A. ASPECTS OF CLARIFICATION

The purposes of clarification and fining during wine processing include removal of excessive levels of certain wine components, achieving clarity, and making that clarity stable especially from a physicochemical viewpoint. The noun *fining* is used in winemaking to describe the deliberate addition of an adsorptive compound that is followed by the settling or precipitation of partially soluble components from the wine. The materials used for these reasons are collectively referred to as fining agents, even though the solutes that they address and the mechanism of their removal vary considerably. The need to employ such treatments is often determined not only by compositional aspects of the musts but also by the winemaking practices that have been employed.

Examples of such fining reactions are: (1) The removal of tannic and/or brown polymeric phenols by proteinaceous fining agents such as casein, isinglass, albumin, and gelatin; (2) the adsorption of wine proteins by exchanging clays such as the bentonites; (3) the depletion of monomeric and small polymeric phenols by polyamide materials such as polyvinylpolypyrrolidone (PVPP, trade name Polyclar AT) and nylon; (4) the elimination of unpleasant odors by copper sulfate or other procedures, and (5) the removal of fine colloidal particle and incipient precipitates by the sieving effect of other gelatinous materials.

In each case, the adsorbent (or fining agent) has several adsorption sites on each bead or molecule and a number of solute molecules are either adsorbed to its surface or exchanged into its interior. The mechanism is usually one of hydrogen bonding between exposed carbonyl groups at the surface of the adsorbent (the protein) and hydroxy groups of the phenol (or tannin). Several of the agents currently in use (such as the proteins and the gums) are colloidal in nature and as the adsorption occurs their solubility is reduced, resulting in precipitation of the solute/agent complex from the solution.

The amount of solute removed by a certain addition of an agent will depend on the solute/agent pair as well as the concentration of
The solute in the wine and the quantity of the agent added. In special circumstances there is a direct relationship between the amount of agent added and the amount of the component removed, but in general, this will not be the case. The more usual condition will be one in which increasing levels of addition will result in further depletion of component concentrations, but with decreasing effectiveness. For this reason, it is necessary to understand the equilibrium that is established between the solute and the agent to understand the way in which the solute concentration is reduced as the agent addition is increased.

It is important to realize that the fining of wines by the addition of an adsorptive agent does not mean that the solute concentration is reduced to zero. The equilibrium nature of adsorption is such that as the component concentration is reduced, the tendency for further adsorption is also reduced and the agent becomes increasingly less effective. In most, if not all cases of fining, the solute concentration is merely lowered to a point at which it remains below a solubility condition (in a stability test) or a taste threshold (in a sensory test), and at such a concentration it is considered to be acceptable.

The addresses of equipment companies mentioned in this chapter can be found in Appendix I.

1. Characterization of Hazes

The need for fining and/or clarification will depend on the nature of the components that are responsible for the haze. Some haze particles can be insolubles such as fine dust, small fibers of grape pulp, and yeast or bacteria that remain in suspension due to very small settling velocities or charge repulsions that prevent more compact settling from occurring. Others can be partially soluble components that have precipitated from solution due to limited solubility at the ethanol content of wine and lower temperatures. Examples would be fine tartrate crystals and protein and polysaccharide hazes or finely dispersed precipitates of large-molecular-weight tannin materials that are often combined with some proteinaceous components. Clarification is generally considered to provide insignificant compositional changes compared with fining in which compositional changes are sought to prevent further precipitation. Fining can also be used to modify (improve) the sensory or stability attributes of wines even though existing clarity may not be an issue.

2. Adsorptive Phenomena

The adsorption equilibrium that is established in solution is a reversible distribution of the solute between the liquid and solid (or colloid) phases. The adsorption equilibrium relationship, often referred to as an adsorption isotherm, since the data is obtained at one temperature, can usually be quantified by one of the following equations, due to Langmuir and Freundlich:

\[
\frac{x}{m} = \frac{(x/m)_{\text{max}}}{K_L + [S]}
\]

\[
\frac{x}{m} = K_F \times [S]^{1/n}
\]

where \(x\) is the mass of the solute (or adsorbate) on \(m\) mass of solid (or adsorbent); and \(S\) is the equilibrium solute concentration in the liquid after the equilibrium is established. It is this equilibrium level of the solute that is the concentration that will remain in the wine after fining. These relationships determine the way in which the solute concentration \((S)\) determines the amount of material to be removed \((x)\) for a given addition \((m)\) of the fining agent.

The constants \(K_L\) and \((x/m)_{\text{max}}\) (or \(K_F\) and \(n\)) are properties of the adsorption pair, and can be determined by plotting double reciprocal plots \((m/x)\) against \((1/S)\) for the Langmuir equation, log-log plots of \((x/m)\) against \((S)\) for the Freundlich equation, or by using general nonlinear regression methods.