Alternatives to refrigeration

Practical commentary around the use of CMC

When it comes to options for cold stabilisation, there are a number of additives that can be used by winemakers to achieve results. Laffort global product manager for fining/stabilisation **Sami Yammine** and Laffort Australia technical manager **Alana Seabrook** examine one cost-effective solution.

Tartrate instability

Tartrate instability is the phenomenon that occurs at a specific temperature when tartaric acid salts become super-saturated: their concentration is higher than the quantity theoretically soluble. Under cooler conditions this state leads to the formation of crystals. All types of wine can incur tartrate instability including white, red and rosé wines.

Precipitation of these crystals can be favoured by exposure to cold, colouring matter (blending vintages with younger wines), and deacidification treatments before bottling. Wines that are tartrate stable may become unstable after filtration due to the clogging of protective colloids that prevent tartrate formation in filtration.

Tartaric acid itself is not commonly found in nature and concentrations range from less than 6g/L in cooler climate grapes and 2-3g/L in warmer climate grapes (Ribéreau-Gayon *et al.* 2006). Tartaric acid can form up to five different salts which all vary in their solubility in alcohol-based solutions:

- potassium hydrogen tartrate (KHT) or Potassium bitartrate
- neutral potassium tartrate (K2T)
- neutral calcium tartrate (CaT)
- potassium and calcium tartrate double salt
- mixed salt potassium and calcium tartromalate.

Tartaric acid, potassium bitartrate and neutral potassium tartrate will exist in different levels at different pH (Figure 1). The pH of a wine will determine whether that pH will increase or decrease should KHT precipitate. Depending on alcohol levels, pH3.6 KHT precipitation will lower the pH. Below pH3.6 KHT precipitation will increase the pH (Ribéreau-Gayon *et al.* 2006). At pH3.6 KHT precipitation is fast and the pH should remain the same.

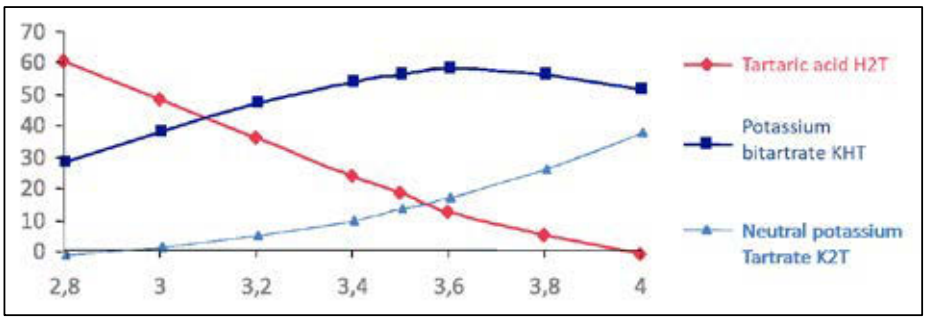

Figure 1. Tartaric acid, potassium bitartrate and neutral potassium tartrate over a pH range of 2.8-4.0.

Table 1. Subtractory and inhibitory methods of preventing tartrate precipitation in wine.

Subtractory	Inhibitory
Cold treatment (with or without seeding cream of tartar)	Metatartaric acid: POLYTARTRYL® (Inhibition of crystal nucleation and growth)
Electrodialysis to remove K+ ions	Sodium Carboxymethylcellulose (CMC): CELSTAB® (Inhibition of crystal nucleation and growth)
	Naturally occurring Yeast mannoproteins (MANNOSTAB®) (Inhibition of crystal growth)

There are various methods employed to test the cold stability of a wine. The treatment options for these wines can broadly be categorised into two groups: subtractory (physical removal of constituents responsible for precipitation) or inhibitory (inhibition of KHT crystal nucleation and/or growth phase).

E466 Carboxymethylcellulose (CMC)

Sodium carboxymethylcellulose (CMC) was approved for winemaking in Australia in 2011 as a crystalisation inhibitor. There are many variations between commercially available CMCs, with the degree of substitution and length of the polymer chain (molecular weight) being very different (Bowyer *et al.* 2010). OIV regulations (OIV resolution 366/2009) outline the molecular weight (indicating the length of the polymer) has to be between 17 and 300 kiloDaltons, correlating directly to the viscosity of the solution and therefore ease of use. The degree of substitution of glucose units within the CMC chain is again outlined by the OIV (must be between 0.60 and 0.95). This directly affects the solubility of the CMC which will in turn impact the effectiveness of the treatment.

