A GUIDE TO THE FINING OF WINE

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Introduction

Wine is a product of both the vineyard and the techniques the winemaker uses. Occasionally, aspects of the wine need to be refined more dramatically than can be dealt with by field adjustments or simple blending because not every growing season or fermentation goes the way the winemaker wants. Fining is a technique that is used to remove unwanted juice/wine components that affect clarification, astringency, color, bitterness, and aroma; the technique works for both red and white winemaking. Although fining is a useful technique to master, it is an indicator that there may be a problem in your vineyard or winemaking. However, in some cases the only solution available is fining. This guide will help you analyze the various problems that occur during the winemaking process and determine what fining agents are available to solve them (Table 1).

<table>
<thead>
<tr>
<th>Problem</th>
<th>Description</th>
<th>Fining Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S, thiols</td>
<td>Stinky (rotten eggs, stagnant water, onions)</td>
<td>Copper sulfate</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>Haze (gelatinous masses)</td>
<td>Enzymatic treatment</td>
</tr>
<tr>
<td>Proteins</td>
<td>Haze (off-white flakes)</td>
<td>Bentonite</td>
</tr>
<tr>
<td>Tannins (excess)</td>
<td>Astringent</td>
<td>Protein</td>
</tr>
<tr>
<td>Catechins</td>
<td>Bitter</td>
<td>PVPP</td>
</tr>
<tr>
<td>Browning, stink</td>
<td>Off-color and aroma</td>
<td>Carbon</td>
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</table>

Table 1. Wine production problems that can be solved with fining.

Fining for Clarification

Primarily done during white wine production, fining for clarification helps remove partially soluble compounds that make a wine cloudy or form a precipitate at the bottom of the bottle. Clarification fining also helps speed up the settling process if added post-fermentation. Two of the most common sources of hazing that can be modified with fining are proteins and polysaccharides. These problems are generally remedied post-fermentation, although pre-fermentation fining can help alleviate problems caused by fruit infected with mold.

Protein-caused hazing

Bentonite is a fining agent generally regarded as safe (GRAS) by the federal government to add to wine (21CFR182). Formed through the weathering of volcanic ash, bentonite is a clay made of soft phyllosilicate mineral. Silica, aluminum, and magnesium are the main components of bentonite, but it is also associated with the cations calcium and sodium. There is evidence that sodium bentonite from the United States has a larger swelling capacity than calcium bentonite found in Africa and Europe, which allows sodium bentonite to adsorb proteins more effectively (Blade and Boulton 1988).

Because bentonite’s layered structure allows it to absorb water readily, it is usually added to wine or juice as a clay–water suspension. It is also common practice to hydrate bentonite and wait 2 days before using it. Bentonite itself has no overall charge because it is associated with either sodium or calcium cations. Thus, when added to wine, the fining agent behaves much like an ion exchange system. Positively charged particles such as proteins exchange with the metal cations and the bentonite–protein complex settles to the bottom. Mixing is generally required for the most efficient use of bentonite, and even after settling it can be remixed to adsorb more proteins.

Proteins must have a positive charge at juice or wine pH in order to interact with bentonite. The functional groups on proteins that are positively charged at wine pH are amine groups such as those found in the amino acid residues lysine and arginine. Thus, it is not surprising that arginine or lysine can be depleted by bentonite fining, leading to more prolonged fermentations (Bach and Hoffman 1978).

Research to explain how the physical volume of protein has an effect on how well it interacts with bentonite indicates that ethanol separates the silicate layers, allowing larger proteins to adsorb to the bentonite (Achaerandio et al. 2001). Thus, at higher concentrations of ethanol, the protein binding capacity of bentonite is improved for larger proteins that otherwise would not fit. The trend in making wine with high ethanol content (exceeding 14% in some cases) is compatible with such results. Smaller proteins do not bind at greater levels with increased concentrations of ethanol. Bentonite fining done with juices prior to fermentation will not result in enhanced protein binding capacity either.

