

Methods for Tartrate Stabilization of Wine*

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In the last issue (Jan/Feb, 1994) of Vineyard and Vintage View, the formation and precipitation of potassium bitartrate (KHT) was explained. In this issue, various methods of stabilizing wine, with respect to KHT, will be discussed. Precipitation of KHT in bottled wine is not considered desirable and therefore winemakers employ various methods to prevent this problem. The common stabilizing methods include chillproofing or cold stabilizing, contact processes, and ion exchange. In some cases, the addition of certain compounds, such as metatartaric acid and carboxymethyl cellulose (CMC), has been successfully tried to prevent KHT precipitation. Metatartaric acid is not very stable and its inhibitory effect is temporary.

Cold Stabilization or Stabilization by Chilling

In a conventional method of cold stabilizing, a wine is chilled to a temperature just above its freezing point and is held at that temperature for two to three weeks. Chilling the wine lowers the solubility of KHT and facilitates its crystallization and precipitation. During cold storage the rate of KHT precipitation is rapid in the initial stage and it slows down with time. This is attributed to the reduction in KHT saturation level. The temperature and the storage time necessary to stabilize a wine depend on the kind of wine. For example, wines containing sugar and/or higher amounts of alcohol would require a lower storage temperature than the dry table wines with 11 to 12% alcohol. Other factors such as the concentration of acids, cations, anions, pH, and various complexing agents will also affect the tartrate stability and precipitation. To minimize the influence of complexing agents and colloidal substances on KHT precipitation, the wine should be clarified by fining and filtration before chilling and cold storage. As stated earlier, storage of wine close to freezing for two to three weeks is considered sufficient to remove excess KHT. However, the wine should be tested for bitartrate stability to determine the length of storage time. To separate the crystalline deposit of KHT following cold storage, the wine should be cold filtered. This is necessary to avoid redissolving the KHT. It should be noted that since oxygen is more soluble in cold wine (than at cellar temperature), great care should be taken to minimize oxygen pickup. Nitrogen or CO₂ blanketing and/or sparging is advisable.

A wine can be chilled by using refrigeration. Using insulated tanks can save the energy and cost of refrigeration. Many wineries take advantage of low winter temperatures to chill the wine. Installing fans to pull in the cold outside air can be helpful in lowering the cellar temperature and chilling the wine. This method of relying on Mother Nature to obtain cooling can be economical, but it may not be convenient and effective. For example, one may not be able to lower the temperature to the desired point or may not be able to hold it for the desired length of time. Sometimes cooling the entire cellar can interfere with other cellar operations.

Wine stabilization by chilling is widely practiced in the wine industry. The process is time consuming and can also be costly. Although there are other methods which are fast and in some cases economical, many winemakers prefer stabilizing high quality wines by chilling.

Stabilization by Ion Exchange

Wine stabilization by an ion exchange treatment is practiced by many large wineries. The process is suitable for producing bulk wines. When properly applied, the wine can be stabilized without significantly affecting the quality. However, some winemakers believe that it adversely affects the quality of a high quality wine, especially one with delicate flavor.

The ion exchange treatment consists of passing the wine through a column containing resin in cationic or anionic form. In cation form, the resin may be charged with sodium (Na⁺) or hydrogen (H⁺), or a mixture of Na⁺ and H⁺. When the wine is treated with cationic resin in sodium form, the Na⁺ of the resin is exchanged with K⁺ (and other cations such as Ca⁺⁺ and Mg⁺⁺) from the wine. This results in the formation of sodium bitartrate which is more soluble. There is a slight reduction in acidity. The increase in sodium content of the wine could be undesirable. In such a situation a mixed resin in Na⁺ and H⁺ form could be used. This would limit the amount of Na⁺ in the wine. However, the acidity of the wine would increase due to the exchange between the H⁺ ion (from resin) and the K⁺ ion (from wine). This may be suitable for treating low acid wine, which would benefit from increased acidity while being stabilized.

When a wine is treated with anionic resin in hydroxyl (OH⁻) form, the OH⁻ ion is exchanged for the tartrate anions (and other anions). This lowers the tartrate content of the wine. By passing the wine through both cation (H⁺ form) and anion (OH⁻ form) exchange resin, one exchanges H⁺ and OH⁻ ions for potassium and tartrate ions. Thus the net result is the exchange of bitartrate for water.

Procedure

In the ion exchange procedure, a cation exchanger resin in Na⁺ form is commonly used. The resin is prepared by treating it with 10% sodium chloride (common salt). The column is washed with ion exchanged water to remove chloride. Wine is then introduced from the bottom until the column is full and the air removed. Then the wine is introduced from the top and allowed to flow downward. As the wine flows through the column it picks up Na⁺ and loses K⁺ to the resin.

There comes a point when the resin is exhausted of its Na⁺ ions. This is referred to as the "break point". It is important to detect the break point by monitoring K⁺ levels in effluent wine at various intervals. After the resin is exhausted (as indicated by the presence of potassium in outcoming wine), it is washed with water and can be regenerated again.

After repeated use the resin loses its exchange capacity. When this occurs the resin is soaked in a hydrogen peroxide solution to remove contaminants.

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The ion exchange method of stabilizing wine is rapid and economical. It is specially suited for stabilizing very large quantities of wine.

Contact Process

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 sediment. In a supersaturated solution (e.g., wine) the crystallization process occurs in two stages. In the first stage, also referred to as the nucleation phase, 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 the 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. This research has shown that the addition of 4 g/L of powdered KHT is sufficient to render a wine stable. Adding 4 g/L of powdered KHT gives 17 million KHT fragments/ml (Rhein & Neradt, 1979). Adding KHT in amounts less than 4 g/L will require a longer time to stabilize the wine. Using higher amounts than 4 g/L of KHT is not recommended because it is uneconomical, rather difficult to remove, and the improvement in KHT reduction is marginal.

Table 1 contains the data showing 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 (8).

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 .67 g/L (i.e., 36.8%). Increasing the rate of KHT to 12 g/L reduced the tartaric acid level by .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, 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 to 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 powder, 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 of particles 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 %.

Particle size	Commercial KHT from German source, Unused	Commercial KHT from Spanish source, Unused	Commercial KHT from Spanish source, After 5 uses	Commercial KHT from Spanish source, Ground after 8 uses
≤ 5µm	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
≥40 µm	57.0	61.5	96.0	49.5

Source: Neradt (1980).

Fouling of KHT Crystals

Fouling of KHT crystals occurs when, during the crystallization processes, certain colloidal substances occupy the active sites on the crystal surface and, as a result, 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 fouled 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 the 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.

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 stabilizing temperature is generally between -4 to 0°C (24.8 to 32°F).
3. Chilling the wine may cause precipitation of unstable material (especially in red wines). In such a case, polish filtration of a 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 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 up.
6. Agitate the wine thoroughly. Agitation promotes crystal growth.
7. Allow 1 1/2 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 a 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, then 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 KHT powder can cause microbial contamination of the wine. To prevent contamination, the KHT slurry should be stored with 500 ppm SO₂.

Wine stabilization with the 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.

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	656
	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).

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 so 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 adsorbed 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 the 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 metatartaric acid.

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.

*Previously published in *Vineyard & Vintage View*, Mountain Grove, MO.