FINING AGENTS PART 2: NON-PROTEINACEOUS FINING AGENTS

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In Part 2 of this series on fining agents, we analyse the non-proteinaceous fining agents. This includes a discussion of the structures of fining agents and what they are typically used for, including the new egg albumin alternative, BIOLEES

INTRODUCTION

Continuing the theme of a discussion of fining agents commonly used in the wine industry, we now move on to the second family of fining agents, those that do not contain proteins. Typically these agents are inorganic (with the exception of tannin) with quite specific purposes in some regards. Some are very simple to prepare and use, with physical processes constituting the bulk of the fining process, whilst others involve very complex chemistry.

COMMON NON-PROTEINACEOUS FINING AGENTS

Bentonite

A comprehensive article on bentonite was published in 2007 (Bowyer and Moine-Ledoux, 2007). Bentonite is a hydrated aluminium silicate and a member of the smectite class of clays, and is comprised mainly of oxides of aluminium and silicon. In montmorillonite, the relevant substructure for beverage fining, occasionally aluminium is replaced with a different metal such as iron, manganese or magnesium, generating a deficiency in positive charge. Overall, therefore, the lattice takes on a net negative charge, ready to react with positively charged proteins in wine in an ion exchange process with the inter-laminar cations. In many bentonites used for wine fining the dominant cation is sodium, leading to high swelling and exchange capacity at the expense of slowly-formed diffuse lees with more aroma removal from the juice or wine.

In some bentonites, such as LAFFORT's Microcol CL-G®, calcium is the dominant inter-laminar cation, with consequent reduced swelling and exchange capacity, with the benefits of vastly superior lees compaction and minimal aroma stripping. The difference in settling qualities between sodium and calcium bentonites can clearly be seen in figure 1. In the case of the Microcol CL-G®, the settling is very rapid, which in turn requires that for correct use as a fining agent it be resuspended immediately prior to and during addition, with additional stirring or agitation in the tank to ensure complete dispersion. In fact, the settling is so rapid that if complete dispersion is not ensured a below-optimal result will be obtained in terms of protein removal. The physical differences between two types of bentonite can be seen in figure 2, where Volclay KWK and LAFFORT Microcol CL-G are compared. Note the differences in grain size, composition and colouration, reflecting the level of consistency and refinement of each product.

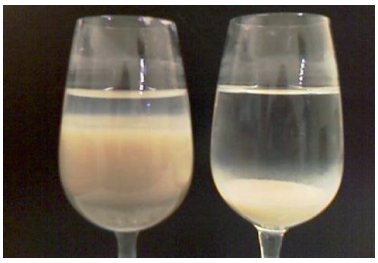

Figure 1. A comparison of the settling characteristics of two different types of bentonite after 2 weeks of standing. The sodium bentonite, on the left, has diffuse lees with greater depletion of wine aromatics but higher protein

exchange capacity, whilst the LAFFORT calcium bentonite Microcol CL-G® has compact lees, greater retention of wine aromatics but lower protein exchange capacity.

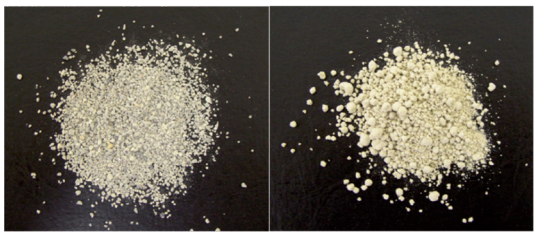

Figure 2. A comparison of the physical appearances of Volclay KWK® and LAFFORT Microcol CL-G®.

Carbon

Carbon is a fairly unglamorous, yet sometimes necessary, fining agent. It is essentially purified charcoal, although some carbonaceous agents are available on the market with remarkably specific attributes, such as Toxical® by LAFFORT. Whereas carbon is typically used for the removal of colour or odour in wines or juice, Toxical contains an active silica component and was initially developed for removing ochratoxine A, a fungal toxin, from juice and wine, yet found renewed application in removing the characters of smoke taint as observed in the vintages of 2003 and 2007 in Australia.

