

Cold Stabilization by Contact Process*

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Grape juice and/or wine can be considered as a supersaturated solution of KHT. Under certain conditions such as low temperature storage, the dissolved KHT becomes insoluble and small crystals settle to the bottom in the form of a sediment. In a supersaturated solution (e.g., wine) the crystallization process occurs in two stages. In the first stage, also referred to as nuclei or seed crystals are formed. It is important to note that for nucleation to occur in a supersaturated solution the concentration of KHT must reach a critical level. Below this level (such as slightly supersaturated wine) nucleation will be slow. In the second stage the nuclei grow into crystals. The crystal growth occurs when the KHT ions migrate to active sites on the surface of the seed crystals and are incorporated into a crystal lattice. If for some reason the active sites on the crystal surface are blocked (due to adsorption of colloids) crystal growth is impeded. Certain phenolic compounds and polysaccharides present in wine have been shown to impede crystal growth.

It has been shown that in a supersaturated solution the rate of nucleation and crystal growth depends on the degree of super saturation. In a contact process of stabilization, powdered KHT crystals are added. These crystals serve as seed crystals and crystal growth begins immediately. Thus the addition of KHT eliminates the nuclei induction phase and this speeds up the time required to stabilize the wine. Many trials have been conducted to determine the optimum amount of KHT needed to stabilize wine. The research has shown that the addition of 4g/L of powdered KHT is sufficient to render a wine stable. Adding 4g/L of powdered KHT gives 17million KHT fragments/ml (Rhein & Neradt, 1979). Adding KHT in amounts less than 4g/L will require a longer time to stabilize the wine. Using higher amounts than 4 g/L is not recommended because it is uneconomical, rather difficult to remove, and the improvement in KHT reduction is marginal. Table 1 shows the effect of KHT additions (in increasing amounts) on K⁺ and tartaric acid levels in wine.

Table 1. Decrease of potassium and tartaric acid levels in wine as a function of KHT additions.

KHT additions g/L	K ⁺ mg/L	DK ⁺ mg/L	H ₂ T g/L	DH ₂ T g/L
Control	1150	-	1.82	-
Chilled, none	1150	-	1.82	-
1 g/L	1020	130	1.34	0.48
2 g/L	1020	130	1.34	0.48
4 g/L	970	180	1.15	0.67
6 g/L	970	180	1.12	0.70
9 g/L	960	190	1.10	0.72
12 g/L	960	190	1.08	0.74

Source: Neradt (1980)

As the results indicate, the addition of 4 g/L of KHT decreased the tartaric acid level by 0.67 g/L, i.e., 36.8%. Increasing the rate of KHT to 12 g/L (3 times) reduced the tartaric acid level by 0.74 g/L or 40.6%. Thus increasing the KHT addition three times the suggested level (4 g/L) gave marginal improvement in tartaric acid reduction. A similar trend is observed with reference to K levels.

Cost of KHT

At 4 g/L, 33 1/3 lbs of KHT will be needed to treat 1000 gallons of wine. At a price of \$2.11/lb (estimated price), the cost of KHT powder to treat 1000 gallons of wine will be \$70.26. In practice the KHT crystals can be recovered from the wine and used again. Generally, the KHT powder can be reused between five and eight times. For red wines the number of times KHT can be reused is much less. If the KHT can be reused five times, then the cost of treating wine would be reduced to about \$14.00/1000 gal or 1.4¢/gal, which is a small expense to achieve wine stability.

With repeated use the KHT crystals grow and become larger in size, thus increasing the amount of contact time required to stabilize a wine. For this reason wet grinding of the crystals is recommended. Neradt (1980) reported that in a commercial KHT power, about 40% of the particles were less than 40 µm in size. After five

uses this fraction was reduced to less than 4% (due to crystal growth). However after grinding, the fraction (i.e., particle size less than 40 μm) increased to about 50% (Table 2). In practice one may be able to reuse KHT crystals about five to ten times before grinding. For more frequent uses, i.e., over five to ten times, wet grinding would be necessary to reuse the crystals.

Table 2. Particle size distribution of KHT in %.

Commercial KHT from Spanish source				
Particle size	Commercial KHT from German source, unused	Unused	After 5 uses	Ground after 8 uses
$\leq 5 \mu\text{m}$	5.0	0.5	0.2	2.5
5-15 μm	10.0	4.0	0.3	2.5
15-40 μm	28.0	34.0	3.5	45.5

Fouling of KHT Crystals

Fouling of crystals occurs when, during the crystallization processes, certain colloidal substances occupy the active sites on the crystal surface and, consequently, halt crystal growth. The fouling substances include certain pigments, polyphenols, proteins, and polysaccharides. The extent of crystal fouling depends on the amount and types of colloidal substances present in the wine. Pretreatment of wine, such as clarification, fining, and filtration, will reduce the level of colloidal material and thus minimize the fouling of the KHT crystals with repeated use. The fouling or blinded crystals can be washed to remove the contaminants. The washing or rinsing will cause a loss of KHT depending on the temperature and amount of water used in washing. Generally, the loss of 3 to 6% of KHT has been noted in the washing of the crystals.