The Laffort CMC (CELSTAB®) is produced to comply with OIV specifications (referenced by FZANZ standard 4.5.1) and has optimal characteristics in terms of molecular weight and degree of substitution. The recommended rate, 1mL/L, is based on these properties. CELSTAB is not recommended in red wines for tartrate instability as it can interact with colouring matter and prevent tartrate inhibition. CELSTAB may be used for rosé if it is colouring matter stable, however adding CELSTAB to 100mL of wine and left at 4°C for 48 hours is recommended to ensure there is no residual colouring matter for it to bind to and form a haze (Figure 3, see page 82).

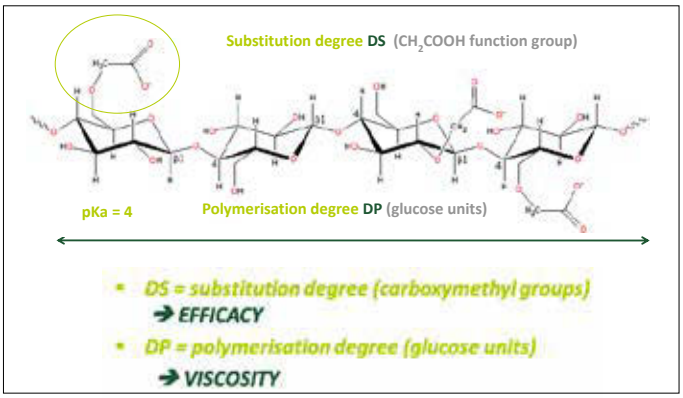

Figure 2. Sodium Carboxymethylcellulose molecule.

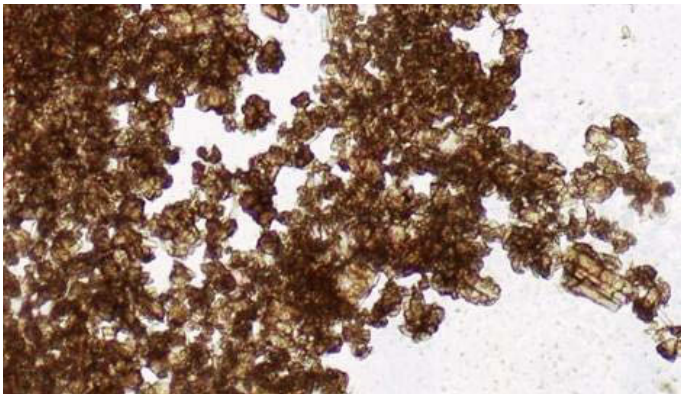

Figure 3. Effect of CELSTAB on a colour matter unstable rosé (Picture sourced from SARCO laboratories, France).

In white wine, CELSTAB is recommended as a cost effective and efficient potassium tartrate stabilisation treatment, removing the requirement for refrigeration to tartrate stabilise a wine. CELSTAB should be the last treatment to wine before final filtration and bottling, excluding polysaccharide additions for mouthfeel (i.e. Stabivin®SP), SO_2, CO_2 and ascorbic acid.

Calcium salt precipitation?

Calcium concentration should be below 60mg/L. It is recommend to test juice as early as possible, during fermentation if necessary. Wine de-acidification with calcium carbonate, treatment with calcium-based products in the vineyard, soil type, poor quality calcium bentonite and skin maceration can elevate calcium levels above 60mg/L ppm in test treated wines. Elevated calcium levels can cause calcium tartrate precipitation, and CELSTAB is not efficient in stabilising this type of precipitate.

Heat stability

Wine must be protein stable (heat stable) as measured on filtered wine. CMC can interact with proteins and form a haze (McManus *et al.* 1981) (Figure 4). Wines that have been treated with Lysozyme, which is a heat-unstable protein, should be bench trialled for CELSTAB compatibility. Additional bentonite may be necessary since elevated protein levels can cause a haze with CELSTAB.

