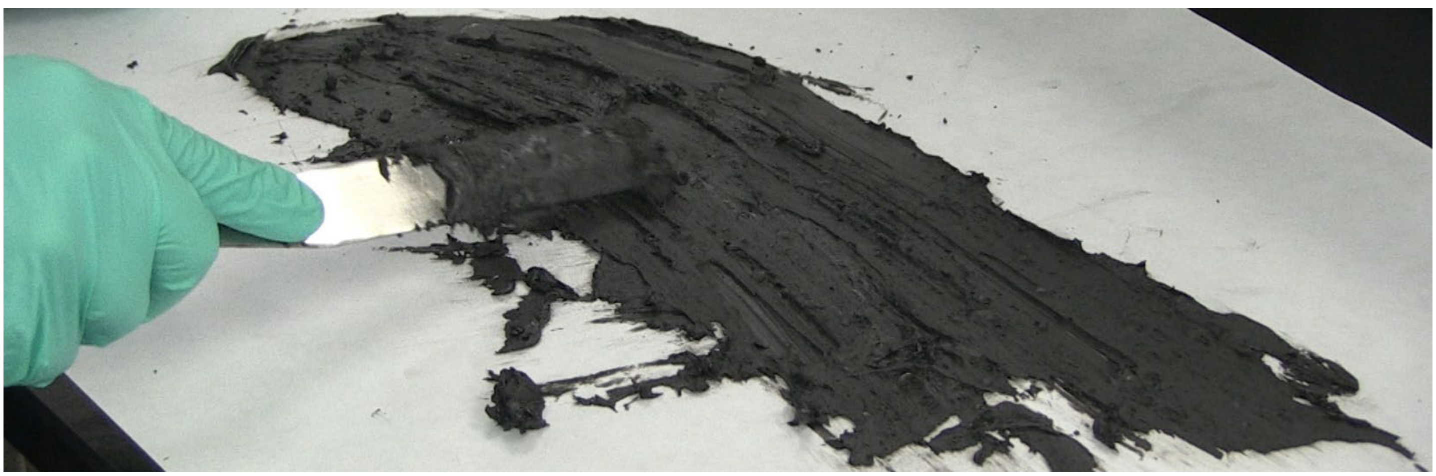
AN ELLSWORTH ADHESIVES COMPANY

TECHNICAL BULLETIN

Resin Crystallization

Those who regularly use epoxies or polyurethanes are likely familiar with resin crystallization. This phenomenon is possible in all epoxy resins and hardeners as well as many urethane resins. It is the phase change of a material from a liquid to a solid crystalline state. These resins are supercooled liquids and are naturally solid at room temperature. Exposure to extreme cold, temperature cycles and other factors may induce crystal growth and revert the materials back to their natural solid state. Crystallization is difficult to predict or eliminate entirely. It happens without warning and may only affect part of a given lot of material. While it may be only an inconvenience with two components systems, it can cause major problems with one component systems. Understanding the causes of crystallization and methods of fixing it can turn this major problem into a minor inconvenience.



What Causes Resin Crystallization?

Resin crystallization occurs similarly to other crystal growth. High purity, low viscosity, impurities, extreme cold, and temperature cycles all increase its probability. The presence of a “seed” often initiates the crystallization process. Here are five factors that contribute to the crystallization process in epoxy resins:

- **High Purity**
  A high purity resin has been stripped of all chemical byproducts and contaminants and falls within a given range of molecular weights. The presence of by-products and a wide range of molecular weights serves to broaden the temperature transition range between liquid and solid. High purity resins have a narrow temperature range during which they transform from liquid to solid. An analogy is pure water, which transforms from liquid to crystalline solid (freezes) at 0 °C. Yet with the addition of another chemical (table salt), the water freezes at much lower temperatures. The closer a high purity resin gets to the point where it

changes from a liquid to a glassy crystalline solid state, the greater the chance minute crystals will start to form. These crystals act as seeds and in combination with other factors can rapidly change the liquid to a solid.

- **Low Viscosity**
  Low viscosity resins are very low in molecular weight and short chained. The lower the viscosity the easier the liquid epoxy can move and orient itself around seed crystals. Materials with high molecular weight and high viscosity are longer chained and less prone to crystallize. Storing a seed-free liquid at low temperatures (0 °C) will slow molecular motion and impede crystal formation and growth. Diluents and modifiers generally increase the rate of crystal formation and growth, however there are significant differences in the tendency to crystallize between diluents. Other additives such as pigments, fillers, and wetting agents can also affect the rate of crystal formation and growth. Generally, if one prevents the introduction of seed crystals into a resin handling system, crystallization will be a rare event unless one is handling high purity resins.

- **Impurities**
  Impurities, usually minute particulate matter, can often act as "seeds" in unfilled systems, initiating the formation of resin crystals which then continue to propagate. Fillers rarely initiate crystallization due to their large size and high content. In fact, they often inhibit crystallization.

- **Extreme Cold**
  While cold does impede growth by slowing movement, extreme cold (-40 °C) accelerates crystal formation once seed crystals have formed. If low enough can cause complete crystallization.

- **Temperature Cycles**
  Temperature cycles as little as 20 to 30 °C can create a vicious circle that is the most common cause of crystallization. Once the material is warmed molecular motion is enhanced allowing liquid epoxy to orient itself around "seed" crystals. Subsequent exposure of an oriented material to cold temperatures will then accelerate crystal growth. Once started the crystallization typically progresses to completion resulting in a solid mass. The fluctuations that occur between daytime and nighttime temperatures can initiate and/or accelerate the crystal growth process. These can occur during transit, while sitting on a loading dock, or on the production floor.

Fixing Resin Crystallization

Crystallization in base resins and two component formulations is a major inconvenience but not an unfixable. Heating these materials several hours at 50 to 60 °C easily reverses the phenomenon. All the crystals must be completely melted as any microscopic un-melted crystals will act as "seeds" and cause the crystallization to return in days. Along with gentle heating the material should be stirred, and the container sides and bottom scraped ensuring all crystals have been melted and the heat is evenly distributed. If crystals reappear, apply heat and re-melt. One component systems should not be heated as product damage or curing may occur. Controlling and monitoring shipping and storage conditions is critical for minimizing temperature fluctuations. Good housekeeping is another factor, as container spouts, spigots, and closures must be kept free of resin buildup to prevent crystal formation. While epoxy compounders and end users have heightened their awareness to crystallization, it remains very difficult to accurately predict or eliminate. If crystallization remains a recurrent problem, products less prone to crystallize may have to be evaluated as alternatives.