

'TCA, probably Contemporary Wine's worst Threat'

By Ernesto de Serdio. MAY 2002

Wine spoilage is a recurrent issue arising in wine loving circles and considered anathema by fine wine producers who sometimes effortlessly strive to fight all factors that will ruin their hard work on the fields and moreover, their wine masterpieces. For one may spare no resources for the making of a piece of art, be most careful and yet be hit where it hurts most: at the table, at the grand opening. Whether at an important wine tasting contest or simply in a top-notch restaurant or at home, for an impressive dinner, there is nothing more offensive for tasters, consumers and producers alike, than their wine being rated as 'spoiled'. Needless to say that the commercial, image and even moral implications can be disastrous, depending on the type of wine, price, marketing expenditure and, in general, global aims.

Though wine spoilage can derive from multiple factors, there seems to be in modern winemaking a culprit that is taking most, if not all the blame: cork. It does not matter if the wine shows too high volatile acidity or suffers from too much sulphur dioxide or hydrogen sulphide or stinks to wet dogs (highly affected by *Brettanomyces*); most neophytes, many non-professional wine-lovers and even some praised experts tend to point their accusing fingers to corks. Regardless of this malefic circle, for which corks are permanently loathed, it is no less true that the latter are the principals behind one of the most common flaws in today's wines: corked wines or cork-taint. But, despite the name, corks are not the only cause leading to such an important defect. Easily spotted, it confers on wines mouldy to wet flavours that normally mask other characteristics of wines and in far too many instances, makes them undrinkable.

A little history may be of interest now. Though corks' properties and beneficial effects as liquid stoppers have been known for centuries, their widespread use as closures for glass bottles of wines is attributed to Dom Perignon in the XVIIth century who observed how traditional wooden bangs covered with oil-soaked rags were not reliable stoppers for his beloved sparklers. Up until the beginning of the XXth century it was widely thought that cork was an ideal innocuous means of preserving wines in their bottles. Any contamination, off-tastes or smells were allocated to blemishes of the wine itself and never to corks. But with the rise of the 1900's various scientists pointed out in their studies that the regular bad tastes and smells reminiscent of dampness, wet wood and/or mustiness were caused by corks. It was then that the term 'corked' ('goût de bouchon') was coined. Moreover, French researchers as Mathieu (1900) or Bordas (1904) went as far as stating that this acute spoilage was due to corks being tainted with micro-organisms and related it to a common cork bark disease called 'Yellow Stain'.

For years to come the 'goût de bouchon' was something consumers had to make do with. Research continued to be carried out especially in what concerned the motives that originated the yellow stain disease in unprocessed cork bark. In the early stages authors pointed out that fungi (moulds) of the genera *Aspergillum* and *Penicillium* could be responsible for the contamination and so the cork industry reacted by bleaching and boiling cork planks thoroughly in the thought that these procedures would eliminate undesirable micro-life. Over time, advanced technology applied to winemaking and wine-related research made possible to determine the compound that generated such untasty feature in wines. A quantum leap was done with the use of ever more accurate gas chromatogram mass spectrometers that could easily detect chemical compounds found in wines that had previously been hidden to human knowledge.

By 1981 a group of few investigators had the certainty that organochlorinated compounds produced the off-smell and taste popularly known as 'cork-taint'. Among these and besides TCA were many like 2,4-dichloroanisole (DCA), 2,3,4,6-tetrachloroanisole (TeCA),

pentachloroanisole (PCA), 2,4,6-trichlorophenol (TCP), 2,3,4,6-tetrachlorophenol (TeCP) or pentachlorophenol (PCP). Of these compounds many acted also as precursors for TCA, but sensory analysis showed that TCA had the lowest perception thresholds for humans and therefore was, and indeed is, considered to be the main cause for bad corky flavours. Another certainty was that, despite the name the flaw had had for centuries, cork itself was not responsible for cork-taint, but only TCA-contaminated corks and that cork was only one (though important) among several 'vehicles' harbouring these molecules, which were naturally present in nature by the thousands.

