

# Azodioxides as Inhibitors and Retarders in Photoinitiated-Cationic Polymerization

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Inhibitors are an important component of UV-curable adhesives. Active-center chain addition polymerizations are generally strongly exothermic. Inhibitors are used to control the reactivity of monomers avoiding runaway conditions. In addition, they also extend storage lifetimes and make purification and transportation possible. Azodioxides are used as free-radical inhibitors, not only due to their inherent inhibition/

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retardation characteristics, but also because they possess the unique property to be thermally reversible between azodioxide and dinitroso structures. The azodioxide structure can sequester a hydronium ion formed from a photoacid generator (PAG), which can be subsequently released during thermal isomerization of the azodioxide to the dinitroso form.

This paper describes recent results that show that azodioxides can also function as inhibitors and retarders in photoinitiated-cationic polymerization. Some examples will be presented of practical formulations and end-use applications in which azodioxides are used as inhibitors/

retarders in the photoinitiated polymerization of epoxides.

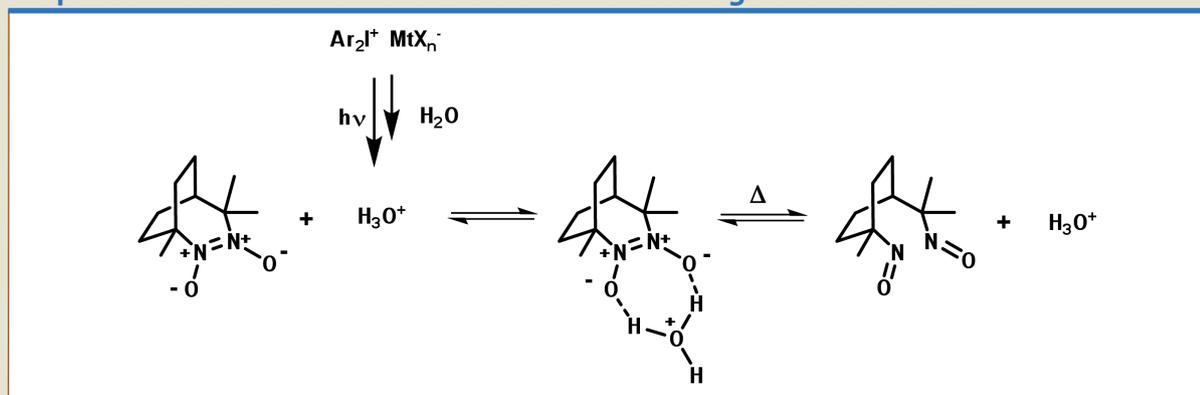
Ultraviolet (UV)-curing is a photochemical process in which high-intensity UV light is used to rapidly cure or “dry” inks, coatings and adhesives. Offering many advantages over traditional drying methods, UV curing has been shown to markedly increase production speed, lower reject rates and reduce processing costs.

UV-curable adhesives work by absorbing radiant energy from a light source and converting it to chemical energy that results in polymerization. While UV-curable adhesives can exhibit lower bond strength compared to other adhesives, they are preferred by manufacturers due to their high transparency, exceptional stability and rapid cure. In addition, they can be used to bond temperature-sensitive and difficult-to-assemble materials, as well as perform various other bonding, sealing, coating or encapsulation functions. Because UV-curable systems can also offer good gap-filling capabilities, flexibility, strength and variable viscosities, these materials have recently become a popular option for use in the fabrication of medical devices.

Inhibitors make up an important component of UV-curable adhesives. Active-center chain addition

## FIGURE 1

### Proposed mechanism for reversible thermal cleavage of azodioxides



polymerizations are generally strongly exothermic and inhibitors/retarders are used to avoid dangerous runaway conditions. They also extend pot life, storage lifetimes and help make purification and transportation of highly reactive photopolymer systems possible. In fact, it is safe to say that the commercial uses of UV-curing technology would not be possible without them.

As shown in Figure 1, in the Azodioxides form, they are sufficiently of particular interest as polymerization inhibitors/retarders in the UV curing of epoxide formulations due to the fact that they undergo reversible thermal cleavage to the corresponding dinitroso compounds. In the azodioxide form, they are sufficiently basic to capture and sequester protons generated by photolysis of the cationic photoinitiator. This function is reversed upon heating.

