in shipping containers, chemically treated wooden pallets and packaging materials⁵ — and are readily absorbed by cork through the air or from contact with contaminated material. There is also a risk that the corkwood itself may contain trace quantities of chlorophenols, resulting from the widespread use of chlorinated pesticides in agriculture during the 1950s and 60s.

• Controlled environment

Given the right conditions, these chlorophenols may be converted to TCA; hence the need to maintain industrial hygiene throughout the entire production, distribution and bottling processes.

FIGURE 3 – DIFFERENT WAYS OF TCA FORMATION



Trichloroanisole (TCA) is formed by the action of microorganisms on chlorophenols present within the corkwood or in the environment.

As mentioned, a moist environment is required for the microorganisms capable of forming TCA to grow and thrive. By keeping the raw corkwood and finished corks in a humidity-controlled environment (ensuring a cork moisture content of less than eight per cent), it is possible to severely restrict mould growth⁶.

Conclusion

The incidence of TCA taint in wine is under continual investigation, with estimates varying from 0.5 percent to five percent or higher. While the processes and sources of TCA formation are complex and varied, cork producers are increasingly confident that, with the initiatives currently under way, the major causes of TCA in corks will be eliminated, and cork-induced taint will cease to be a problem for the wine industry.

¹ Suprenant A and Butzke C E (1996). 'Implications of Odor Threshold Variations on Sensory Quality Control of Cork Stoppers', Proceedings of the Fourth International Symposium on Cool Climate Viticulture & Enology, Rochester, 16-20 July 1996, VII, 70-74.

² Buser, H, C Zanier and H Tanner (1982). 'Identification of 2,4,6-Trichloroanisole as a Potent Compound Causing Cork Taint in Wine', J. Agric. Food Chem., 30, 359-362.

³ Simpson, R F (1990). 'Cork taint in wine: a review of the causes', Aust. NZ Wine Ind J, 5, 286-296

⁴ Maujean, A P Millery and H Lemaesquier (1985). 'Explications biochimiques et metaboliques de la confusion entre gout de mois', Rev. Fr. Oenol. 99, 55-62

⁵ Whitfield, F, T H L Nguyen and C R Tindale (1989). 'Shipping container floors as sources of chlorophenol contamination in non-hermetically sealed foods', Chem. Ind. (London), 458-459.

⁶ Daly, N M, T H Lee and G H Fleet (1984). 'Growth of fungi on wine corks and its contribution to corky taints in wine', Food Technology in Australia, V 36(1), 22-24.