

## The Case for NOT Ignoring Select Secondary Antioxidants

The more things change the more they stay the same. The field of stabilizers for plastics and coatings has evolved in the last fifty years from a large selection of primary and secondary antioxidants to a handful of choices grandfathered into a select family and grade line in the global industry. This is especially true of polyolefin polymers. The family of polyethylene, polypropylene and poly butane-1 contain the largest concentration of primary and secondary antioxidants. Condensation polymers contain more secondary antioxidants than primary antioxidants, the remainder of polymers being developed have ignored the utility of antioxidants.

When we speak of secondary antioxidants we speak of a group of peroxidolytic antioxidants which are additives that catalyze the decomposition of hydroperoxides. The majority today are low and medium molecular weight aliphatic and aromatic phosphites and phosphonites. The second group include Sulphur compounds which give acidic species upon oxidation with hydroperoxides. The family of dialkyl thiodipropionates is the most important of this class. It is this class of additives that were used for many years providing synergisms with primary higher molecular weight antioxidants as long term thermo-oxidative stabilization to polyolefin resins like polypropylene. In addition prior to higher molecular weight primary antioxidants these were utilized with low molecular weight primary antioxidants as processing stabilization systems and as synergistic combinations with ultraviolet absorbers prior to the introduction of hindered amine light stabilizers. The usage of both Sulphur and Phosphorus based secondary antioxidants has been shown to be valuable additions to stabilization packages. Furthermore, there has been reported poorly studied conclusions on the downside of these additives that have forced a decrease in their usage over time. One such misconception in the industry is the severe antagonism with Hindered amine light stabilizers. It is true basic hindered amine light stabilizers (HALS) are affected by acidic additives that reduce the performance as light stabilizers but the evidence was based on limited studies and by academics using conditions and measurements not typically used in the industrial sector. Current studies show that inhibition of HALS can occur from primary and secondary antioxidants, various lubricants, acid acceptors, pigments, fillers and catalyst residues from the polymer. Therefore, there are many other variables that can influence the performance of HALS. By avoiding thioester type additives unnecessarily restricts the formulator in producing a solution that could lead to a new product line. It is known in the art that Sulphur additives contain different levels of Sulphur. This difference in content determines both performance as a synergist but also which polyolefin benefits the most from solubility and compatibility in the matrix. Among the key Sulphur additives today that have broad applicability DSTDP, DMTDP and DLTDP are the dominant.

Other important Sulphur additives are the liquids which have unique ability to solubilize other phenolic antioxidants and are utilized in coatings to enhance both long term thermo-oxidative stability but thermal degradation during oven baking that can alter the spectral activation energies of a coating resin, thereby changing its intrinsic light stability.

Understanding the chemistry and mechanism of Sulphur additives allows the formulator the ability to tailor the concentration with the right type and concentration of the primary antioxidant and correct acid acceptor for the intended end use application. This is true when designing long term thermo-oxidative and light stabilization systems in environments where the temperatures reach 40°C and above and found to benefit from the addition of a Sulphur additive. This is also true when dealing with high energy photon radiation in the sterilization of polyolefin molded parts allowing for long term storage stability in the dark to prevent yellowing and embrittlement.

The known synergisms with other additives and their cost performance benefits should not be ignored because of a lack of understanding or preconceived ideas about their problems.

This is especially evident when odor issues are mistakenly attributed to Sulphur compounds when it turns out that the problem was actually due to interactions with acid acceptors and primary antioxidants or other additives in the matrix that undergo thermal degradation and in-situ interaction with other additives. This is especially true with dehydration catalysts like basic magnesium aluminum hydroxy carbonates and their related chemistries. It has been shown that changes in acid acceptors from traditional metallic stearates to more basic buffers in the system not only lead to odor but discoloration (yellowing) and pinking (canary yellow) by interactions with primary antioxidants.

All stabilization systems are multiple components systems and require knowledge of chemical interactions and transformation prior to combining these into a master batch or to manufacturing of resins in the plant. Heat history and residence times determine outcomes as do purity and chemistry of the additives. When it comes to Sulphur additives purity and levels of Sulphur are key to performance. Never assume each vendor manufactures these additives by the same method. Method of manufacturing determines impurities, quality and performance.

In our opinion, the need to revisit Sulphur additives in many of the new applications being globalized expands the portfolio of products and performance while expanding market share. Current perceptions and paradigms that avoid markets due to limits imposed on existing formulations by those who have preconceived notions threaten business and new opportunities.

Joe Webster

Stabilization Technologies LLC