Fining is the addition of a reactive or absorptive substance to remove or reduce the concentration of one or more undesirable constituents. Fining agents are added for the purposes of achieving clarity, color, flavor and/or stability modification in juices and wines. Fining agents are grouped according to their general nature.

1) Earths: bentonite, kaolin
2) Proteins: gelatin, isinglass, casein, albumen
3) Polysaccharides: agars
4) Carbons
5) Synthetic polymers: PVPP, nylon
6) Silicon dioxide (kieselsols)
7) Others - including metal chelators, enzymes, etc.

Many fining agents contain an electrical charge. If this charge is the opposite of the particles in suspension, then neutralization and absorption may occur. In a fining operation, small particles of suspended solids are induced to coalesce so that they form larger particles which, because of their density relative to that of the wine or juice, settle from solution. In most cases, the fining agent adsorbs suspended material and exerts some clarifying action by virtue of formation of particles of high density, thus increasing filterability.

The effectiveness of fining is dependent upon the agent, the method of preparation and addition, the quantity employed, the pH, the metal content, the temperature, the age of the wine, and previous treatments. Fining is a surface action performed by the agent (adsorption); therefore, the method of hydration and addition of the agent is of extreme importance. Four common methods of adding fining agents are:

1) uniformly and slowly through a 'Y' on the suction side of a positive displacement pump while transferring or mixing;

2) uniformly and slowly through an 'in line' proportioning pump;

3) uniformly and slowly through a 'T' into a Guth-type tank mixer; or

4) added slowly in slurry form to a barrel using a dowel to stir in a figure-8 motion through the bung hole.

Bentonite is the most commonly used fining agent in the wine industry. Its principle uses are for the clarification and protein stability.
A major problem encountered in juice and wine production, particularly white wines, is protein stability (the removal of heat-sensitive proteins). This form of instability is possibly second only to potassium bitartrate as the most common nonbiological defect in commercial wines. Bentonite fining removes both stable and unstable proteins. The goal is to lower the unstable protein content to a level at which precipitation in the bottle will not occur, while using as little bentonite as possible. The use of bentonite to obtain protein stability is a somewhat confusing issue due to the variation in bentonites, the nature of wine proteins, and the vastly different procedures by which protein stability is determined.

Bentonite is volcanic material which was deposited millions of years ago in broad layers, which weathered and changed from a fragile glassy state into a mineral. This mineral is classified as a montmorillonite, which is named after the small French town where it was first discovered. In this country, bentonite is principally mined in Wyoming - hence the term 'Wyoming clay'. The type of bentonite, the source, and its purity influence its properties.

Bentonite is a complex hydrated aluminum silicate with exchangeable cationic components: (Al, Fe, Mg) Si₄O₁₀ (OH)₂ (Na⁺,Ca++)++. The most commonly used form in the United States is sodium bentonite. Sodium bentonite has enhanced protein binding ability over calcium bentonite.

Bentonite exists as small plates (1NM by 500 NM) which when hydrated separate to form a colloidal suspension with enormous surface area. Its subsequent activity in solution is like that of a multiplated, linear, long-chained, principally negatively charged molecule. The mechanisms of protein removal are absorptive interactions between positively charged proteins and negatively charged plate surfaces. Some bentonite absorption of uncharged molecules also occurs. Additionally, due to the fact that the platelet edges are positively charged, some limited binding of negatively charged proteins may occur (see Figure 1).

Bentonite may indirectly adsorb some phenolic compounds via binding with proteins that have complexed with phenolics. However, the amount of phenols removed is usually not great. Bentonite is known to affect red wine color directly by binding with positively-charged anthocyanins, which results in up to 15% color removal. Bentonite color removal is dependent upon the temperature and age of the wine. Bentonite removes more color from younger wines than gelatin, for example, while the opposite is true for older wines. This is due largely to the greater action of bentonite on colloidal color material found in younger wines (Bergeret 1963). Fining certain red wines with 1/2 to 1 pound of bentonite per 1000 gallons is said to enhance membrane filterability. Presumably, this is due to a reduction of the colloidal particles in suspension.

