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Technical Data Sheet
Epoxy Crystallization

All epoxy resins are susceptible to a natural occurrence called crystallization. This phenomenon is similar to what happens to honey left undisturbed for long periods. Crystallization starts out slowly, with single tiny seed crystals forming at places called nucleation sites within the material. From these seed crystals, other crystals start forming and moving outward.

In epoxies, crystallization shows up as cloudiness, free floating crystals, clumps of crystal masses or in extreme cases the liquid can turn to a hard, brittle solid. Crystallization can occur in virtually all resins and hardeners.

The liquid polymeric materials that are common to all epoxy formulations are classified as super cooled liquids at room temperature. Because of their composition, they remain liquid at room temperature because the rate of crystallization, or solidification, takes place at a relatively slow rate. If certain conditions occur that allow the formation of small seed crystals in the material, then the rate of crystallization increases.

Because of the complexity of crystal formation in nature, crystallization can be very difficult to predict and control when working with epoxy adhesives.

Some of the factors that can contribute to the formation and propagation of crystals are:

Low viscosity and molecular weight
Lower viscosity epoxy polymers are shorter molecule chains with lower molecular weights. These molecules are more mobile, and can flow and move more easily around seed crystals that have formed in the liquid. Higher viscosity polymers have less mobility, so the growth of crystals around seed crystals is much slower.

Because conductive epoxy systems have such a high loading of solid silver filler, the polymer system must be made using large amounts of very low molecular weight epoxy additives to allow for complete wetting out of the silver particle. For this reason, silver filled epoxies are more prone to crystallization

High purity
So called “high purity” resins required by many high end electronic assemblies are more prone to crystallization. These resins are made by applying heat and vacuum to strip out low molecular weight components and liquid impurities. Epoxies contain residual liquid by-products and have a wide range of different molecular weight molecules. The temperature range, where it will transition from a liquid to a solid (crystallize), is very broad. Removing these by-products and low molecular weight components by heat and vacuum leaves a very narrow range of molecular weights, and results in a much narrower temperature range in which the material will transition from liquid to solid. As an example, pure distilled water will freeze relatively quickly at $0^{o}C$. Adding another material, such as alcohol or dissolved salt, will broaden the temperature range over which solidification occurs, and in order to get complete solidifying, it needs to cool to a lower temperature. High purity material starts to form seed crystals more readily as you approach the given temperature, and once formed, crystals continue to form more rapidly as it continues to cool.

Solid Impurities
Small solid impurities in an epoxy can act as seeds, and cause other crystals to start forming around them. Larger particles, such as the silver used to fill conductive adhesives, generally do not act as seeds. However, most silver

materials contain small amounts of sub micron particles that can act as seed sites in the polymer.

Extreme Cold

While cold storing an epoxy material can slow down the rate of crystal formation by slowing down the movement of the molecules, extreme cold storage even for short times can cause rapid crystal formations if small seed crystals are present.

Temperature Cycling

Temperature cycling is perhaps the most frequent cause of most crystallization. Warming a material slightly allows the molecules to move around and contact seed crystals. The amount of temperature cycling required to induce crystallization is relatively small. A temperature swing of only 20^{o}C can begin the crystallization process. As a result, temperature during shipping and warehouse storage must be taken into consideration. When epoxy materials are shipped by air, the combination of extreme cold in the cargo portion of a plane and exposure to multiple warm to cold temperature cycles can accelerate crystallization greatly.

Accommodating Crystallization in Epoxies

Crystallization can be very frustrating to deal with in epoxy adhesives, because it cannot be attributed to one single factor, and its occurrence can be arbitrary. It is possible to have a shipment with hundreds of small containers of epoxy, and discover only a few of them randomly placed throughout the box will have varying degrees of crystallization.

Fortunately, two part epoxy systems can be treated easily to revert them back to a liquid state so they are suitable for use.

Simply heating the silver filled epoxy to 50^{o}C for a short time is enough to revert it back to a liquid state. It is important to heat the epoxy long enough to make sure that all of the seed crystals have been liquefied. Once heating is complete, the material should be allowed to return to room temperature before mixing, or the excess heat will begin the crosslinking reaction more quickly when the two parts are mixed.

If a one part adhesive appears to have crystallized, it must be scrapped because it is not possible to revert crystallization. A warming process on a one part adhesive would begin the crosslinking reaction, which hardens the material.

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