Late tannin additions

A protein stability test is necessary if tannins are added in the last stages of wine preparation before bottling (following barrel ageing or a late addition of finishing tannins). The addition of tannins can cause the formation of a thermo unstable complex with any remaining proteins (McManus *et al* 1981), thus creating protein haze that the CMC can bind to. As a consequence, the tannin addition can also render the CMC less efficient and render the wine more susceptible to tartrate instability.

Factors around filtrability, clogging and colloidal load

There is no correlation between filterability and wine turbidity; a clear wine can clog filters. It is essential to assess several

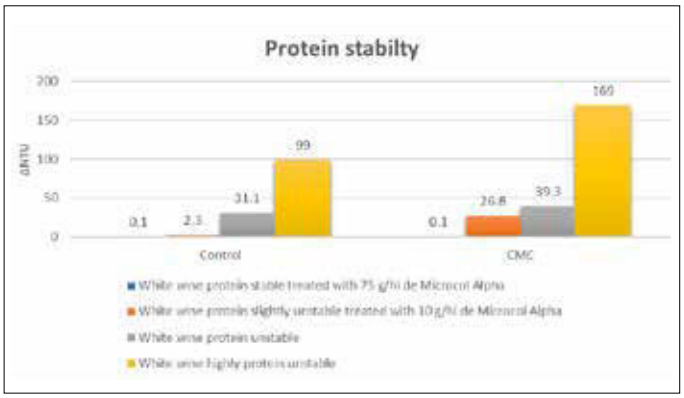

Figure 4. Level of protein stability after the addition of CMC (SARCO laboratories, France).

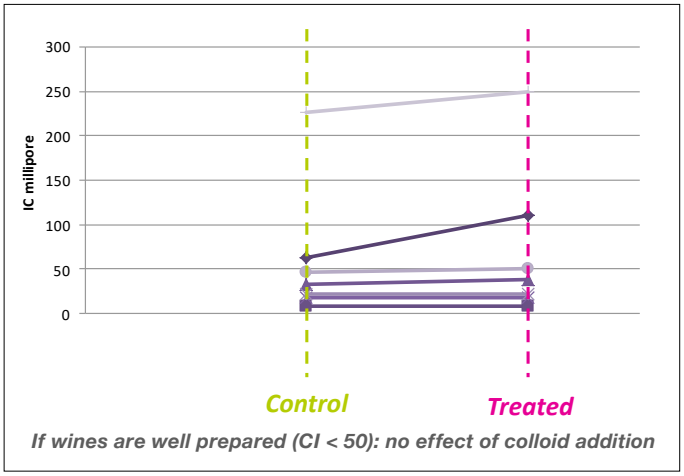

Figure 5. Effect of protective colloids on filterability (SARCO laboratories, France).

parameters when preparing a wine for filtration. Colloidal load refers to unstable colloids that are partly comprised of anthocyanins in the form of flavylium (charged +) ions, tannins, polysaccharides (including pectins) and proteins (+). The colloidal load of a wine will affect its filtrability/clogging index.

Products added to a wine may affect its filtrability/clogging index. Depending on the nature of the products, CMCs and mouthfeel-enhancing and stabilising polysaccharides may add to the colloidal load of a wine and increase the clogging index. However if this colloidal load is low to start with due to the use of enzymes, fining, bentonite and appropriate temperatures at filtration, the addition of colloids should not impact the clogging index (Figure 5).

How can I decrease the colloidal load of my wine?

1. Enzyme addition - action on filterability. Ensures pectin and/or glucan chains breakdown to improve settling (racking).
   a. pectinases
   b. β. glucanases
2. Fining - decreases the load. Ensures settling of particles in suspension (colloids) present in the wine. The addition of negatively charged bentonite allows for the stabilisation of particularly unstable compounds and makes them precipitate.

Table 2 shows the interaction of a protein stable wine after the addition of 0.4g per 1L of tannins and CMC.

	Control	Tannins 4 g/hl + CMC 10 cl/hl
Turbidity after 48 hours	0,9	10

3. Racking - decreases the load. Lees removal

Other factors that affect filterability

- Temperature - the colder the wine the harder it can be to start with.
- Degassing - Reduction of the CO_2 load ensures minimal degradation of the cake during DE filtration.

Application

Initial tartrate instability can be measured by a refrigeration test (-4°C for 3 days), DIT* (STABILAB) or conductivity test and must be <4%. The clarity of the wine must be <3.0 NTU. Pad or cross-flow filtration is highly recommended.