In the early 1990's there was general unanimity that the major chemical responsible for cork taint was the defiant 2,4,6-trichloroanisole, also known as TCA. At the same time, rigorous statistical analysis showed that cork-taint afflicted wines were more than was thought: one out of 12-15 bottles (though many producers still deny these facts). As New World wines began to soar in global markets, this proportion seemed rather high for producers to cope with. Australians and North Americans led the first moves to tackle the issue and prestigious institutions like the University of California Davis or The Australian Institute of Wine Research implemented intensive research programs for alternative closures. Meanwhile in the Old World, increase in quality and quantity of wines marketed, had also led to whole batches from renowned wineries suffering from corkiness, many of which from serious producers were removed from the market. The cork industry, dominated by Portuguese, Spanish and French producers, was at stake.

Whilst New World research moved into innovative closures based on 'plastic' (thermoplastic elastomers), Old World analysis were centred in the determination of the causes generating contamination and possible cork-treatments that would avoid it. Cork producers such as world's largest 'Amorim & Irmaos' did not hesitate to set up independent research agreements with reputed organisations, including supra national projects, to solve the issue. At last the enemy had been identified and the industry had to move fast.

In 1997 the conclusions of project 'Quercus', under the auspices of the European Union, were very illustrative about cork taint. It was proved that 'yellow stain' was a significant cause for TCA, but the main (but not the only one) fungi responsible for it was the *Armillaria Mellea* species (Honey Mushroom) which grows on dead oak stumps and/or bark and easily spreads through the forest litter. *Armillaria* genus has the capability of producing chlorinated compounds and therefore is a precursor for TCA. On top of that it was acknowledged that besides 'yellow stain', there were many other sources for TCA and that moist environments were ideal for TCA-producing moulds and microbes to progress.

But before we go into the new techniques to fight such a slippery foe and how to prevent it, let me emphasise on the essentials: What on earth is TCA? TCA, as has already been stated, stands for 2-4-6 Trichloanisole, a volatile chlorinated compound of organic origin (organochlorinated): that is to say, produced by a myriad of microorganisms, mainly fungi, and present in various forms in Mother Nature. The undesirable effects on wines are clear, but just to give you an idea of the relationship between quantity and rate of 'infection', just point out that TCA in wines is measured in parts per trillion. Its nanogram size explains as to why it has been a hidden enemy for so long. Recent tests carried out by Professors Christian Buzke, Adam Suprenant and Thomas Evans of The UC Davis, all at the forefront of investigation of TCA effects on wines, have shown that human sensory threshold begins at concentrations superior to 4.6 ng/L (4.6 parts per trillion). For concentrations of only over 15 ng/L, the wine can be completely ruined. So in words of Professor Buzke: 'just one half-tablespoon of pure TCA could destroy all of the wine produced in the United States.'

In fact TCA is also believed to originate from fungal and microbial degradation or waste generation when fungi and/or microbes interact with chlorinated compounds. The latter can be of natural or industrial origin. So now we have the havoc wreaking couple: fungi and microbes, which can naturally generate chlorinated compounds even in unpolluted environments, and natural or artificial chlorinated 'precursors'. When both factors get together, wine is defenceless. Professor Miguel Cabral of The University of Porto and Head of Research and Development at Amorim, has ratified the most common acknowledged path for TCA generation: the interaction of certain fungi with trichlorophenols (TCP) in a process known as biomethylation. TCP, in turn, can be formed by the interaction of naturally-occurring phenols with chlorine or can result as a breakdown residue of chlorinated pesticides and wood preservatives (such as pentachlorophenols). Furthermore, certain microorganisms are able to convert glucose and other common carbohydrates first into shikimic acid and then, in the presence of chlorine, into TCP.