Experiments with sparkling wine made in the “methode champenoise” style showed that bentonite fining of the initial wine (prior to secondary fermentation) had no effect on the wine volatiles. Researchers actually found that the normal losses and changes to aroma during aging were more
Polysaccharides are another cause of hazes in wine. Of the several different types of polysaccharides found in grapes, the majority are derived from the berry cell wall. Polysaccharide abundance is determined by solubility and tissue breakdown. Most polysaccharides are insoluble in ethanol conditions so there are few left in wine. Type II arabinogalactan proteins are the most abundant polysaccharide-like compounds. Glycoproteins are compounds with a protein core and polysaccharides attached to their exterior. The significance of the polysaccharide component to the protein is the additional solubility provided by the sugar groups. Type II arabinogalactan proteins are one of the only polysaccharides left in finished wines and are thought to persist because they are found in such low concentrations (20 and 50 mg/L).

Other polysaccharides present in juice and wine are arabinogalactans, rhamnogalacturonans, xylglucans, galacturonans, and pectic polysaccharides. Juice yield is often improved by the breakdown of polysaccharides, which continues after grape crushing. Water that is trapped within polysaccharides by weak chemical bonds is released during their breakdown.

The polysaccharide content of wine is limited by its solubility in ethanol. During the course of fermentation, many polysaccharides precipitate and settle to the bottom of the fermentor. The removal of polysaccharides is done with enzymes that have unique chemical reactivity to particular compounds. The main strategy is to use a mixture of enzymes (containing cellulase, hemi-cellulase, protease, pectinase, and/or beta-glycosidase), termed the “kitchen sink” method.

These enzyme cocktails break down several different classes of polysaccharides simultaneously and for the most part are very efficient. However, beta-glycosidase enzymes cleave the glucose of anthocyanins and destabilize them (Bloom and Thomassen 1985). Beta-glycosidase enzymes are also made by yeast but are not particularly stable and have little or no effect on the sensory properties of finished wine (Delcroix et al. 1994).

Another difficulty with enzymes is that they are only effective under specific pH, temperature, and ethanol conditions. Even more problematic is that the quantity and composition of grape polysaccharides varies from season to season. Empirical experimentation is required each season to determine the most effective way of removing excess polysaccharides. Varying the amount of enzyme is generally a good enough solution. However, if the grapes have been infected with the Botrytis cinera fungus, the amount of type II arabinogalactan glycoproteins increases threefold, while arabinogalactan is also increased by up to 25%, making it difficult to enzymatically treat. This leads to a lower filterability of the infected wine.
Fining for Astringency

To understand how protein fining works on astringency, you must first understand the basics of astringency. Astringency is not a flavor, but a tactile sensation that arises from reduced mouth tissue lubrication. Tannins are thought to cause this delubrication by binding and precipitating with salivary proteins (Gawel 1998, Noble 1998). Fining to remove tannins from wine is generally done when a wine is judged too astringent; it primarily applies to red wines since the amount of tannin in white wines is negligible.

The astringency consumers expect varies by cultivar and wine type. Wine that is to be consumed immediately should have a moderate to low level of astringency to match consumer expectations. Wines intended to age can be fairly astringent at release, as they will become less astringent over time.

Determining whether a wine is too astringent is generally left to the winemaker’s judgment, but can also be verified or tested with a sensory panel. Chemically monitoring wine tannin can help you understand how changes in astringency relate to how acceptable a wine is to consumers.

Fining for astringency acts in a similar way to how the sensation is caused in your mouth. To reduce the astringency of a wine, you add protein. Just like salivary protein, the protein added to wine coagulates with the tannin to form an insoluble complex. After time it settles to the bottom of your barrel or tank as a precipitant.

Although fining is a useful technique to reduce astringency, it is always preferable to simply not extract too much tannin during winemaking or blend with less astringent wines.

