

## **Hindered Benzoates The Forgotten Alternative to Hindered Amine Light Stabilizers and Known Synergisms.**

**Hindered Benzoates especially p-hydroxy benzoates containing tertiary butyl groups historically have shown great potential as light stabilizers to replace hydroxy substituted benzophenones and other UVA classes in the eighties during the introduction of hindered amine light stabilizers i.e. secondary low molecular weight hindered amine Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate.**

**Although the classic hindered benzoate commercialized in the eighties did not undergo Photo-Fries rearrangement like (2,4 Di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate) the utility of several p-hydroxy benzoates investigated prior to the introduction of HALS (hindered amine light stabilizers) was considered**

**candidates worth serious consideration due to light performance properties in combination with secondary antioxidants e.g. phosphorous and sulfur chemistries. Later the discovery of synergisms with oligomeric HALS made p hydroxy benzoates an alternative to conventional UVA absorber combinations especially in color sensitive systems.**

**The mechanism is more related to controlling rates of in-situ oxidation of UVA in polymeric systems thereby slowing down the rate of hydroperoxide decomposition and controlling the rate of hindered amine to the nitroxyl species and formation of a new phenolic antioxidant species in-situ.**

**Again, what was discovered 25 years after the introduction of hindered benzoates should validate the fact we still know little about the potential of existing light stabilizer chemistries and need to recognize more study is required to fully isolate the full potential of these known and little utilized chemistries.**

**This brings us to Plasmonic Mechanisms and permanence of light stabilizer systems. The discovery of a rare scientific Phenomenon called Hyperchromicity or the increase in the absorbance of a chemical species in both polar and nonpolar systems followed by a red shift called bathochromic leading to in-situ control of the rate of consumption of the organic Ultraviolet absorber not seen or reported in the literature suggests again what little we truly understand.**

**In both examples we need to understand that alternatives to existing hindered amine light stabilizers is potentially viable based on the needs and end use application requirements and specifications.**

**So, for example when 0.10% Oligomeric HALS is used as the bench mark comparison we find that comparable light stabilizer performance is achieved with combinations of 0.05% each of hindered benzoate and phosphite and or thioether.**

**In addition, FDA approval for indirect food additive addition was approved many years ago under Title 21 178.2010 at levels not to exceed 1 percent by weight in Nylon resins, 0.75% in Nylon 12, 0.55% in vinyl polymers, and 0.5% in polyolefins. Therefore, the FDA argument is a non sequitur.**

**There is little argument that hindered amine light stabilizers continue to dominate the landscape globally. However, we tend to forget alternatives and the potential to look at potential synergisms and new mechanisms that could lead to new technological breakthroughs that lead to better and cheaper systems in a competitive landscape.**

**In 1987 studies consistently reported those in the field of study of light stabilizers that hindered amines were found to be consistently antagonistic towards p hydroxy benzoates. However, years later in 2005 the opposite was discovered.**

**These studies were done with tertiary and secondary oligomeric HALS and found to have lower effectiveness in combination with a hindered benzoate versus the HALS alone.**

**However, at the time of these studies it was shown that hindered benzoates were synergistic with both hydroxy substituted benzophenones, and secondary antioxidants like phosphites and thioesters (thioethers).**

**The conflict between antagonisms and synergisms between hindered benzoates boils down to additive concentration and ratio of the additives with the HALS for synergism to occur. The same can be stated for the synergisms between hydroxy substituted benzophenones and secondary antioxidants.**

**Therefore, paradigms have shifted from absolutes that lead to rigid formulation based on false premises done by others to a shift in attitudes based on new information.**

**In conclusion it is our opinion that thirty years of research into light stabilizers for polyolefins and vinyl resins shows what little we truly understand.**

**In addition, with dramatic changes in intangible assets and competent people in the field of study coupled with little product development and research being carried out today the industry has lost its direction and options have become more limited by fixed systems with little innovation.**

**It should be remembered that a persons needs are best shaped by their understanding of what is potentially feasible/possible.**

