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Evaluation of Ultraviolet Absorbers for Coatings and Plastics

There appears to be some confusion among those who sell Ultraviolet Absorbers (UVA) and those who purchase them for a particular end use application in our global market. We hear that my product is failing and it contains 1% of a hydroxyl-substituted benzotriazole or hydroxyl-substituted benzophenone after six months outdoors in a six mil polyethylene film.

We hear that our UVA is migrating or blooming after we produce the film or we no longer find the UVA at the right concentration in multi-layer films or coatings after storage in the dark. We hear that the UVA absorber recommended did not protect the substrate or provide the intended protection for the end use application initially or during the first six months of use. We also hear the product containing the UVA has changed color in storage or in the application and product claims are causing us market share and legal problems.

These and many more instances of complaints regarding Ultraviolet absorbers (UVA) continue to increase in the last few years. It appears when reviewing these complaints we find those left in the coating or plastics fields have forgotten the basics of proper evaluation of UVA additives for the intended application.

Before we discuss the basics for the proper evaluation of Ultraviolet Absorbers we need to reflect on the chemistries that have been available and where we are today.

Prior to Hindered amine light stabilizers commonly referred to as HALS or HAS additives we had Ultraviolet absorbers (UVA). Early in the science of light stabilization we had hindered benzoates, hydroxyl-substituted benzotriazoles, hydroxyl-substituted benzophenones. The usage of these three common types

of UVA became dominant in plastics and early lacquer coatings. They became grandfathered into many plastic and coating systems for years. Then we began to see the introduction of oxanilides, benzylidene malonate esters, cinnamates, salicylates, nickel and cobalt quenchers cyano-acrylates and other less common miscellaneous chemistries. In recent years the introduction of hydroxy substituted triazines and multiple binary and tertiary blends of UVA in the market. All of these chemistries are not to be confused with hindered amines which do absorb below 290 nm but fall into a separate class of light stabilizer with a totally different mechanism of action.

The intrinsic colors of organic ultraviolet absorbers change with crystal structure and size but range from white to tan to yellow and red shade yellow to green. The nickel quenchers are all green and the cobalt quenchers were blue.

The end use application for these UVA in the past ranged from very thin section plastics and coatings to thick injection molded parts and pipes. End use applications for plastics ranged from fibers, slit tapes, films, sheet, thermo-forming, injection molding, bottles, rotational molding. Virtually all end use applications that required protection from damaging light and lifetime durability in the intended end use application used conventional UVA.

In the coating field they were most commonly used in cellulose nitrate lacquers, wood coatings, and in mono-coats and later in TSA OEM coatings as substrate protection of the coating under layers e.g. E coats, pigments, surface primer replacement.

Market and Technical experience in selection of the right UVA for the application required a broad knowledge base of the chemistry, system interactions with other additives, spectral coverage, physics of transmission and absorbance and absorptivity and cost benefit performance relationships.

Today price of the UVA is the driving factor with little guidance on selection and application requirements.

With the known limitations of conventional organic UVA this complicates both the choice and evaluation. Factors such as molecular weight, volatility, migration, blooming (bleeding), discoloration, purity (quality), solubility, bathochromic (red shift to longer wavelengths), hypsochromic (shift of absorption to a shorter wavelength or blue shift), shifts in polar and nonpolar systems, hyperchromic or increase in absorption intensity versus Hypochromic effect a decrease in absorption intensity in response to a systems polarity, absorptivity and molar extinction coefficient, rates of in-situ consumption, transformation products and initial toxicity and FDA approval and now the issue of biotoxicity and bioaccumulation and lastly price all enter into the selection process. In addition, consideration of synergisms and or antagonism from the organic UVA are considerations rarely considered. Therefore, a total systems approach is required in the selection process besides price.

In one of many examples of past recommendations by vendors is the Target and Wal-Mart bug light manufacturer who asked the additive vendor for a light stabilizer system for the polymer coating over the glass lamps used in the bug light zapper. This device attracts mosquitoes and other insects that bite and are a nuisance and then zaps the bugs in the cage. The vendor provided a recommendation that would protect the polymer coating and purchased enough material to produce 500,000 units. The units were sold by the retailer and shortly after the complaints started and units returned. The bug light was not attracting the bugs. Eventually all units were returned by the retailer and the manufacturer shortly went out of business.

