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Carboxymethylcellulose for crystal stabilisation
-Recommendations for practical use-

Every year anew, crystal stabilisation is a challenge due to the still earlier bottling of wine and the always farther distances to cover to consumers. To obtain crystal stability, the wine producer has the choice between numerous processes. It is however important to consider costs, operational prerequisits, such as production equipment and facilities and what is required of a wine's crystal stability before finally deciding on a method. In table 1 current stabilisation methods and their advantages and disadvantages are compared. Hereby the long-term effect and the impact on filtration capacity are of particular interest.

Since August 1st 2009 there is a further method of application which can be used for crystal stabilisation: the addition of carboxymethylcellulose, CMC. It is not new, already in the 1980s trials with this substance in wine were conducted and its positive effect against tartar precipitation was proved (see WUCHERPFENNIG, *et al.*, 1987). In the frame of different theses, also in cooperation with the Erbslöh Geisenheim AG, the application of CMC in practice was successfully tested (see STOCKE, 1985). Yet the product was not legally approved in Europe at that time. It was only in March 2006, when the subject was taken up again on recommendation of the champagne producers. In Resolution 2/2009 the OIV recommended the use of CMC for crystal stabilisation in wine and in August 2009 CMC was legally admitted in the EU (VO 606/2009). The legal basic conditions are stated in figure 1.

What is carboxymethylcellulose?
Carboxymethylcellulose (synonym: cellulose gum) is a polysaccharide, obtained as modified cellulose from plant fibres. Already for many years, CMC is used in the food sector as thickening agent (E466) in the production of ready-made sauces and soups, yoghurt, etc. The polymers consisting of anhydroglucose units (see figure 2) are of different solubility dependent on the degree of polymerisation and substitution and form more or less viscous solutions. Solubility in water is rather poor and in ethanol CMC is insoluble, thus solubility in wine must be evaluated as poor too.

Why is CMC applied in wine?
Due to its molecular structure CMC acts, similar to metatartaric acid, as protective colloid, which attaches to the surface of dissolved potassium hydrogen tartrate and thus prevents crystal growth. The great advantage of carboxymethylcellulose as against metatartaric acid is its temperature insensitivity. While metatartaric acid decomposes under warm storage conditions or with frequent temperature variations and loses its efficiency, this is not the case with CMC (see RIBÉREAU-GAYON *et al.*, 1977). This means, with CMC lasting crystal stability is obtained. Natural acidity and potassium are preserved, analogical to the application of metatartaric acid, which is, besides the small process costs, an advantage of CMC vis-à-vis the energy-consuming minicontact process.
With strongly oversaturated wines (ST 1 > 18°C) the effect of CMC is limited and also with an increased addition full stability cannot always be guaranteed. Pretests and parallel measurements with the minicontact process are a reliable means of assessment in this case. The effect of carboxymethylcellulose against calcium tartrate is limited.

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As already mentioned before, carboxymethylcelluose is poorly soluble in wine and handling of the highly viscous solutions during running operation in the production plant is difficult with regard to dosage and cleaning. In the frame of the OIV recommendation the possibility of industrially manufactured liquid products was taken into account. These have a lot of benefits for the user (see figure 3).

Results from the practice:
The stabilising effect of carboxymethylcellose can be tested by means of two methods. With the OIV method the wine to treat is stored over several days at - 4°C and is checked every day for crystal precipitations. If the wine is free from crystallisation for more than 6 days, it is considered crystal stable. In figure 4, this is shown by a comparison between metatartaric acid and carboxymethylcellulose. The trial wine used had a potassium hydrogen tartrate saturation temperature of 18 °C. As expected, the application of CMC led to sufficient stability. The application of metatartaric acid also showed an improvement compared to the untreated control yet to a smaller extent due to the high oversaturation of the wine. The long-term effect of metatartaric acid is not as good as that of CMC, in practice however, this is not necessarily considered in a negative way, because assessment depends on the individual requirements of the respective production plant. Shorter stability periods may indeed be sufficient for large wineries where most of the wines are produced for rapid consumption within the next few months.