Proteins used for fining astringency

Most of the available fining proteins are by-products from other food industries (see Table 2). As a result, the proteins are generally cheap and usually a mixture. Recently in the United States and Europe, concerns have been raised about the addition of animal proteins to wine due to the disease known as bovine spongiform encephalopathy (Mad Cow disease). The conditions under which raw collagen is denatured during the manufacture of gelatin were shown not to affect the protein that causes bovine spongiform encephalopathy (Shreiber 1997). In 1997, the Food and Drug Administration recommended stricter guidelines to avoid contaminated gelatin (Shreiber 1997). This has led to research into the use of proteins derived from plant sources (Maury et al. 2003).

Table 2. Commercially available proteins and their chemical characteristics.

<table>
<thead>
<tr>
<th>Protein</th>
<th>Range of Application (mg/L)</th>
<th>Weight (daltons)</th>
<th>Isoelectric Point (pI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casein</td>
<td>60-240</td>
<td>20-30 KD</td>
<td>3.7-6.0</td>
</tr>
<tr>
<td>Gelatin</td>
<td>30-240</td>
<td>60 KD</td>
<td>4.8-4.85</td>
</tr>
<tr>
<td>Ovalbumin</td>
<td>30-240</td>
<td>46 KD</td>
<td>4.55, 4.9</td>
</tr>
<tr>
<td>Conalbumin</td>
<td>30-240</td>
<td>60 KD</td>
<td>6.8, 7.1</td>
</tr>
</tbody>
</table>

The plant proteins tested so far are derived from wheat and white lupin. Gluten, a wheat protein, has been effective as a red and white wine fining and clarification agent (Maury et al. 2003, Marchal et al. 2002). Although not widely commercially available, the plant-derived fining agents may prove to be a valuable alternative to those from animal proteins. Gluten could be an exception because it is a well-documented allergen. It is not clear at this point how much plant-derived fining agent residue remains in finished wine. If it is established that less than trace quantities are found, specific allergen labeling might be avoided.

Tannin protein reactivity

The degree that tannins bind to proteins has to do with tannin size and subunit composition and protein chemistry. Once added to wine, proteins coagulate with the large molecular weight tannins primarily responsible for astringency. Larger tannins generally precipitate more readily with protein than smaller tannins. Tannins that have subunits containing gallic acid esters (seed tannins) interact easier with protein (Sarni-Manchado et al. 1999a), while proteins that are rich in the amino acid residue proline are some of the most effective at precipitating tannin (Oh et al. 1980, Hagerman and Butler 1981).

Proline-rich proteins are found in human saliva and the connective tissue of different mammals (Lu and Bennick 1998). This connective tissue in its denatured form can be purchased as gelatin and is one of the most common fining agents. The proline residues place kinks in the backbone of the protein, which gives the protein a more string-like structure that allows easier access for tannins to bind. Although larger proteins are typically better at precipitating tannin than smaller proteins, some small proteins that are rich in proline precipitate tannin as effectively as larger proteins.

Grape seed and skin tannins have average polymer lengths of 10 and 32, respectively (Kennedy et al. 2000, Souquet et al. 1996). The average polymer length of seed tannins that precipitate with salivary proteins is 5.8 subunits (Sarni-Manchado et al. 1999b). However, the size of tannin that each
of the different enological proteins will precipitate with is yet to be defined. The fact that most proteins are mixtures also complicates efforts to target specific molecular weight classes of tannin. Nevertheless, the overall ability of a protein to remove tannin is highly efficient.

**Protein charge**

The isoelectric point (pI) of a protein is the pH at which its net charge is zero. Protein structure is made up of many amino acid residues, and each of these residues has its own charge status. In most cases, the pH of a solution controls the acid residue charge status.