Investigation into the recommendation and analysis of the polymer coating over the light bulbs found the presence of 1% of a UVA from the hydroxy-substituted benzotriazoles. There was no other light stabilizer present in the polymer coating. The coating thickness over the glass bulb was 25 mils thick. Based on the thickness and concentration of the UVA the percent transmission of those wavelengths needed to attract the insects was less than 1%. Therefore, the polymer coating was protected from degradation but the purpose of the bug light zappers was compromised by the wrong recommendation. This is just one example among hundreds of asking the right questions before making any

recommendations to the customer. The consequences of this action not only destroyed the customer but the potential of a long term business of supplying the customer a product and sustained sales.

In another example a coating for automotive having an E coat, surface primer, base coat and top coat failed in the field having been formulated in the lab and tested for long term durability. After scaling up and baking the cars in the oven a unseen change was occurring in the E coat that over time caused premature paint fading and delamination in a fraction of the time predicted by lab tests.

The coating itself contained very high loadings of a hydroxy-substituted benzotriazole well known in the coating industry and hindered amine light stabilizers at levels that would have predicted well over ten years life out doors.

However, within five years, several million cars were recalled.

After many months of finger pointing by the coating customer and the vendor it was discovered that both coating customer and vendor were at fault. The coating customer had decided without the knowledge of the vendor that saving money was more important so elimination of the surface primer changed the state of the coating system and the E coat. The vendor was making recommendations based on conditions reported by the coating customer and increasing the loading to compensate for the failure. However, the vendor did not know most of the UVA was being baked out of the coating at higher temperatures and faster residence times in the oven. Therefore, a large majority of the UVA was being baked out of the coating and no post analysis of the level in the coating was measured to insure proper loadings in the final product.

In addition sufficient heating and residence times in the oven changed the thermo-oxidative stability of the E coat making it much more susceptible to light damage over time. The solution to the problem was obvious once the facts were determined. Either restore the surface primer or provide thermo-oxidative stabilization to the E coat. Change the oven conditions back to previous guidelines and eliminate loss of the volatile UVA or use a less volatile UVA in the system having comparable absorptivity and wavelength protection.

In this example those involved did not know about activation spectra of coating polymers or the effect of temperature on changes in the chemistry of the polymer that made it more susceptible to longer wavelengths of light. The knowledge that various plastics and coating polymers are intrinsically susceptible to both photo- and photo-thermal degradation is key in the selection of any UVA or light stabilization system.

In any recommendation never assume you have all the facts. The best solution comes from knowing the customer and the product they are introducing. Know the end use requirements of that product and guarantee being given by the retailer.

Furthermore, never assume the customer knows what they truly need. The vast majority of customers looking for a solution rarely have knowledge about the products they are using. Remember a person's needs are best shaped by their understanding of what is potentially possible. Therefore, technical sales and technical managers must know more about the customer needs and fulfill the need. If you provide the customer what they perceive they want you may never sustain the long term business with that customer because their true need was never satisfied.

Making any recommendation for the use of either UVA or HALS (hindered amine) light stabilizer requires a basic understanding of both the mechanisms of these two classes and the limitations and antagonisms and synergisms that occur in both plastics and coatings.

First and foremost the activation spectra of the polymer. Measurements on the intrinsic absorption of various polymers show both structure and impurities in the polymer initiate degradation and are dependent on the wavelength of the energy. A list of these wavelengths is well known in the art and is a valuable guide in the initial selection of the proper chemistry of the UVA being selected.

The next step is the nature of the polymer. What is the processing temperature and residence time and total heat history or what is the solubility of the monomer used, what is the cross linking agent and is the polymer polar or nonpolar and how polar or nonpolar is the polymer? Next is the thickness of the plastic. Is this a fiber, thin film, orientated slit tape, injection molded, rotational molded, thermo-formed or compression molded. The same for any coating system where thickness is generally one mil or less in OEM coatings and thicker in cap stocks over molded plastic or flame coats. Thickness is critical and is a limitation of organic UVA. The photo physics of any UVA is limited by thickness and reaches a point of diminishing returns. Remember the UVA is being used in both plastics and coatings in many cases to provide substrate protection especially in thin coating systems. Therefore, depending on the susceptibility of the substrate being protected and the nature of the top coat a limited concentration of UVA is reached for a particular wavelength and concentration.