Despite the vast literature on protein instability, the actual protein levels at which wines will remain protein-stable are unknown. Wine proteins are a mixture of proteins derived from the grape and from autolysed yeast. Protein nitrogen content of wines varies between 10-275 mg/l (Boulton 1980). Variety, vintage, maturity, condition of the fruit, pH, and processing methodology affect the must and wine protein content. Yeast proteins, however, have not been shown to play a role in white wine protein clouding.

It appears that about 1/2 of the total white wine protein content is bound to a minor quantity of grape phenolics (flavonoids), and this portion is thought to be responsible for protein haze (Somers and Ziemelis 1973). White wines contain relatively large insoluble proteins that slowly precipitate from solution. Most white wines are too deficient in phenols to cause initial protein precipitation. Protein haze may be
due to the fraction of residual wine proteins that have been rendered prone to precipitation by their interaction with small quantities of reactive phenols. Bentonite removes equal amounts of both protein fractions.

In order to understand bentonite's ability to remove proteins, it is important to understand the nature of juice and wine proteins. Wine proteins can be characterized by size and electrical charge. There are as many as 8 protein fractions that range from 11,000 to 28,000 molecular weight units (Boulton 1980).

This is a depiction of a wine protein.

\[ \text{\includegraphics[width=0.2\textwidth]{wine_protein.png}} \]

At a certain pH, the positive and negative charges of each protein fraction are equal and the protein is least soluble. This pH value is known as the isoelectric point, or isoionic point, of the protein.

The lower the difference between the juice or wine pH and the isoelectric point of the protein fraction, the lower is the net charge on that protein fraction and the lower is the solubility of that fraction. If the juice or wine pH value is quite different than the protein isoelectric point than the protein charge is great and the greater is the ability of that protein to electrostatically bind to fining agents. Therefore, the isoelectric properties of proteins influence not only their natural tendency to precipitate but also their affinity to be removed with various agents. Two examples of the relationships between wine pH and isoelectric points are given in Table 1.

If the wine pH of Malvasia Istriana is 3.2, then the protein fractions above 3.2 pH will all be positively charged and those below will be negatively charged. The positively charged proteins will react with a fining agent of mainly the opposite charge (\(-\)) such as bentonite. In the case of Malvasia Istriana, there would remain three protein fractions which, because of their negative charge, would not be easily removed by the use of bentonite. Those protein fractions with isoelectric points closest to pH 3.2 have a limited charge and would not electrostatically bind to bentonite.

The isoelectric points of the protein fractions in White Riesling wine are generally at elevated pH's, as indicated. The pH of White Riesling wine is usually below pH 3.6, thus assuring that each protein fraction will be positively charged and bound with negatively charged bentonite.

Protein clouding in white wines is a greater problem when the wine pH is near the isoelectric point of the various protein fractions. This is due to the fact that bentonite will remove, preferentially, the most positive proteins. The electrostatic charge of various protein fractions explains the observable phenomena of not being able to stabilize certain wines with the use of bentonite alone, or only with excessive amounts that can strip wine character.
Table 1

PROTEIN ISOIONIC POINTS
Adopted from Anelli 1977

(Examples of the isoelectric points of several wine cultivars. Unbracketed numbers are pH, bracketed numbers are the percentage of the total protein fraction at the various isoelectric points)

<table>
<thead>
<tr>
<th>VARIETY</th>
<th>ISOIONIC POINT</th>
</tr>
</thead>
<tbody>
<tr>
<td>MALVASIA</td>
<td>2.5 (18)</td>
</tr>
<tr>
<td>ISTRIANA</td>
<td>7.1 (5)</td>
</tr>
<tr>
<td>WHITE</td>
<td>3.6 (19)</td>
</tr>
<tr>
<td>RIESLING</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 is an example of the considerable protein variation among grape cultivars. Within the average range of wine pH's, the lower the pH the less quantity of bentonite is usually needed for stabilization. Due to a change in the wine pH relative to the isoelectric points of proteins, such activities as chill proofing, blending, malolactic fermentation, etc., can render a previously stable wine unstable.

