Technical Awareness – Mercaptan Skinning (January 2019)

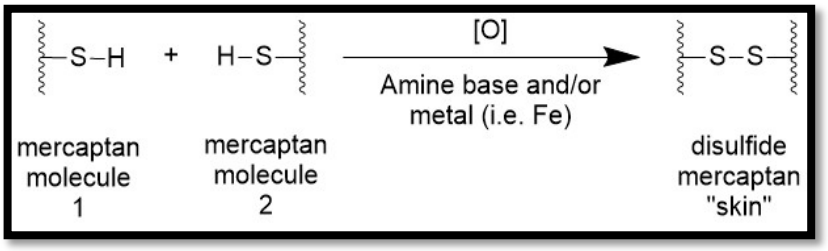
One issue occasionally seen with polymercaptans is skinning. Skinning occurs when a solid layer of crosslinked polymer forms on the surface of material stored in a container. For polymercaptans, skinning is a result of an oxidation process. A nitrogen blanket is effective at significantly reducing the tendency of polymercaptan blends to skin.

TECHNICAL DISCUSSION

Polymercaptan resins can oxidize to form disulfides. This oxidation process is most apparent when it happens on the surface of material. The first step of the process is the oxidation of the mercaptans to produce sulfide radicals. The radicals couple together to give the disulfides. As more molecules are linked by disulfide formation, a skin eventually forms on the surface. While this chemistry can occur in the bulk of the material, it typically is a surface phenomenon.

The disulfide formation is extremely slow in the pure mercaptan. There are two common ways that the skin formation is promoted in formulated products. The first is by metal catalysis. The second is by catalysis by amines and other bases. Since amines are accelerators or co-curatives with the mercaptans, formulated blends of polymercaptans exhibit the tendency to skin.

Among metal compounds, iron compounds are good oxidation catalysts because of their ability to cycle between oxidation states. Gabriel mercaptans are treated to remove iron so that the level is about 1 ppm of iron. Some formulators use fillers in their adhesive formulation which can be a source of iron / metals that act as oxidative catalysts and promote skinning.



It's up to the formulator to develop a proper mitigation scheme if a filler causes skinning. Some iron chelators are known to form such strong complexes that they will not undergo the oxidation-reduction cycle.

Base-catalyzed (especially amine-promoted) skinning is another potential problem area. As we stated earlier, amines are necessary to accelerate the reaction of the mercaptans with the epoxies. However, the literature indicates that the mercaptide anion is a primary intermediate in the oxidation of the mercaptans to disulfides. As shown in the diagram, the process involves a number of reactions, but for each mole of oxygen consumed, two moles of disulfide are generated.

Since the mercaptide anion is important in curing epoxies, we cannot stop the process at this step. Blanketing with nitrogen is the most effective way in slowing the skinning by removing the oxygen from the process.

For more information, please call 1-866-800-2436 (CHEM)