In figure 5 the minicontact process, the second method to evaluate crystal stability, is shown. In this example the wine has a potassium hydrogen tartrate saturation temperature of 20 °C, the limiting area of carboxymethylcellulose application. This is made clear by the results obtained by checking the stability over a storage period of 10 months at 17 °C. The control values show a high difference in conductivity which means, the wine was extremely instable. At first good stabilisation was obtained by the metatartaric acid added. However due to the decomposition of the metatartaric acid this was no longer the case after 10 months storage at warm temperatures, whereas the wine treated with CMC remained stable. Yet a tendency towards deterioration of stability could be observed since the difference in conductivity had increased after 10 months storage. As already mentioned, the stabilising effect by CMC is not sufficient with increased oversaturation. A higher dosage could help in this case, but the impact on filtration has to be controlled.

The chemical structure of CMC makes clear that any addition of such polymers to the wine always affects filtration. Through careful selection of the carboxymethylcellulose filtration capacity along with maximum stabilisation effect can be optimised. Besides thoroughly chosing the optimal CMC type, the contact time of the product until filtration is conducted during practical use is an important parameter. As shown in figure 6, a filtration step directly after addition results in a significant deterioration of filtration capacity, whereas already after 4 days filtration capacity is comparable with the untreated wine. With higher dosages in case of wines with stronger crystal instability, a prolonged reaction time (> 4 days) can equally minimise the impact on filtration.

Summary:
With the approval of carboxymethylcellulose a further method of crystal stabilisation is available for use. Since CMC is poorly soluble, a product in liquid form for convenient handling makes sense to assure homogeneous distribution in wine and thus to obtain a safe stability effect. The main advantage of CMC is the lasting prevention of potassium hydrogen tartrate precipitations due to temperature insensitivity and the stability of this substance over long storage periods. Stabilisation against potassium hydrogen tartrate precipitations is also possible with wines with tartar saturation temperatures up to 18 °C. Effectivity against

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calcium tartrate precipitations is limited. Dependent on the degree of oversaturation, the dosage must be adjusted and filtration capacity of the wines must be evaluated.

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Table 1: Comparison of crystal stabilisation methods

Crystal stabilisation method	Low process costs	Environmentally friendly	Easy application	Effect against Ca-crystals	Long-term effect	Impact on filtration	Preservation of natural acidity
Contact process	-	-	-	+/-	+	-	-
Metatartaric acid	+	+	+	-	-	+/-	+
CMC	+	+	+*	-	+	+	+
Mannoproteins	-	+	-	?	?	+	+

* as liquid product (VinoStab®)

- Max. dosage: 10 g/100 L sodium carboxymethylcellulose
- Legally admitted for the treatment of white, rosé and red wine as well as sparkling wine
- Chemical characteristics according to the OIV purity specifications of 2009
- Application possible as powder product or granulate or as viscous liquid

Fig. 1: Legally approved basic conditions for CMC addition in wine

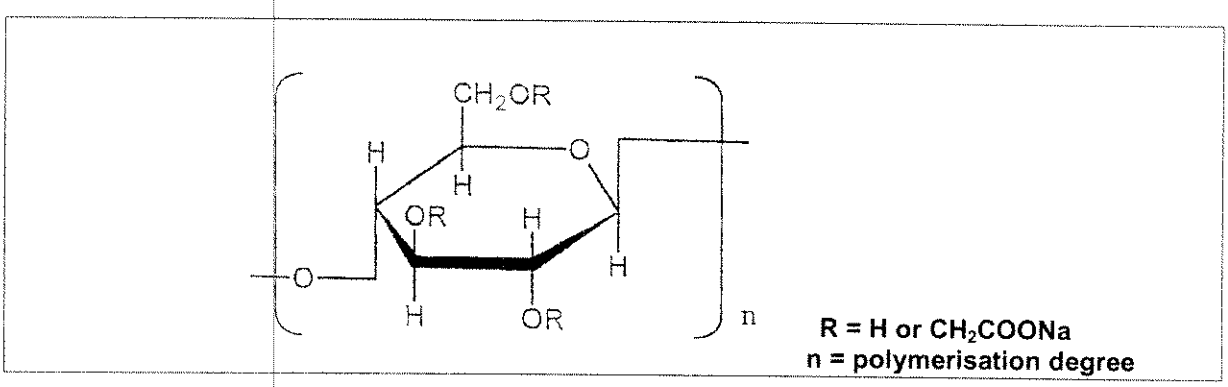

Fig. 2: Chemical structure of carboxymethylcellulose

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- Easier application and homogeneous distribution in wine
- Direct addition possible
- Higher CMC concentration with addition of the product realised by industrial manufacture (minimised water input)
- Positive impact on wine filterability
- Less personnel necessary since no labour-intensive cleaning of mixing containers
- Improved hygiene – remains of product are difficult to remove and quickly tend to microbial spoilage
- No risk of slipping caused by product dust