Proteins are generally less soluble and have been demonstrated to co-precipitate tannin maximally at their isoelectric point. Of the proteins available for commercial scale fining, the milk protein casein has the closest isoelectric point (3.7) to wine pH. Gelatin and albumin proteins are exceptionally soluble at their isoelectric point, whereas casein is not.

**Protein selection for fining**

Although most protein preparations for fining are mixtures, you can purchase more pure fractions of proteins from commercial vendors. One of the most well known but least understood fining practices is the use of egg whites. Egg whites contain a mixture of polysaccharides and proteins, and are chosen primarily because of availability and ease of use. However, it is often difficult to reproduce the same results due to variations in egg volume and consistency. Purified forms of egg white proteins can also be purchased (ovalbumin and conalbumin). Casein is probably the best protein available because its isoelectric point is close to wine pH and it does not leave a residue in wine (Boulton et al. 1996).

Gelatin is a good protein for fining because it is rich in proline and reacts quite readily with tannin. However, gelatin can take a long time to form insoluble complexes with tannin, and it leaves a protein residue. In addition, gelatin does not react with many protein dyes, making it difficult to detect residual protein in your wine. Gelatin also must be added to wine within a specific temperature range (see manufacture details for exact temperatures).

Despite their limitations, there are many gelatin preparations available. During the manufacture of gelatin, a combination of chemical processes alters protein size and purity. The raw proteins undergo both enzymatic (protease) and chemical hydrolysis (boiling). Manufacturers claim that choosing proteins of different sizes allows the user to remove specific classes of tannin. A study performed to test this theory using gelatins that underwent hydrolytic cleavage confirmed via gel electrophoresis that the proteins were of different molecular weight. The protein fractions showed small differences in their ability to precipitate tannin, except for the largest protein fraction that did not precipitate as much tannin (Maury et al. 2001). The researchers reasoned that the higher molecular weight proteins had structural conformations that lowered their ability to bind tannins.

**Addition amounts**

Table 2 provides information about the amounts of pure proteins that you can add to wine. It is important to note that federal guidelines limit the amount of egg whites to 2 lbs (907.2 g) in 1 gal of brine solution containing 1 oz (28.35 g) of potassium chloride (KCl), while the maximum dosage of the egg white brine solution is 1.5 gals per 1,000 gals of wine, or 3 lbs of egg white per 1,000 gals.

Protein products obtained from different manufacturers generally provide information about how much to add. However, it is advisable to perform trials with your fining agents before scaling up. Small-scale trials with a range of fining agents and different additions allow the winemaker more control and knowledge about how the fining agent(s) will alter the wine. The additions should be varied from low to high and a variety of fining agents tested to make an informed decision.

**Tannin removal efficiency**

The relationship between how much tannin is removed by a specific amount of protein varies according to both the individual characteristics of the tannins and proteins involved and their interaction. Gelatin fining is documented to remove from 10 to 20% of an initial tannin concentration (Maury et al. 2001).

**Duration of fining**

The time required for tannin and protein to interact is very fast, taking anywhere from 15 minutes to an hour, whereas the time for the particles to settle can take between 2 and 3 days. The duration of the settling period is dependent on the wine density, volume, temperature, and protein amount added (Boulton et al. 1996).

**Timing and distribution of addition**

Fining earlier rather than later helps prevent losing polymeric pigments (the source of desired coloration in wine) through co-precipitation with protein. This class of polymeric pigment is preferentially formed over smaller non-protein precipitable polymeric pigments during wine aging (Harbertson et al. 2003, Adams et al. 2004).
The fining addition needs to be distributed throughout the wine evenly. This can be achieved by pumping the wine over progressively while slowly adding the fining agent. A dosing valve can be placed between the pump and tank that will allow you to vary the amount of fining agent that is distributed into the wine.

Wine is generally filtered after the wine is racked away from the solids to ensure that there are no protein instability problems during wine aging. Measuring protein concentration and heat stability before and after fining can also help avoid future instability.