Carbon has a very high surface area, very small pores and operates on an adsorptive mechanism. Carbon works as a hydrophobic species, in a similar manner to the first stage of protein-tannin interaction (Bowyer, 2008). Carbon also has activity towards small phenolics and anthocyanins, as larger phenolic molecules cannot diffuse into the porous regions of the particles. In the Rebelein analysis for residual sugar in wine, for example, when analysing a red wine decolourising carbon is used to remove the colour from a red wine and thus avoid interference in the detection of the end-point of the titration (Iland et al., 2004).

PVPP

PVPP is the acronym for "polyvinylpolypyrrolidone", a synthetic polymer formed from vinylpyrrolidone (figure 3). The polymer is not soluble in aqueous ethanol solutions like wine, (nor water/juice) and is very rapid in its action. It selectively targets small phenolics species, which are usually associated with bitterness. This is because the relatively rigid structure of the polymer does not allow for interaction with larger phenolics species: only smaller phenolics are able to gain access to the hydrogen-bonding sites within the polymer's structure. PVPP is also said to strip aroma and flavour at excessive addition rates, works well at low temperature and can be used on juice or wine.

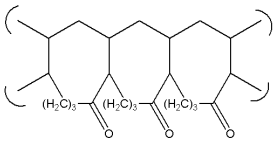

Figure 3. The chemical structure of PVPP.

Within the brand Polyclar®, two types of PVPP are available: Polyclar V® and Polyclar VT®, the latter of which is shown in figure 4. The only difference is the grain size, with the latter having a more coarse structure, enabling it to settle and not require filtration for removal.

Figure 4. Polyclar® VT, a coarse-grained version of PVPP, designed for removal from wine or juice by racking.

Silica Gel

Silica gel is a colloidal suspension of silica (figure 5). Commercial solutions are typically around 30 % concentration. Silica gel is used as a co-fining agent, most commonly with gelatine: it is added prior to the gelatine to avoid over-fining. The silica particles carry a negative charge, so in the presence of positively charged proteins (like gelatine) flocculation occurs, followed by precipitation.

Figure 5. Silica gel, in this case LAFFORT Siligel®. Typically, silica suspensions are made at 30 % concentration.

Tannin

Tannin is used in two distinct modes in wine or juice fining. It can be used as a co-fining agent with proteinaceous fining agents such as gelatine, in a similar manner to silica gel, where the purpose is to prevent over-fining and aid flocculation. Tannin can also be used to remove protein from white juice and red must.

Grape juice contains several chemical species, including protein. The protein content of any given white juice varies according to grape variety (Ribéreau-Gayon et al., 2006), hence the bentonite load required to effect protein stability also varies for any given wine. Given that it is known and accepted that proteins and tannins interact during fining processes (Bowyer, 2008), it is equally plausible that adding tannin to a white juice will also cause protein removal, reducing the bentonite load required and thus preserving aromatics and overall wine quality. Figure 6 illustrates the reduction in protein load of a model solution after being treated with various types of tannin at the same dosage rate, whilst figure 7 shows the reduction in bentonite load required to protein stabilise a wine after tannin treatment at the indicated dosages.

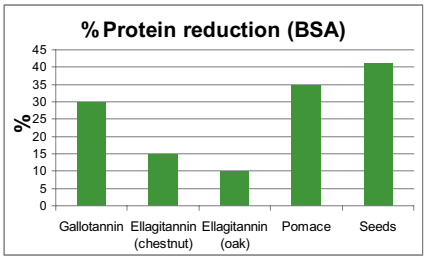

Figure 6. The reduction in protein load (BSA) in a model solution after equivalent doses by mass of different types of tannin.

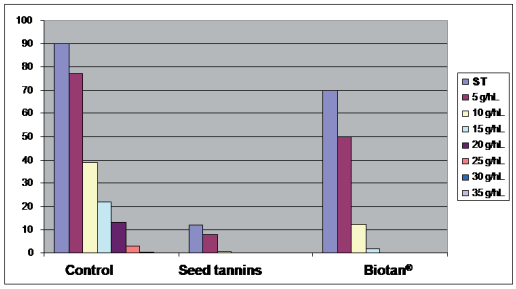

Figure 7. The reduction in bentonite load required to protein stabilise a wine after pre-treatment with tannins at an equivalent dosage. The tannins used were seed tannins (extracted from grape seeds) and LAFFORT Biotan®, which is a blend of grape seed and skin tannins.