The method of preparation significantly affects bentonite's ability to remove proteins. Bentonite is made up of small platelets that are separated by a layer of water molecules. During hydration, the charged platelets repel each other and pop apart. As this occurs, swelling begins. Water molecules partially neutralize the exposed surfaces holding them apart, thus exposing the large reactive surfaces.

**Figure 1**

Bentonite Hydration and the Formation of the 'House of Cards'

Most bentonites should be hydrated by very slow addition to water to avoid clumping. One hydration procedure that has been recommended involves mixing bentonite into 46°F water, 96 grams/l, or about 1/2 pound per gallon, then agitating and reheating to 60°C once daily for 3 days prior to use. This allows the platelets to disperse and to form a gel.
Most winemakers prepare bentonite by simply adding it slowly to hot water and letting the slurry stand for a day or two prior to use. However, some bentonite suppliers suggest merely cool water hydration. The winemaker should consult his bentonite supplier.

When properly dispersed, bentonite sets up a network commonly known as the 'house of cards' (see Figure 1). This network encases droplets of water, which prevent the bentonite from coalescing or flocculating with itself. In order for bentonite to be effective in binding with proteins, the bentonite platelets must be separated into a homogeneous suspension. This is the primary purpose of 'aging' bentonite prior to use. The bentonite-to-water ration in the slurry is usually 5-6% wt/vol. The total quantity of water must not exceed 1% of the wine volume treated.

Because bentonite's protein binding activity is due to its exposed surface area, slurries for laboratory trials must be prepared exactly the same as suspensions used for cellar finings. For example, waring-type blenders used for laboratory preparations exert a shear force that affects the hydration and separation of the platelets which cannot be duplicated in the cellar.

Bentonite of various types exists in different geographical locations, is mined from different depths, and comes in different levels of purity, particle size, adsorption capacity, and swelling ability. The type and source of the bentonite used can affect protein removal. This is generally the result of variations in the swelling capacity and cation exchange capacity of the bentonite. There can be slight differences in bentonite from one shipment to another. This makes it imperative that the same lot of bentonite be employed for both laboratory trials and cellar activity.

There are several 'types' of bentonite. Volclay is a trade name for western bentonite of varying grades. KWK is a term for a particular volclay used in the food industry which is surface mined, has a high cation exchange capacity (binding ability), high swelling ability, low grit content, low iron, and a high level of purity. Due to these features, KWK bentonite appears to be the most desirable form for the wine industry. KWK's binding capacity averages 80-100 milliquivalents per 100 grams while other volclay grades range from 65-80 and average around 70. The higher the milliquivalent capacity, generally, the greater is the potential for protein binding.

Agglomerated KWK bentonite is now in fairly common use in the wine industry. It is produced by drying high disperson bentonite, grinding this through a 325 mesh screen and agglomerating or binding this powder with a sodium silicate spray. Standard bentonite, hydrated in warm water, requires 48 hours or longer to separate and 'open up'. Agglomerated bentonite has the ability to unfold at a much faster rate, thereby reducing the time period required for hydration. Presumably this is the result of the sodium silicate acting as a protective colloid for each plate, thus increasing solubility. Additionally, agglomerated bentonites form a slurry which is much less viscous than standard nonagglomerated bentonites which may enhance the ease of addition.