As hygienic conditions in wineries dramatically improved over the XXth century, the use of chlorine-based cleaning substances soared. Bleach was thought to be the perfect cleanser, the ultimate response for protection against micro-life. Only in the 1990's was there sufficient evidence that fungi reacting with chlorine compounds resulted in high levels of TCA. Common fungi and bacteria of the genera *Trichoderma*, *Aspergillum*, *Penicillium*, *Armillaria*..... sporulate vividly and rapidly. Their spores are found everywhere and cork lenticels (small 'breathing' cavities within corks) are a perfect hiding place for them and the organic matter they need to develop. Given cork's inherent resistance to liquid leakage and high temperature, spores lodged in inner lenticels of cork can easily resist boiled water treatments. Furthermore, they are provided with the best of temperatures and humidity to grow. If, on top, chlorinated bleaching was the common method used for sterilisation by the industry, the Molotov cocktail was served.

So there is widespread acknowledgement that the chemical precursors of TCA and the factors contributing to its formation are varied. To put in more simple words: TCA contamination is not exclusive because of corks. Spores can be found all over the place in the winery, including glassware, wooden and cardboard items or even steel (to a lesser extent). On the other hand statistical research throws that some 70%-80% of cork-tainted wines have been infected via cork stoppers. Corks may be infected from the onset, in the forest, or by other most likely contributory sources such as infected wood, cardboard or wooden utensils, chlorinated drinking water, hypochlorites found in commercial cleaning and bleaching products or, even, saline water.

How to prevent it? Well, there are measures to be taken at different levels of the winemaking industry. First, by the cork industry. The objective is simple: reassure the production of cork closures that are TCA free. For this sake, decontamination and protection of bark and elimination of chlorine is essential. Most cork producers today have switched to non-chlorinated water for boiling and washing, and hydrogen peroxide and ozone for cleansing and deodorising corks. Use of chlorinated pesticides has been obliterated in oak tree forests and moisture-controlled cork storage facilities have been put into place. Some new types of stoppers have been developed that have proven to be incredibly taint-resistant as are the 'Twin-Tops'. These are made of cylindrical agglomerate cork bodies with natural cork disks glued to each end. Thorough checks are implemented to detect minuscule concentrations of TCA at different levels of the production process. Some companies are even applying new microwave heating or hydrodynamic extracting techniques that seem to minimise micro-life development in the inner cork. In this field, progress has been spectacular in the last few years.

Since chlorophenols and spores are ubiquitous (found, for example, in shipping containers, chemically treated wooden pallets and bottle racks or packaging materials), all efforts implemented by cork producers are to no avail if contamination occurs at oak ageing, bottling or even thereafter, at racking or laying down. So, the wineries and the cooperage and packaging industries come next. Most concerned wineries have been substituting all their wooden bottle racks for steel or aluminium ones. New wineries make use of very little wood at all for their facilities and when they do they take care it is not chemically treated (thus avoiding chlorophenols). Cleansing is being carried out with non-chlorinated detergents. Same applies for the cooperage and cardboard (packaging) industry. The consensus is unanimous for conscious winemakers. But there is still a lot to do for some wineries and smaller companies are still reluctant to invest against the plague

Last but not least, at commercial and consumer levels care should also be taken. It is true that cork wine capsules may prevent contamination, though not completely. Cork's porosity and insulating properties are proverbial therefore making it easily prone to air contamination. Intensive cleaning with chlorinated detergents at home or at the shop may damage cork stoppers and hence the precious liquid. But what about synthetic stoppers? Would they not erase the problem? There is now a lot of talk about 'New-corks' and even a handful of prestigious Californian and Australian wineries have switched to them, in the belief that corks, and only them, are responsible for 'cork-taint'. Though there are no track records still on their impact in wine ageability, long-term resistance and overall behaviour, they do not assure that the flaw was not there in the first place (recent lawsuits filed against French firm Sabaté for its composite taint-free corks -Altec-, quickly jump to mind). And first and foremost, their producers seem to forget that wine means tradition, the very best of it, in this fast moving world and that cork & wine have been happily united for centuries..... Besides, what would have happened to the low-yield, low-growth, majestic cork oak tree forests if wine had not been there to their rescue? You tell me.