The key factor at this stage is Absorbance per unit thickness or Percent Transmission per unit thickness at a particular wavelength that is being protected. It is not enough to know the UV spectra of the UVA which typically shows where the UVA absorbs and its Absorbance in a particular solvent. The need to know the molecular weight of the UVA determines the absorption of that UVA in a particular solvent. Therefore, instead of Absorbance we tend to look at absorptivity measured in liters/gram-cm. This follows Lambert Beer Law of $A = a b c$, where A is Absorbance, a = the absorptivity, b = the thickness and c = the concentration. Absorptivity versus wavelength provides the person a broader tool and harmonizes the key factors needed to compare price of the UVA and wavelength being protected.

The following example gives a comparison between UVA-1 and UVA-2.

The two UVA have comparable volatility (by TGA) and both are soluble in Polar systems. However, UVA-1 is \$10/pound and UVA-2 is \$15 per pound. The customer requires protection at 355 nm. Looking at Absorptivity versus wavelength in a polar solvent we determine that UVA-1 has an absorptivity of 35 l/gm-cm at 355 nm but UVA-2 has absorptivity of 48 l/gm-cm.

All other physical chemical properties being comparable, it comes down to the price for the two UVA and the \$10/pound seems to be the choice by the customer purchasing the additive for their department. However, when we do the math we see the real differences.

The absorptivity of UVA-2 is 37% stronger than UVA-1. Therefore, UVA-2 can be used at lower levels to reach equivalency of UVA-1. When we calculate the difference UVA-2 cost \$9.45/pound using a loading that gives the same transmission as UVA-1 at 355 nm.

In another example UVA-1 costs \$40/pound and UVA-2 cost \$20 per pound.

The customer requires absorbance at 300 nm with zero transmission in a 1 mil coating. Both UVA have the same TGA and solubility in nonpolar solvents but their limitations in solubility restrict the amount that can be put into the coating solvent. The Absorptivity of UVA-1 is 100 l/gm-cm and that of UVA-2 is 50 l/gm-cm. Therefore, UVA-1 is twice the price but double the absorptivity but UVA-1 is more soluble in the coating system by 20%. Based on the thickness of the system 1% of the UVA-1 is required and 2% of UVA-2 is required to provide zero percent transmission at 300 nm. However, UVA-2 is 20% less soluble than the expensive \$40 UVA. Even though UVA-2 is cheaper and requires double the loading the issue of solubility in a particular VOC/HAP solvent for that system limits its use. The use of another solvent is not possible due to restrictions on the solvent system used.

In plastic systems especially films and molded parts like bottles for packaging which require a transmission specification the same math and issues prevail.

In blow molded or injection molded bottles light continues to penetrate even pigmented systems. Therefore, the addition of a UVA to prevent light penetration of a particular wavelength is added to insure zero transmission of harmful light do not compromise the light sensitive ingredients. Although most of the end use packaging needs do not require FDA approval others like pharmaceutical and specialty products require regulatory guidelines. These guidelines today have extended beyond the scope of most organic UVA that

absorb in the wavelength range of 300 to 400 nm. Today the needs of the global community are changing and the needs range beyond 400 nm into the 410-460 nm and 550 nm region depending on needs.

For example rancidity of oils and oils in foods require protection at 410nm, 430nm and 450nm. The key transmission is 430 nm with a transmission of 25 mil bottles of less than one percent and lifetime retention of this transmission for 1 year outdoors.

The same has specification has been imposed on thin films for retort packaging and military packaging in countries with higher environmental temperature of 40C and higher UV radiance.

Standard organic UVA are limited by the wavelength range and their intrinsic volatility and migration and blooming and rapid in-situ consumption. The increased thermal gradient and UV irradiance stress plastics and the conventional organic UVA they contain and this change is becoming relevant in many parts of the globe.

