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Coatings manufacturers are facing many challenges in the industry today and are expected to fill these requirements to be successful. To meet these needs, producers are looking to new technology from material suppliers to help differentiate their systems. With the ever changing economic climate and increased globalization, the need to implement new performance technologies to meet these concerns is required as well as their suppliers.

Today, the development of paints and coatings focuses mostly on three main areas, including the increase in overall performance, meeting environmental regulations, and maintaining low costs for end users. Increased functionality, longer durability, and use of thinner films are some main areas where performance improvements are occurring. It is anticipated that governments will continue to place pressure on the coatings industry to create products with less impact on the surrounding environment. Technology will help support this change and eliminate older, less environmentally sustainable systems. Reducing costs with technology usually relates to the elimination of specific manufacturing steps in the preparation or application of paints. However, some approaches allow for the overall reduction in the amount of dry films required in a system, therefore also lowering costs.

Light stability and durability to weathering during service is a key characteristic of coatings. Maintaining exterior appearance translates to more valuable automobiles, buildings, equipment, decorative articles, etc. Substrates, resins, pigments, and other coating components are sensitive to UV light due to the presence of chemical functionalities and/or impurities that absorb specific electromagnetic radiation. Light stabilizers help to mitigate degradation through the prevention of light absorption as well as minimize any subsequent radical oxidation reactions.

Light stabilizers based on 2-hydroxybenzophenone were some of the earlier chemistries used for UV absorption. These products also found use in coatings and are still being used today, based on the need for performace. 2-Hydroxy-2-phenylbenzotriazole chemistry was introduced and increased the performance of organic materials. The introduction of ortho-tert-alkyl substituted* and, later, ortho-cumyl groups, promoted UV absorption to some of the most stabilized potential today. Triazine chemistry also added another 1980 to stabilization from UV light by providing significant improvements in durability.

 Hindered Amine Light Stabilizers (HALS) were first introduced in the 1970s into polymers, and n-alkyl based versions were used in coatings in the early 1980s. In the early 1990s, commercial versions of n-alkoxy HALS became available for use in coatings for better performance and less interaction with other coating components. All of these improvements have led to very durable coatings and plastics due to changes in the fundamental and auxiliary chemistry related to the core light stabilizing molecules.

**Protection from UV Light**

Pushing the envelope for the protection of substrates, coatings resins and components requires maximizing three critical factors related to the chemistry of a UV absorber. First, the absorbing chromophore must be significantly stable or photostable, simply to continue performing as a light stabilizer. Beer's Law dictates that the amount of light absorbed is directly proportional to the concentration of absorber, the path length (thickness of the coating, in this case), and the extinction coefficient of the absorbing molecule. Maximization of this extinction, through chemical design is the second priority for product design and can be used to help reduce the concentration required in the formulation.

Finally, the absorption profile remains a key factor for protecting materials from UV light. Here it is important to take into consideration the UV (or even visible) light that reaches the substrate or coating as well as the relative sensitivity of the substrate and coating. For example, a coating resin could be very sensitive to 250 nm light, but the amount of 250 nm radiation in sunlight may not be sufficient by itself to create any photochemistry. The exact amount of radiation in sunlight, coupled with the absorption sensitivity of resins, pigments, the substrate or basecoat, etc., will determine where a UV absorber should function to alleviate any degradation. It could be anticipated that longer wavelength light absorption could be used to reduce or eliminate any photochemistry from occurring. This theory generally holds true, but as absorption approaches the low end of the visible spectrum at 400 nm, visible absorption occurs. The result would be a yellow tint from the additive's absorption spectrum.

As mentioned in the introduction, triazine chemistry exhibits one of the best photostability behaviors of any known UV absorber chemistry. This stability is reported to be related to the robustness of the intramolecular hydrogen bridge present in triazine UV absorbers.** The proton in benzotriazoles is reportedly more susceptible to base-induced deprotonation, eliminating the excited state-induced proton transfer (ESPT) pathway to the ground state and energy release. The ranking of stability of UV absorber chemistry can however deviate significantly from studies in inert solvents or model systems when used in a specific application. The overall durability of a system can be more dependent upon other factors, such as absorption profile, yielding a more robust system using a less stable UV absorber.