As stated, sodium bentonite is generally employed in this country because it has greater swelling power than calcium bentonite. Calcium bentonite platelets tend to clump together, thus reducing the exposed surface area, and therefore, protein binding. Calcium bentonite precipitates at a slower rate than sodium bentonite but produces more compact lees (Perenczi 1966). Calcium bentonite is employed in Europe in juices and wines where it is more prevalent and where sodium levels are restricted. The sodium content in foods is becoming a large concern. The sodium pickup from sodium bentonite can be expected.
to be 1.7 - 3.5 gr/100 of sodium bentonite. Because of its compact lees calcium bentonite is generally preferred vs. sodium bentonite as a riddling aid in methode champenoise. Indeed, the commonly expressed problem with sodium bentonite is excessive lees production and the loose compaction of those lees. Bentonite lees volumes often range from 5-10%. There are several methods employed to help minimize these problems.

Bentonite needs only minutes to react, precipitating peptides and proteins. Therefore, the winemaker need not let his wine or juice settle following bentonite addition but may remove the bentonite and reacted proteins 'in line' with the proper filtration or centrifugation equipment. Three-quarters of the proteins react to bentonite within the first minute of contact. It may be undesirable to leave bentonite in contact with wine or juice for any prolonged period of time because of the possibility of leaching or 'sluffing off' of proteins from the bentonite platelets.

An additional method of avoiding excessive lees formation in wine is to hydrate the bentonite in the wine to be fined rather than in water. Although this can significantly reduce the bentonite's binding ability because of premature fouling, it often produces about 1/2 the normal lees volume.

Hydrating bentonite in hot water that has been pH-adjusted to about 3.0 produces a bentonite slurry that appears to have a slightly lower swelling ability. This reduction in viscosity of the bentonite slurry may aid in its dispersement into juice or wine. Although lower viscosity reduces bentonite's protein binding ability, the lowered pH is an aid in preventing biological growth within the bentonite slurry. Winemakers should use water that has a low mineral content should to avoid bentonite clumping, which may help reduce lees volume. Dissolved minerals (cations) in the slurry water will preferentially replace the sodium ions clustered on the sodium bentonite clay surface and detrimentally affect the hydration, the viscosity, and the binding ability. Additionally, wines high in metals, particularly calcium, fined with bentonite are said to result in poor lees compaction. Bentonite fining of ion-exchanged wines may result in poor bentonite absorption and lees compaction. Therefore, when planning both operations, bentonite addition should precede ion exchange.

Bentonite may be counterfined with kieselsol (aqueous silicon dioxide) to aid in lees compaction. Some find success in protein-stabilizing and clarifying white juices and wines by fining with 15 ml of a 30% kieselsol solution, 3 grams of gelatin, and 25-250 grams of bentonite per 100 liters (26.4 gallons), depending upon the results of fining trials. Gelatin is a positively charged protein which will bind with negatively charged species such as tannins kieselsols and bentonite. Gelatin can be used to help flocculate bentonite and possibly aid in lees compaction. A discussion of the use of protein fining agents is given by Zoecklein 1988.

Additionally, fining juice or wine that is already relatively free from suspended solids will minimize lees formation and, consequently, the bentonite requirement. Some winemakers prefer multiple fining with bentonite rather than a single large addition (Rector 1981). This approach may be successful in reducing the overall bentonite requirement, particularly if the wine to be fined is free from suspended solids.

A method being used to help solve the problems of excessive lees and flavor stripping caused by fining wine with bentonite is to ferment in contact with bentonite. Fermentation in the presence of bentonite is an age-old practice used in Europe for protein stabilization. Such a practice avoids or minimizes the need for subsequent bentonite
addition into wine. Fermentation in contact with bentonite has several advantages. Possible sensory benefits may result due to the fact that only juice components are adsorbed onto bentonite not fermentation or barrel aging constituents. Fermentation lees have a lower monetary value than does finished wine lees. Thus protein stabilization or partial stabilization during fermentation may be an important economic consideration. The procedure for fermentation of white juice in contact with bentonite is as follows.

1. Settle juice to remove non-soluble solids. This may be done with refrigeration and/or the use of fining agents. A high solids level could foul the bentonite and reduce overall efficiency. Add the desired quantity of bentonite in line while racking.

