Vacuoles:

Vacuoles are void spaces inside the paint film. These void spaces may be filled with solvent vapor, but can also be completely empty, just filled with air. Vacuoles can (normally) not be seen from the outside of the film, but only becomes apparent when the film is cut open. Vacuoles may become focus points for water molecules forming liquid water, and certainly represent a weakening of the film where present.

Cracked Blistering:

This is due to localized loss of adhesion caused by entrapped solvents or solvent vapor in or below the paint coating film, or by osmosis of water. Excessively thick films may also exhibit blistering.

Blistering:

This is the process where the gas/vapor (i.e. solvent entrapment) cannot get through the top layer of the paint film and due to build up of vapor pressure, a blister is formed.
This type of blistering must not be confused with osmotic blistering.

It is necessary to distinguish between blistering, which is application related and blistering which is related to service exposure of the paint coating film.

1) Application related blistering is normally caused by:

---Solvents entrapped in a paint coating film, which has dried/cured on the surface thus, entrapping solvents inside the semi-dry film.

---Air entrapped beneath the paint coating film, typically air in the pores of an underlying coat. Normally such air will force its way through the paint coating film creating “popping”, however, in the case of thick films the air may become entrapped causing blisters.

2) The service exposure related blisters might be classified as follows:

---Blistering in Immersion Service

Perhaps the most common problem in immersion service is blistering of the lining material. Blistering itself does not necessarily denote failure, and often a blistered coating will provide long-term corrosion protection to the underlying steel or concrete substrate. However, a blistered lining will inevitably provide a lesser corrosion protection than a non-blistered lining, all other factors being constant. In time, many blisters will fill with rust, and active corrosion within the blister cavity may occur.

Alternately, the blister may fill with concentrations of permeating chemical species, leading to aggressive attack of the underlying substrate. When the tank is drained, the blisters dry out, stressing the lining film and causing cracks or adhesion loss. As a consequence, blistering should be avoided whenever possible, and in order to do so, it is necessary to have some understanding about blistering mechanisms.

Four types of blistering mechanisms will be discussed here:

osmotic blistering due to entrapped water-soluble salts,

osmotic blistering due to retained solvents,

cathodic blistering, and cold-wall effect blistering.

The first two types of blistering mechanisms are by far the most common and best understood. Blistering due to cathodic disbonding occurs only under very specialized conditions in conjunction with cathodic protection of a coated surface. Cold-wall effect blistering can be readily demonstrated, but the exact cause of the blistering mechanism is not known.

---Osmotic Blistering Due to Entrapped, Water-Soluble Salts

This classic blistering mechanism requires the presence of a water-soluble salt (such as that coming from perspiration, salt contamination near coastal areas, and chemical contamination from nearby industrial plants) entrapped beneath a coating or between coats of a lining system.

As moisture, in time, permeates the lining after it is placed in immersion service, it dissolves the entrapped water-soluble material, rendering an entrapped solution with a high salt-to-water ratio. In contrast, the bulk liquid within the vessel is relatively free of water-soluble salts, and accordingly has a low salt-to-water ratio. The higher the purity of the bulk liquid within the vessel, the greater the tendency for osmotic blistering. This is a particular problem when high-purity, de-ionized water is stored, as in the nuclear power industry, and in condensate systems in power generation facilities. The difference in salt concentrations (the entrapped solution of high salt content and the bulk liquid of low salt content) leads to what is commonly called an “osmotic driving force”. This very powerful force increases the rate of moisture permeation from the bulk liquid side to the entrapped solution side in order to create equilibrium.

Equilibrium will be accomplished when sufficient moisture from the bulk liquid side permeates the lining such that the salt concentrations on either side of the lining (which acts as a semi-permeable membrane) are equalized. In practice, this never occurs, due to the rapid drop-off of the osmotic driving force after initial permeation occurs, and the inelasticity of the lining material, which holds and contains the entrapped salt concentration within the blister cavity. Thus, the ability of the lining material to hold the entrapped salt solution in the blister cavity (much like the skin of a balloon holds air at higher pressure than the outside air) may allow considerable blister pressure to build up within the blister cavity.

When the lining is in service, such blister pressure is countered in some part by the head pressure of the solution. When the vessel is drained and the blister is punctured, often liquid spurts out in a stream as the blister collapses. Alternately, if the blister is not punctured, water may migrate from the blister cavity to the lining surface and evaporate, causing the blister to collapse as well. Thus, for best results, a lining system should be inspected for blisters shortly after draining. Osmotic blistering sometimes will concentrate on flat or horizontal surfaces, or areas where perspiration or falling airborne contamination can settle.

Paradoxically, however, the very act of draining a tank may cause a blistered lining, which otherwise would have been protective if the tank had not been drained, to crack or be exposed to oxygen from the air, which may cause rusting within the blister cavity. Thus, draining a tank to inspect for blisters may be somewhat self-defeating, as the lining “dries out”, shrinks, perhaps cracks, and is exposed to oxygen.