Fig. 3: Advantages of the application of VinoStab® as liquid product

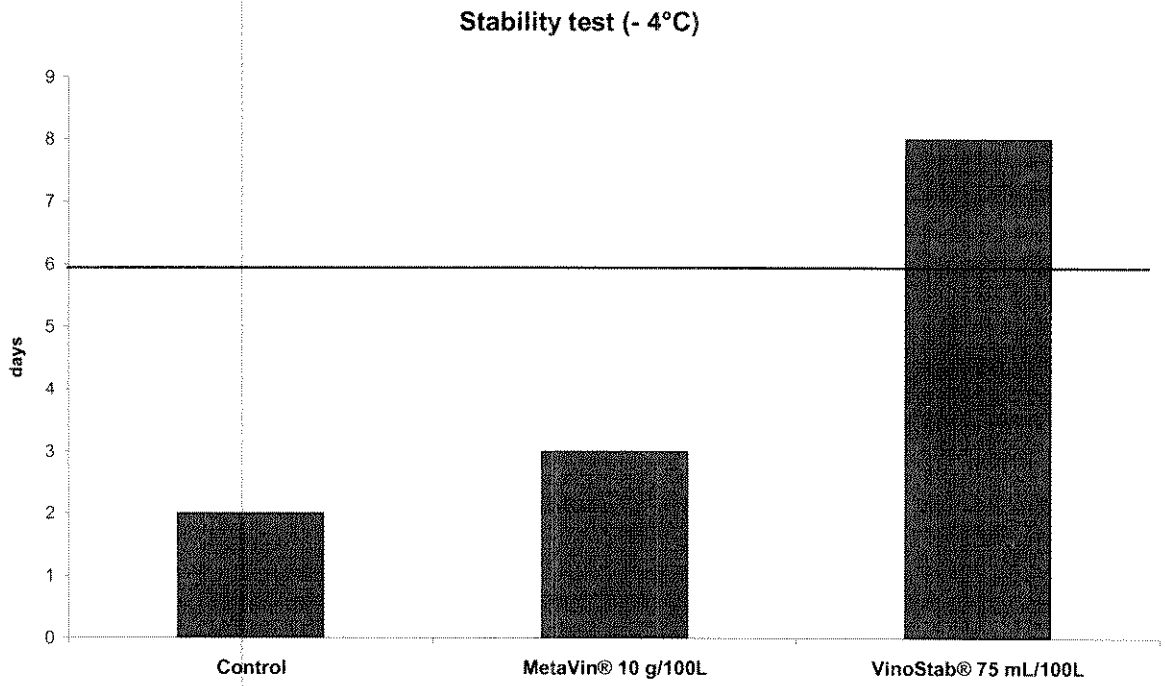

Fig. 4: Stabilising effect of VinoStab® against MetaVin® after 10 months of storage at 17 °C (test wine with potassium hydrogen tartrate saturation temperature of 18°C)