2. Make any yeast nutrient, sugar and/or acid addition need to the juice.

3. Add yeast innoculum on to juice surface. Do not pump mix. The bentonite may bind with the yeast, pull the yeast to the bottom of the fermentor and thus delay the fermentation rate. For this reason, mixing is avoided.

Yeast nutrient addition is a preferable step in fermentations occurring the presence of bentonite. Bentonite may deplete the assimilatable nitrogen content of the must due to electrostatic binding and adsorption. This may result in fermentation sticking and or hydrogen sulfide production (Vos and Gray, 1979). The addition of an exogenous source of nitrogen eliminates these potential problems.

A determination of the quantity of bentonite to add to the juice to attain a protein stable wine is done empirically or analytically. Many winemakers fermenting in contact with bentonite simply add several pounds per 1000 gallons of juice. Analytical methods for specific determination of bentonite levels needed in the juice for subsequent wine stabilization are available (see Zoecklein, et al. 1988). In addition to protein stability, bentonite fining can help prevent copper casse, possibly iron casse, and enhance wine filterability via general removal of suspended solids.

The removal of protein is proportional to the amount of bentonite added. Additions of the equivalent of several pounds of bentonite per 1000 gallons of wine can reduce the protein content from an initial 50-100 mg/l to less than 10 mg/l (Kean and Marsh 1956). Although complete removal of residual wine proteins can generally be achieved by the use of bentonite, it has been recognized that this may not be necessary to obtain protein stability and may detrimentally effect the sensory quality. Bentonite additions to wine exceeding several pounds per 1000 gallons can potentially strip wine body, color - and possibly impart an earthy, freshly 'laundered' smell. Care must be used when attempting to protein-stabilize sparkling wine cuvees with bentonite. The carbon dioxide in sparkling wines is present in a free and unstable state, bound to peptides and proteins (Berti 1981). Bentonite is not specific in its interaction with wine constituents, and significant alterations in wine composition can occur as the result of bentonite fining. Excessive bentonite fining of sparkling wine cuvees can produce a finished product that has both a large bubble size and poor bubble retention as a result of too great a reduction in the protein and peptide content.

Cold stabilization procedures (conventional chill-proofing and seeding) cause both a precipitation of potassium bitartrate crystals as well as proteins. If the wine pH is below 3.65, then chill proofing causes a downward shift in pH (Beelman 1984) and enhances protein precipitation. This reduction in pH and the precipitation of proteins caused by cold stabilization is why some winemakers elect to fine with bentonite during or following potassium bitartrate stabilization. In certain wines, free tartaric acid can be complexed with proteins, polyphenolics, etc.,
inhibiting potassium bitartrate crystal formation. Removal of a portion of these complexing compounds with bentonite can enhance potassium bitartrate stability. Additionally, bentonite fining of wines during cold stabilization allows potassium bitartrate crystals to help compact the bentonite lees. For additional information on potassium bitartrate stabilization and stability evaluations, see Zoecklein 1988b.

Carefully controlled laboratory fining trials must be performed before any agent is added to cellar wines. In evaluating fining trials, the winemaker must note and record how each fining agent alters clarity, less production, less compaction, stability, color, body (front, middle, and finish), astringency, bitterness, the nose characteristics in general, the fruit, the finish, the aging potential, and overall wine palatability. To be able to duplicate laboratory trials in the cellar, the same lot of fining agent must be prepared and used in the same manner.

A final analysis of protein stability should be performed just prior to bottling. Any change in the wine pH and or phenol oxidation could effect protein stability. For a discussion of the protein stability evaluation methods commonly employed in the wine industry, see Zoecklein 1988c.

References

Rector, B., Theories and uses of fining agents, Practical Winery Jan/Feb 1983.

Trade names are used in this publication for information purposes only. The Virginia Cooperative Extension Service, Virginia Polytechnic Institute and State University, and Virginia State University do not warrant those mentioned nor do they intend or imply discrimination against those not mentioned.