Table 3. Cost of tartrate stabilisation Lasanta and Gómez (2012)

	Method	Direct costs (€/hL)	Amortization (€/hL)	Total costs (€/hL)	Rate[e] (%)
Gomez *et al.*, 2002[a]	Cold treatment	0.76	0.19	0.95	100
	Ion exchange	0.07	0.04	0.11	11.58
	Electrodialysis	0.56	0.58	1.14	120
Low *et al.*, 2008[b, c]	Cold treatment	1.38	0.67	2.05	100
	Cold treatment with seeding	3.74	0.69	4.43	216.10
	Semicontinue cold treatment	1.99	0.72	2.71	132.20
	Continue cold treatment	2.60	0.66	3.26	159.02
	Electrodialysis	3.1	1.57	4.68	228.29
Rondeau, 2011[d]	MTA	0.07	–	0.07	7.40
	CMC	0.7	–	0.7	73.68
	MP	3.0	–	3.0	315.78

[a] Adapted from Gómez *et al.* (2002).
[b] Adapted from Low *et al.* (2008).
[c] Currency at April 7, 2012: 0.787 €/AUD.
[d] Extracted from Rondeau (2011).
[e] Rate considering cold treatment as 100.

Add CELSTAB at 1mL per L after pad or cross-flow filtration and at least 48 hours before membrane filtration and bottling. Dilute CELSTAB in two times the dosage volume with wine and mix into wine thoroughly.

Cost

Lasanta and Gómez (2012) summarised the costs of tartrate stabilisation using various methods factoring in direct costs (energy, chemicals, labour, consumables, water, wine losses) and indirect costs (amortisation over 10 years). In all studies considered CMC was lower priced than cold treatment with or without seeding. Low *et al.* 2008 only looked at physical processes but the study was conducted in Australian wineries indicating that the energy and labour costs are likely higher than in 2008 but nonetheless realistic in an Australian context. Figure 5 compares the costs of cold stabilisation with and

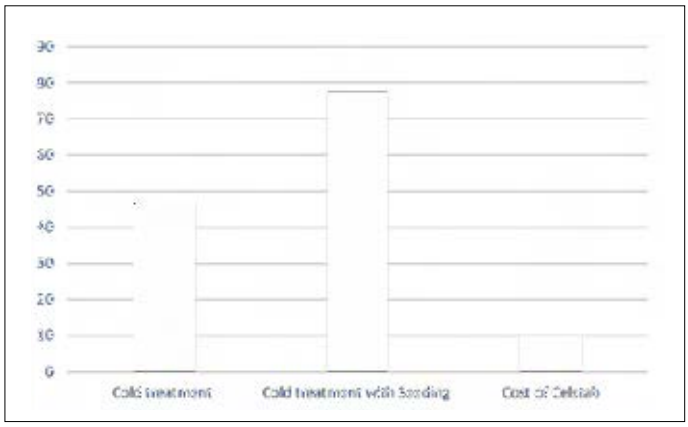

Figure 6. $AUD/1000L of wine. Values from cold treatment and cold treatment from seeding taken from Low et al (2008) in AUD based on Australian labour and electricity costs in 2008. Cost of Celstab based on 2019 cost/L

without seeding in 2008 (Low *et al.* 2008) in AUD adjusted to cost per L, compared with the current cost of CELSTAB in 2019. The figures of AUD$46.9 and $77.5 were derived from the batch cost (Low *et al.* 2008) of $12,900 and $21,300 for 275KL batches. The data is then expressed in $/1000L of wine. It is expected that the energy and labour costs between 2008 and 2019 would have increased significantly, making the cost saving of CMC in comparison to traditional cold stabilisation methods even more impactful. Whilst large businesses may be set up for cold stabilisation, many smaller wineries may not have the resources to achieve the cold temperatures for the amount of time required, making CMC a practical solution.

Conclusion

CMC has been validated by the OIV since 2009 and in Australia since 2011. It is an interesting alternative to cold treatment, since it requires less energy and is inexpensive and easy to implement. It is important to check the quality and suitability of any CMC product prior to its use in wine. Since it is produced from polymeric products and their physical and chemical parameters may vary considerably. CELSTAB ® has been produced and selected with optimal DP/DS for a wide range of applications.

References

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