---Osmotic Blistering Due to Entrapped Solvents

This blister mechanism is quite similar to osmotic blistering by water-soluble salts, except that hydrophilic (water-loving) solvents are entrapped within the film, taking the place of the salts as described above.

Hydrogen bonding attraction between the water molecules in the bulk solution and the entrapped solvent increases the permeation of water through the lining material to the point of solvent entrapment. The amount of water that permeates depends upon the type and polarity of the entrapped solvent, and the permeability and physical nature of the lining material. While, strictly speaking, the driving force is not an osmotic driving force, the effect is the same, and the blister formation is identical. When entrapped solvents are the cause of blistering, the blistering is generally more predominant toward the bottom of the vessel where solvents can accumulate, and solvent volatilization from the lining is retarded. Alternately, in cooler areas or heat sink areas, solvent volatilization from a lining may be retarded, and blister formation may be more prevalent.

---Cathodic Blistering

When coatings are used in conjunction with cathodic protection, either by impressed current or sacrificial anodes, sufficient cathodic protection current must be supplied to protect the metal tank (or pipe), but not so much current to cause cathodic disbonding. As a rule of thumb, a value of –0.85 volts is used to protect steel surfaces, as measured using a standard copper/copper sulfate reference electrode to contact the environment. If other types of reference electrodes are used, the values of the voltage requirement will be different.

If less than –0.85 volts are used, less than complete cathodic protection will be attained on steel. On the other hand, electrode potentials more negative than –0.85 volts will be a waste of energy, as corrosion on steel is stopped at that voltage. In actual practice, however, it will be necessary to maintain a more negative potential at drainage points of cathodic protection current in order to maintain the minimum of –0.85 volts at locations remote from the drainage points (protrusions, edges, and prominences). This is a result of attenuation – voltage drops caused by cathodic protection currents on a pipeline or vessel flowing through the longitudinal resistance of the metal in order to return to the drainage point.

In this respect, large diameter coated pipes or vessels are easier to protect cathodically than are smaller diameter pipes or tanks, because the larger cross-sectional steel area means a lower longitudinal electrical resistance with resulting lower attenuation. However, if a protective over-voltage is applied (approaching the order of –1.2 volts copper/copper sulfate electrode), the possibility of gaseous hydrogen evolution may occur at coating defects on the coating surface. Hydrogen evolution may occur at coating defects on the paint around defects, resulting in a loss of adhesion and exposure of more uncoated steel. If the over-voltage is considerably in excess of –1.2 volts, extensive blistering and disbonding of the coating system may occur. With an impressed current cathodic protective system, increased current density will be required to protect these now-exposed areas. If the protective system is by sacrificial anode, it may not be possible to increase the current density, and corrosion will initiate at areas where the least cathodic protection is available.

---Cold-Wall Effect Blistering

The cold-wall effect results whenever there is a thermal gradient between one side of a vessel and the other side. Often, the interior of a vessel is heated, while the exterior is at a lower or cold temperature.

The water vapor pressure is higher on the warm side of the lining than on the cool side. This vapor pressure gradient causes moisture vapor to pass into the lining more rapidly than it egresses. Condensation occurs on the cold side because of the increased vapor pressure (i.e., saturation or dew point is reached). There is a continuous driving force to transfer and condense water vapor on the cold side because the system cannot reach thermal equilibrium.

On the warm side of the lining, there is greater molecular vibration and higher energy, causing an increased rate of permeation. As permeation proceeds through the lining to the “cold” side, the rate of permeation decreases, but more importantly, cooling and perhaps condensation occurs.

Due to the unequal permeation as a result of the thermal gradient, moisture will ultimately accumulate adjacent to the cold surface beneath the coating. Accumulation will occur at areas of weak adhesion of the coating to the substrate, resulting in liquid-filled blisters. The greater the thermal gradient between the hot and cold sides, the greater will be the size and frequency of the blisters. Additionally, the higher the temperature, the greater the size and frequency of blistering as well.

Studies indicate that coating systems with the lowest permeability are more resistant to cold-wall effect blistering than coating systems with increased permeability. However, the best way to eliminate cold-wall effect blistering is to insulate the vessel, and minimize the thermal gradient across the lining.

Would you assume that the size of the blisters would be greater in fresh water than in sea water, or would you assume the opposite? Please state your reasons.

Salt contamination:

The blisters would be larger in fresh water due to the lower level of salts in the fresh water as compared to the sea water. The concentration difference between the salt contamination under the paint film and the salt concentration in the water is thus greater and more water molecules will pass through the paint film (the membrane) to dilute the underfilm salts until the same salt concentration is reached on both sides of the paint film (the membrane).

We call this osmotic blistering.