Recently the introduction of a new technology based a mechanism of Plasmonic action also called Spectral Enhancer or Modifier has been introduced into the market that shows promise against the existing known deficiencies and limitation of organic UVA. These materials do not have the limitations of organic UVA.

- They are not volatile
- They do not bloom or migrate
- Are very inexpensive
- Are synergistic with other light stabilizers known to be used globally
- Absorb in the range of 200 to 800 nm and do not diminish their absorptivity at any wavelength over time

The materials are very polar in nature and show unique performance in pigment polyolefin using colorants with borderline light stability.

The Spectral Enhancers also absorb strongly in the mid infrared region especially in the thermic region and Far infrared region for military use in night vision invisibility.

Currently, these materials have shown unique synergisms with various hydroxy-substituted benzophenones that cause a red shift of 5-15 nm allowing for protection in the 400-460 nm region against rancidity of food and oils in packaging.

The technology today in the globalized community has evolved in the last twenty years into more expensive organic UVA with wavelengths still in the same region of 300 to 400 nm. The new chemistries are based on absorbance properties in the 290 to 345 nm region. Others are predicated on low volatility and high absorptivity. Both have one thing in common increased cost which limits the utility into specialized thick section fibers.

Spectral Enhancers are changing that dynamic. Lower cost with greater cost benefit performance ratios and broader long-term permanence for longer protection.

True synergisms are rare in the plastic industry and by definition differ among those who claim synergisms. There are patented synergisms and commercial marketing of additive synergisms to sell a product. Both differ significantly.

Spectral Enhancers have known synergisms with other additives and have been illustrated and proven over time. The key observation reported is the significant hyperchromic effect seen between these additives and other UVA. This little observed phenomenon is more common among spectral enhancers and leads to greater cost performance of the commercial UVA and slower in-situ consumption over time extending the life time curve and the initial protection for the end use application.

Therefore, the last category in the selection process is to look for those known synergisms and antagonisms.

Many organic UVA systems prior to the introduction of hindered amines relied on combinations of UVA with other additives to increase the performance and lifetime of organic UVA. There are many co-synergistic additive combinations in the literature and an equally larger number of antagonistic additives that react with organic UVA to destroy their effectiveness.

One classical example is the formulation of orientated slit tapes made of polypropylene homo polymer. Most slit tapes contain a hindered amine light stabilizer for long term protection for the end use intended for the woven slit tapes in outdoor backing or woven bags. However, over the years the resin manufacture will add their own additives to the base resins based on their own customer requirements for the end use application that conflict with the final needs of end consumer.

It is well known in the art that processing stabilizers undergo in-situ conversion during processing and long term storage into chromophores that can initiate secondary pro-degradant reactions to accelerate both thermo-oxidative and photo-oxidative degradation. In the above case, there have been many instances of premature UV failure of oriented slit tapes made of polypropylene homo polymer fully fortified with a hindered amine but have failed prematurely.

The main cause of the problem can be traced back to the type and concentration of these known pro-degradant antioxidants that are excellent in their performance on one phase of the polymer end use but long term are antagonistic. The solution to the problem again is to change the system and if that is not possible, which is the case in our industry you add another additive that blocks the pro-degradant reaction and allow the hindered amine to perform. In the above case the additive of a low level of UVA is the solution to harmonize any pro-degradant additive that absorbs in the region that initiates UV degradation of the base resin.

This case shows once again that all recommendations and selection of any UVA depends on knowing the full chain of custody and end use requirements. Knowledge of the additive systems in any polymer is a must to have all information. However, due to the proprietary nature of most plastic additive systems this is not easily accomplished without good analytical reverse engineering intervention by those who can differentiate and quantify additives in any complex mixed system.

Finally, the loss of experience and the knowledge gained in the last fifty years has not been fully recorded in books or in the open literature. We repeat the same mistakes every five years in the plastic industry and the coatings industry is the recipient of the knowledge gained from the plastic industry especially when most additive companies choose to look at additives for plastics.

The needs of our industry are changing globally and unfortunately few new product solutions have come forth that provide the needs of the industry. Instead additive companies continue finding solutions to problems that do not exist and think they know what fits in a changing market. Needs instead of wants is the key to sustained growth with Ultraviolet absorbers.

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