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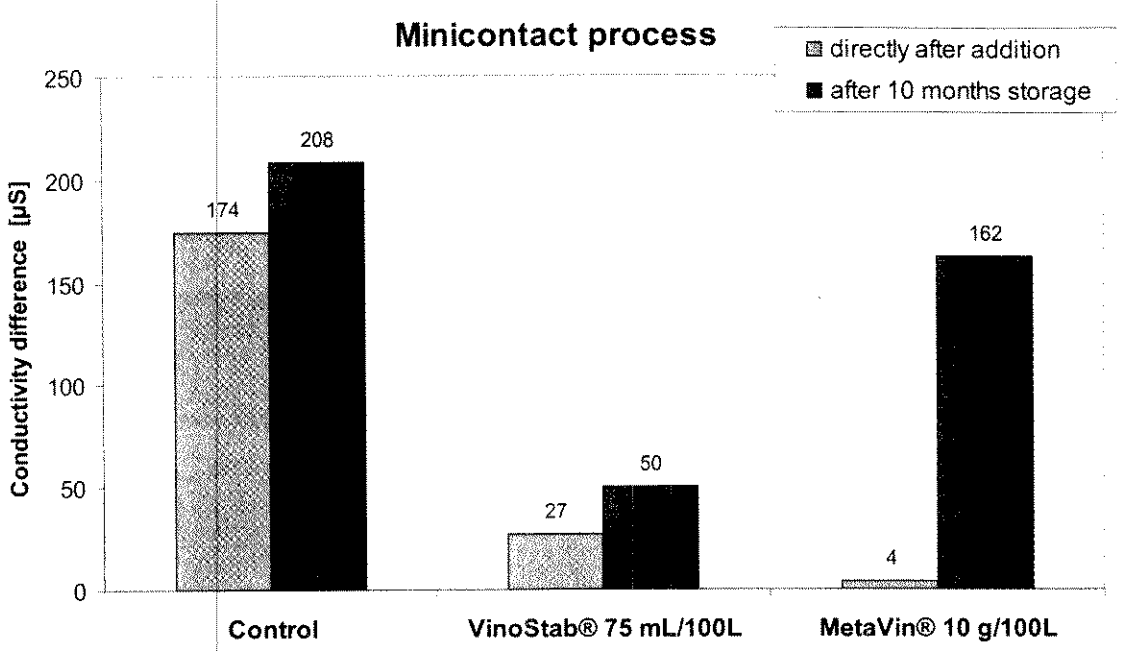

Fig. 5: Stabilising effect of VinoStab® against MetaVin® at direct measurement and after 10 months storage at 17°C (test wine with potassium hydrogen tartrate saturation temperature of 20 °C).

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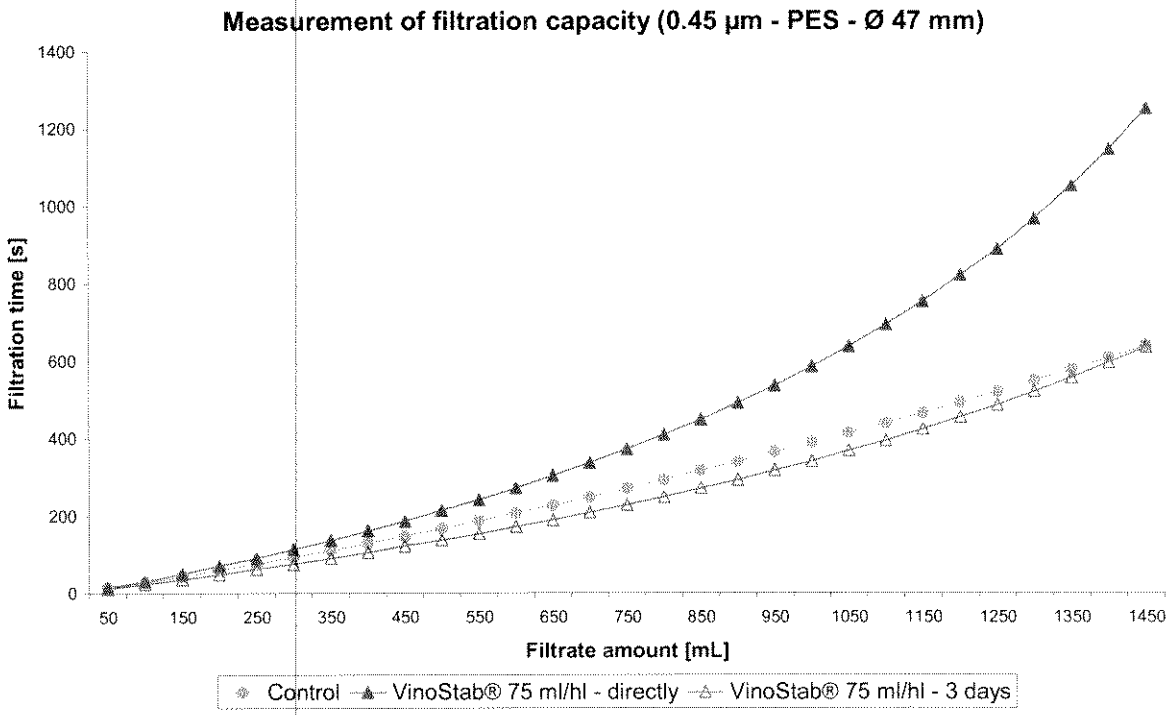

Fig. 6: Filtration capacity of VinoStab® in dependence on contact time until filtration

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