**Assessment of fining**

Monitoring your fining trial is recommended, both with sensory and chemical techniques. Measuring tannin can be done directly or when under duress with a total phenolics analysis. It is best to run a phenolics panel that measures each of the phenolic classes so that you can assess the fining agent impact on the phenolic composition of your wine.

It is simple to measure total phenolics, tannin, and polymeric pigments during a fining trial and before and after fining. There are many methodologies available for measuring phenolics in wine and several can be performed in a laboratory setting. A complete discussion, along with recommended methodologies, can be found in Harbertson and Spayd (2005). If your laboratory does not have the necessary equipment, there are outside laboratories that can help.

**Fining for Color and Bitterness**

**PVPP**

The use of insoluble fining agents such as polyvinylpolypyrrolidone (PVPP, or Polyclar) to wine is fairly common to help reduce oxidative browning in white wines. PVPP is popular because of its large binding capacity (Singleton and Rossi 1965). Most of the research into its efficacy involves the soluble form of PVPP (polyvinylpyrrolidone, or PVP), which can preferentially bind catechins over tannins, thus helping to reduce bitterness and potential browning. However, because of health concerns with PVP leaving a residue in wine, PVPP is preferred. PVPP can be added after crushing or post-fermentation, with better results prior to fermentation; a typical dosage is 4–10 lbs/1,000 gals.

**Activated carbon**

Activated carbon can be used to remove the majority of phenolic classes from wines without specificity. Wines with color problems such as excessive browning or pinkness can be helped because carbon is effective at removing non-polar substances, but weak at removing water-soluble components such as sugar and amino acids. Not many wineries use activated carbon because it can strip wine of both desirable and undesirable components. With wines that have significant problems, this may be an acceptable loss. Activated carbon is used more often on white wines than reds.

**Fining for Off-aromas**

Probably the most obvious types of wine flaws are those that can be characterized as off-aromas. Since the aroma of wine is generally assessed before the taste, often wines with off-aromas don’t actually get tasted. There are a few wine off-aromas that can be removed by fining, while others are unassailable. The most common is hydrogen sulfide (H2S), which causes the rotten egg aroma that winemakers refer to as “reduction.”

Reduction in no way downplays the aroma’s presence, but is a polite way of saying a wine stinks. Some winemakers consider traces of reduction as flaws, while others see them as added complexity. However, there is a fine line between complexity and off-character that each winemaker needs to draw.

Hydrogen sulfide forms by yeast during the reduction of sulfate or sulfite and by the catabolism of amino acids that contain sulfur (such as cysteine or methionine). The presence of elemental sulfur that is used as an anti-fungal agent in the vineyard also contributes to excessive hydrogen sulfide production during fermentation. If used in the vineyard too close to harvest (1 month before or after is safe), methanethiol, another smelly compound, is formed from methionine and sulfite in a reaction catalyzed by iron (Wainwright et al. 1972).

The production of hydrogen sulfide by yeast is a complex process that is controlled by several sets of genes (Spiropoulos et al. 2000). It is naturally made during the fermentation of most musts. Excess hydrogen sulfide is typically produced when yeast lack adequate nitrogen or vitamins. If the aroma persists after the fermentation is completed, some of the sulfur compounds can be removed. Table 3 includes a list of the offending sulfur compounds found in wine, the concentration at which most people can perceive them, and a description of the aroma.

When added to wine in very small quantities, copper sulfate forms an insoluble precipitate (copper sulfide) that can be left behind after racking. The addition should be less than 0.5 mg/L, which is the maximum residual allowed according to federal laws.
The measurement of copper is best left to commercial laboratories because of the equipment required. Some winemakers use copper screens to get the same effect, but this makes it difficult to determine the yield of copper added to the wine. Copper, although a great way to remove sulfur, can also oxidize your wine, so it is important to control its use. Traces of brown/black precipitate will form but are not always observed. Negatively charged proteins may react with copper and so occasionally it will be necessary to add further copper to remove the sulfur compounds. The reaction between copper and H2S is over quickly and a change can be perceived after a few hours.