In a similar manner, the addition of tannin such as LAFFORT's VR Supra® to a red must during fermentation can be expected to remove grape-derived protein early on in the winemaking process. Since this action would otherwise be performed by the native grape tannins extracted increasingly as the alcohol content of the must increases, VR Supra® can thus provide a protective role, aside from acting as an anti-oxidant and colour stabilising agent, and allow far greater retention of the viticulturally-derived tannins in the grape. A scientific investigation to elucidate the exact nature of tannin function in this regard is underway at the University of Bordeaux, sponsored by LAFFORT.

Potassium ferrocyanide

Potassium ferrocyanide is the agent used in blue fining. The process is so named because of the Prussian blue colour which develops under certain conditions of usage. Blue fining is used to remove metal ions from wine, specifically iron (Fe) and copper (Cu), although this is far less of a problem today than it was when brass joints were used in wineries. It is a permitted process in Australia but not in all countries (eg USA). The chemistry associated with the use of ferrocyanide is complicated, but centres on the use of the complex ferrocyanide ion $[Fe(CN)6]2-$ to react with metal ions to form relatively insoluble salts which precipitate. The relative insolubilities of these salts govern the effectiveness of the fining process. The solubility product, a measure of the solubility of a salt, for $Fe4[Fe(CN)6]3$ (formed when Fe(III) is removed) is 10-41, far smaller than 10-16, which is the solubility product for $Cu2[Fe(CN)6]$, hence Fe(III) is removed far more efficiently than Cu(II) (Boulton et al., 1999).

Biolees®

Biolees® is a very new product from LAFFORT that performs two functions in wine: it is a mild fining agent for the polishing of the phenolic structure, in addition to providing a non-fermentable sensation of sweetness. Biolees® is derived from yeast, and is naturally released into wine during yeast autolysis. Biolees® is enriched in the low molecular weight peptide fraction (which has a very low detection threshold of 16 mg/L) that provides the perception of sweetness, and so simultaneously reduces the perceptions of acidity and bitterness, leaving the wine with a more rounded, softer profile. The protein fraction in Biolees, being yeast rather than grape-derived, is thermally stable, so it does not contribute to instability.

When added to a wine, initially a rise in turbidity is observed (figure 8), after which flocculation completes and precipitation occurs, leaving the wine in a state of increased clarification. The sapid peptide fraction is soluble in wine, hence not only is the wine clarity improved, but its structure is softer and rounder.

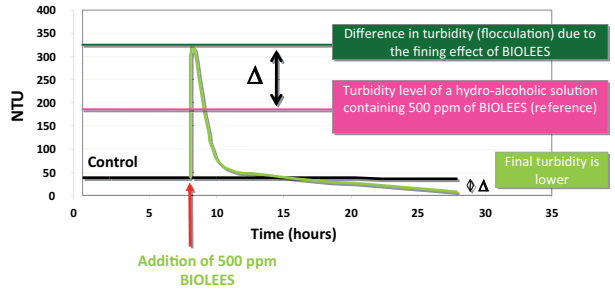

Figure 8. A typical profile for the turbidity changes observed when using Biolees®. Initially, an increase in turbidity is observed as flocculation increases; Turbidity level of a hydro-alcoholic solution containing 50 g/hL of BIOLEES (reference); On completion of the fining action, the wine turbidity level has decreased over the control.

BENCH TRIALS

One aspect of the use of fining agents, be they proteinaceous or non-proteinaceous, is the use of bench trials. It is vital for any fining agent that a trial be conducted in a small scale for every wine to be fined. It is dangerous to simply extrapolate dosages from one must or wine to another without appropriate confirmation of the rate of application and correct fining agent to be used. Since it is well known that the excessive use of some fining agents can be detrimental to wine quality, such practice is not only scientifically and professionally required, it is also commercially justified in terms of return on the winemaking investment and the future image of the quality of Australian wine.

SUMMARY

Fining is an integral part of most winemaking. While some wines are produced without the use of fining agents, these are few and far between. Each fining agent has a role to play in improving wine quality and/or stability. Some are very simple, and some are quite complex, but at the end of the day they are simply there to make the winemaker's job easier, the wine more enjoyable, and therefore strengthen the Australian wine industry as a whole.

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Products discussed in this article are available in Australia through LAFFORT, phone 08 8260 7974 and in New Zealand from Oenological Resources (Greg Wilkin: greg@oenological.co.nz), phone 0213 22290. www.laffort.com

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