Contact Process Compared to Conventional Cold Stabilization and Ion Exchange

In 1979 Rhein and Neradt reported the results of an experiment in which the contact process was compared with chilling and the ion exchange methods. Their data is given in Table 3.

From the results shown in Table 3, it is clear that the contact process yielded significant reduction in tartaric acid and potassium levels; whereas, conventional cold stabilization gave inconsistent results.

Table 3. Tartaric acid and potassium content of a wine before and after tartrate stabilization.

Wine	Stabilizing method	Tartaric acid g/L	K ⁺ mg/L
A	untreated	2.50	720
	contact	1.95	565
	chilling	2.50	715
	ion exchange	2.40	360
B	untreated	2.35	735
	contact	1.75	575
	chilling	2.00	655
	ion exchange	2.25	340

Source: Adapted Rhein and Neradt (1979)

Contact Process Procedure

In order to stabilize a wine using the contact process, the following procedure is suggested:

1. Clarify, fine and filter the wine to remove colloidal material. (Remember this causes fouling of crystals.)
2. Chill the wine to the desired stability temperature. For table wine the stabilized temperature is generally between -4 to 0°C (24.8 to 32°F).
3. Chilling the wine may cause precipitation on unstable material (especially red wines). In such a case, polish filtration of chilled wine may be needed. Filtration before seeding makes later removal of KHT crystals easy.
4. Add KHT powder crystals @ 4/g/L.

5. Provide a CO₂ or nitrogen blanket to minimize oxygen pickup. It is important to remember that a larger amount of oxygen is dissolved at the lower temperature, but the oxidation effect becomes evident later when the wine is warmed.

6. Agitate the wine thoroughly. Agitation promotes crystal growth.

7. Allow 1 ½ to 2 hours of contact time.

8. Take the conductivity reading of the filtered wine sample and compare it with the reading obtained during the laboratory trial. This assumes that a lab trial for a given batch of wine was conducted earlier and the conductivity reading of the wine stabilized to the desired temperature is known. In place of conductivity reading, changes in the tartaric acid level can be determined analytically and compared with the tabulated value to determine wine stability.

9. After the treatment, the KHT can be allowed to settle and the wine can be racked and filtered. If time is too short to allow settling, the wine can be filtered to remove KHT. (The wine should be filtered while cold.)

10. To lower the cost of processing the wine, the KHT crystals should be ground and reused.

11. Repeated use of the KHT powder can cause microbial contamination of the wine. To prevent contamination, the KHT slurry should be stored with 500 ppm SO₂.

Wine stability with contact process has many benefits. The results are reliable and consistent. It is rapid as compared to the conventional cold stabilizing method, and with repeated use of the KHT seed crystals, the process can be very economical.

Tartrate Precipitation Inhibitors

Stabilizing methods such as chilling and the contact process involve techniques to accelerate the precipitation of potassium bitartrate and thus their removal from the wine. Ion exchange alters the composition of KHT, i.e., converting potassium bitartrate to sodium bitartrate. This makes tartrate soluble and therefore prevents precipitation.

There is yet another method that can be used to stabilize tartrate by preventing its precipitation. It is based on the observations that certain colloidal compounds found in wine inhibit the precipitation of KHT. The colloids are absorbed on the active centers on the surface of seed crystals. This stops the crystal growth. There are other compounds (not found in wine) exhibiting similar properties that can be added to wine to achieve tartrate stability. The two compounds in this category are metatartaric acid and carboxymethyl cellulose (CMC).

Metatartaric Acid

Metatartaric acid is produced by heating tartaric acid. Heat causes the transformation of tartaric acid to metatartaric acid. The changes include dehydration, esterification, and polymerization. When added to the wine metatartaric acid retards crystal growth and inhibits the precipitation of KHT. However this inhibitory effect is not permanent. The property is lost with time as metatartaric acid rehydrates to tartaric acid. The change from metatartaric to tartaric acid is influenced by storage temperature. Rankine (1989) reported that in a wine stored at 10°C, the effectiveness of metatartaric acid lasted for 18 months; whereas at 25°C, it lasted for only a few months. This suggests that metatartaric acid could be used to achieve (short term) stability in wines destined for early consumption. The suggested rate for its use is 100 mg/L. It should be dissolved in cold water and added to the wine before polish filtration and bottling. Check current BATF regulations to make sure it is legal to add.
Carboxymethyl Cellulose (CMC).

Sodium carboxymethyl cellulose is a water soluble polymer derived from cellulose. It is more stable than metatartaric acid and is very effective in inhibiting tartrate precipitation. Experiments in Germany and Australia have shown its effectiveness when used at the rate of 15 to 100 ppm. The compound is used in the food industry and is physiologically inert. However, its use at present is not legal.

References

Neradt, F. (1980). Experience with KHT stabilization by seeding (contact process) under production conditions. U.C. Davis Grape and Wine Centennial Symposium Proceedings.

Rhein, O. and Neradt, F. (1979). Tartaric stabilization by the contact process. Am. J. Enol. and Vitic. 30(4) 245-271.

Rankine, B. (1989). Making good wine. Ian McMillan Publishing. Australia.

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