TECH TIP 07

Epoxy Crystallization

WHAT

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WHY

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What is Epoxy Resin Crystallization?

It can often come as a surprise, but crystallization is a problem. The ones who are most aware of it are our customers. Frequently, a jar, bottle or container looks cloudy, turbid or even solid upon inspection. By definition, it is referred to as a phase change from a liquid resin to a solid format. It can be viewed similarly to water turning from liquid into ice and vice versa. Crystallization of epoxy resins is completely reversible, like freeze/thaw cycles of ice and water. As water remains unchanged from repeated cycles, so do the original properties of epoxy resin.

Why Does Crystallization Occur?

Many plastic resins are super-cooled liquids, including epoxy resins. They are solids in format at room temperature but remain in a liquid state below their freezing temperature. Liquids super-cool because crystallization can be too slow of a process or the seed crystals are not readily formed. In general, super-cooled liquid resins have a natural tendency to crystallize at low temperatures. Other factors such as extreme cold, fluctuation in ambient temperatures and thermal cycling can cause seed crystal growth and may induce materials to revert back to their natural, solid state.

Signs of Crystallization

Crystallization appears in the form of cloudiness, free-floating crystals, crystal masses or as completely solidified. Since the crystals are higher density than the liquid resin, they sink to the bottom of the container. At the onset of crystallization, the clear resin begins to look foggy, cloudy, hazy or turbid to milky white. The white sedimentation continues to build, pack and spread, typically from the bottom of the container or from the corresponding side-walls. This sandy-like texture will eventually overcome the entire contents of the container. Once solidified, crystallized epoxy resin can be stored indefinitely in this state.

Causes of Crystallization

Crystallization can be difficult to predict and eliminate entirely. It happens randomly, without warning, and may affect parts of a given production batch (it is normal for a few containers from the same batch to show differing degrees of crystallization deposits). Understanding the factors that contribute towards crystallization helps with knowing how to deal with it. According to our suppliers, the tendency for liquid epoxy resins to become crystallized depends on the purity of the resin, resin viscosity, additives, moisture content and temperature history (extreme cold or thermal cycles).

High Purity

Typically, high purity resins are more easily crystallized than impure resins. A narrow molecular weight distribution is indicative of the former, while broader MW distributions the latter. One model for high MW impurities is the addition of anti-freeze into water. It has the effect of lowering the melting temperature, thus making it harder to crystallize. The same can be said with adding high MW oligomers or isomers into an epoxy resin formulation. Avoiding crystallization of resins due to their purity is more of a formulating challenge and not for our customers. We would rather our customers understand that it is an indication of purity and homogeneity and not be viewed as a negative byproduct.

Low Viscosity

In general, higher MW resins result in higher viscosities and are less prone to crystallize. The rate of crystallization is also much faster in a lower viscosity resin. Lowering the temperature increases the viscosity and thus, reduces the molecular motion and rate of crystallization. Storing "crystal seed free resin" at 0°C is one method to reduce the rate of crystallization but, this may be less than optimal. As explained above, 0°C might be enough of "extreme cold" or may be viewed as enough of a thermal cycle, to cause hidden seed crystals to propagate into a solid mass.

Additive – Solid Fillers

Solid, inorganic fillers sometimes can act as seeds for crystal growth. Precipitated calcium carbonate has been shown to increase the rate of crystallization (eg. ISO 4985, "Plastics – Liquid Epoxy Resin – Determination of Tendency to Crys- tallize"). Other fillers like alumina and silica can have a similar effect. Even the scratch of a side-wall of a glass or metal container can be enough of a "filler" to promote seed growth.

Temperature

While cold temperatures can reduce the crystal formation/growth by slowing movement (increased viscosity), extreme cold accelerates crystal formation once seed crystals have been formed.

Thermal Cycles

Temperature cycles of as little as 20-30°C are the most common cause of crystallization. Once the material is warmed, molecular motion is enhanced allowing the liquid epoxy to orient itself around the seed crystals. Subsequent exposure of an oriented material to cold temperatures will then accelerate crystal growth. Once started, the crystallization typically will go to completion resulting in a solid mass. The temperature fluctuations that occur between night and day can start or enhance the crystal growth process.

Solutions

As stated earlier on, crystallization of epoxy resins is more of an inconvenience rather than a problem. Subjecting the resin to a temperature of 40-50°C for a few hours is generally sufficient for re-melting the crystals. It is important to be certain that all of the crystals have been melted away and can no longer act as seeds before cooling to room temperature. This can be done by closely examining the container sides, bottom and areas around the caps for any signs of crystallization the could nucleate additional growth. If possible, it is recommended to clean the bottle caps and bottle neck with solvent (isopropyl alcohol – IPA or acetone) after each use in order to prevent seeds from developing. The same applies for spigots, spouts, pumps, piping and valves. Controlling and monitoring shipping and storage temperatures is a good way to prevent crystallization from fluctuations in temperature. Good housekeeping is also a great way of preventing this.

IMPORTANT NOTE: *Re-melting of the crystals should only be preformed on the resins side (part A) of the epoxy. In rare cases, it may be necessary to warm a part B or single component system. Please consult our Technical Experts for specific heating recommendations. Pre-mixed and frozen systems should not use this technique as it may cause premature curing or cross linking.*

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