Other sulfur-derived off-aromas are thiols and alkyl sulfides. It is important to note, however, that not all thiols are considered off-aromas. In Sauvignon blanc, several thiols (4-mercapto-4-methylpentan-2-one, 3-mercaptohexyl acetate, 3-mercaptohexan-1-ol) have been identified that provide its characteristic aromas (Tominaga et al. 1998). Using copper with Sauvignon blanc may strip these distinctive odors, but it may be necessary in some cases. Thiols have a free sulfhydryl group (-SH) and can be bound by copper and removed, but alkyl sulfides (-CH2-S-CH2-) have alkane groups attached to sulfur that hinder copper’s ability to bind sulfur.

The most prominent alkyl sulfide is dimethyl sulfide, which is a very disagreeable aroma, reminiscent of rotten cabbage or the seaside at low tide. In model solutions it is possible to use sulfite in conjunction with ascorbic acid (vitamin C) to cleave the disulfide and trap oxygen radicals, thus preventing the reformation of the disulfide so copper may be used to remove the thiol. However, many winemakers report no appreciable reduction in dimethyl sulfide with this method. Researchers found that interconversion of sub-threshold levels of disulfides to supra-threshold amounts of thiols at room temperature took 700 days (Bobet et al. 1990), making it an unlikely option for most wineries.

Yeast hulls have been promoted as a means of removing sulfur aromas—including dimethyl sulfide—but there is limited published evidence to support the claim (Palacios et al. 1997). Aeration of wine is another popular way to remove hydrogen sulfide. The loss of aroma is due to volatilization of hydrogen sulfide and formation of disulfides that have a greater sensory threshold concentration and thus are seemingly odorless. However, if enough disulfides form at a high enough concentration to be appreciated, your wine will have an off-aroma. This is especially problematic because disulfides are so difficult to remove. Further, under reductive conditions, disulfides can be reduced back to mercaptans, which have a lower threshold.

One of the most difficult aspects of sulfur defects is there are no methods available in a typical winery to measure them. Gas chromatographs must be equipped with special detectors for sulfur that only commercial laboratories can usually afford. Since the threshold of most of these compounds is very low, the best alternative detector is your nose. Thus, monitoring your cellar for sulfur aromas is probably the most effective option short of sending samples to a commercial laboratory. Routine tasting of the wines in your cellar and marking suspect barrels with chalk can also help to monitor your products for sulfur aromas.

**Conclusion**

There are many problems that can be handled with fining. Careful monitoring of your wine and characterizing its development during production will help in maintaining high quality. In some cases (i.e. sulfur), this may be impossible with chemical methods, but smelling and tasting also work. However, it is important to note that addressing vineyard issues such as vine nutrition and site selection can help prevent some of these problems. Please see Moulton and King (2005) for guidance specific to Washington vineyards.
References


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**Glossary**

**Astringency**: a tactile sensation that arises from the reduction of the lubrication of the tissues in the mouth.

**Bentonite**: a clay made of soft phyllosilicate mineral, formed through the weathering of volcanic ash.

**Copper Sulfate**: a copper salt that is used to remove sulfur aromas.

**Fining**: a winemaking technique that removes certain unwanted wine components.

**Isoelectric Point**: the pH at which the net charge of the protein is zero and usually results in reduced solubility for the protein.

**Hydrogen Sulfide**: a sulfur compound that has an odor reminiscent of rotten eggs.

**Polysaccharides**: a heterogeneous group of complex sugar polymers that are generally derived from grapes.

**Polyvinylpolypyrrolidone**: an insoluble fining agent that removes low molecular weight phenolics such as catechins from wine.

**Tannins**: a heterogeneous class of polymeric phenolics that are capable of binding proteins; a major source of astringency in wine.