### Experimental

An example of this unique functionality is performed by incorporating an azodioxide (supplied by Hampford Research under the trade name UVTS-52) into a “demonstration” cationic UV-cure formulation containing a blend of cycloaliphatic

epoxy resins with (4-octyloxyphenyl) phenyliodonium hexafluoroantimonate (OPPI) as a photoinitiator. Additionally, a small amount of a fluorinated surfactant was also added in order to improve the flow and leveling characteristics of the formulation. The test solution was prepared by blending both the azodioxide inhibitor and photoinitiator directly into the epoxy resin under high shear mixing at a rate of 3,600 rpm. Tests showed that continuous mixing for 40-45 minutes was necessary to completely dissolve the azodioxide. During this time, the temperature of the sample formulation increased from ambient (26-27°C) to a maximum of 37-38°C. Care was taken not to allow the solution temperature to exceed 40°C.

A baseline test UV cure was performed using a formulation containing only the epoxide blend and photoinitiator. A drop of the formulation was placed on an 0.010- inch thick aluminum plate which was irradiated with a single pass under a Fusion 300 W/in “H” lamp at 10-feet-per-minute line speed. The measured thickness of the drop was 0.070 inch. As expected, the result was complete top-to-bottom vitrification without discoloration.

Follow-up testing was performed using a series of 0.8-mil wet film drawdowns on 0.011 inch aluminum plates, both with and without the azodioxide additive. The aluminum plates were placed on a metal block, which acted as a heat sink. By effectively transferring the heat away from the epoxy coating, the azodioxide inhibition properties were maintained. The coatings were irradiated via a single pass under a “filtered” Fusion D-lamp at a rate varying from 10 to 47 feet per minute.

In all cases, formulations prepared without the use of inhibitor exhibited complete top-to-bottom curing, whereas samples containing the azodioxide remained liquid after UV exposure. The exposed uncured materials were then placed in a bake oven and heated to 100°C, at which point complete curing was achieved. It should also be noted that the thermal reversibility characteristics of the azodioxide inhibitor were maintained even after standing for several hours after the initial UV exposure.

An additional series of tests were designed to determine the effect of temperature on both UV exposed and unexposed surfaces. Solutions were prepared, as before, with epoxy resin,

photoinitiator and inhibitor. One set of samples was exposed to UV radiation, while the second was not. All the samples were then placed in a forced air oven heated to temperatures ranging from 50 to 100°C. At 100°C, a complete cure was achieved almost instantly where at lower temperatures (85°C) the required exposure time to achieve full cure was as high as five minutes.

At temperatures below 60°C, full cure was never achieved, suggesting there is a threshold temperature requirement for unblocking the initiator. None of the unexposed samples cured, indicating irradiation was necessary to “activate” the cure in the presence of the azodioxide.

It was later determined that it was not necessary to expose the entire surface to high temperature in order to initiate curing, and a complete through-cure can be achieved by heating a very

small area. This was demonstrated simply by filling the channel of a Teflon mold with 1g of the liquid monomer containing the photoinitiator and azodioxide inhibitor.

The monomer solution in the channel was irradiated with UV light for 90 seconds. As previously observed, curing was effectively suppressed by the azodioxide. Polymerization was then initiated by touching the hot tip of a soldering iron to the irradiated liquid at the end of the channel. The heat generated from the local polymerization was sufficient to allow the release of the previously photogenerated initiating protons. This resulted in the subsequent polymerization of the monomer solution throughout the length of the tube.

### Conclusion

The advantages of photopolymerized adhesives in industry have been

well documented, but their use has been limited primarily to “line-of-sight” applications. Through the incorporation of a thermally reversible inhibitor, potential uses now include structural applications—the assembly of electronics, toys and appliances. Further benefits of azodioxides as room-temperature pot life stabilizers have also been realized in laboratory tests.

For more information, visit Hampford Research Inc. at [www.hampfordresearch.com](http://www.hampfordresearch.com). ▀

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