The synthesis of extensions to existing versions of triazines is also fairly general, starting from cyanuric chloride. UV1 and UV2 are commercial materials that were developed based on the variation of aromatic constituents around the triazine core. Electron donating groups and extended π systems were used to vary absorption maxima and increase molar extinction, respectively.
Advanced Light Stabilizers for the Next Century's Needs

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day's coatings industry is driven by three main factors: technological advancement, environmental compliance, and economical performance. Light stabilizer chemistry has advanced over the years and has entered a new era with the introduction of products relating to these factors. Advanced triazine take advantage of the known high epoxidation values as well as photostability and have extended now to longer wavelengths with even higher absorption characteristics. The latest hindered amine light stabilizers (HALS) are able to react into these technologies to that their migration is limited to the level they are intended to protect. Finally, a new technology has been developed to render these intrinsically hydrophilic chemistries compatible with water for enhanced performance and ease of use in today's low VOC systems.

INTRODUCTION

Coatings manufacturers are facing many challenges in the industry today and are expected to fill these requirements to be successful. In order to meet these needs, producers are looking to new technology from material suppliers to help differentiate their systems. With the ever changing economic climate and increased globalization, the need to implement new performance properties or effects at a faster pace also places significant pressure on manufacturers as well as their suppliers.

Today, the development of paints and coatings focuses mostly on three main areas, including the increase in overall performance, meeting environmental regulations, and maintaining low costs for end users. Increased functionality, longer durability, and use of thinner films are some main areas where performance improvements are occurring. It is anticipated that governments will continue to place pressure on the coatings industry to create products with less impact on the surrounding environment. Technology will help to support this change and eliminate older, less environmentally sustainable systems. Reducing costs with technology usually relates to the elimination of specific manufacturing steps in the preparation or application of paints. However, some approaches allow for the overall reduction in the amount of dry films required in a system, therefore also lowering costs.

Light stability and durability to weathering during service is a key characteristic of coatings. Maintaining exterior appearance translates to more valuable automobiles, buildings, equipment, decorative articles, etc. Substrates, resins, pigments, and other coatings components are sensitive to UV light due to the presence of chemical functionalities and/or impurities that absorb specific electromagnetic radiation. Light stabilizers help to mitigate degradation through the prevention of light absorption as well as minimize any subsequent radical oxidation reactions.

Light stabilizers based on 2-hydroxybenzophenone were some of the earlier chemistry used for UV absorption. These products also found use in coatings and are still being used today, based on the need for performance. 2-Hydroxy-2-phenylbenzothiazole chemistry was introduced and increased the performance of organic materials. The introduction of ortho-tetralyl substituted and, later, ortho-cumyl groups, promoted UV absorption to some of the greatest stabilization potential today. Triazine chemistry also added another 1980 stabilization from UV light by providing significant improvements in durability.

Hindered Amine Light Stabilizers (HALS) were first introduced in the 1970s into polymers, and α- n-alkyl based versions were used in coatings in the early 1980s. In the early 1990s, commercial versions of α-alkoxy HALS became available for use in coatings for better performance and less interaction with other coatings components. All of these improvements have led to very durable coatings and plastics due to changes in the fundamental and auxiliary chemistry related to the core light stabilizing molecules.

PROTECTION FROM UV LIGHT

Pushing the envelope for the protection of substrates, coatings resins and components requires maximizing three critical factors related to the chemistry of a UV absorber. First, the absorbing chromophore must be significantly stable or photopermanent, simply to continue performing as a light stabilizer. Beer's Law dictates that the amount of light absorbed is directly proportional to the concentration of absorber, the path length (thickness of the coating, in this case), and the extinction coefficient of the absorbing molecule. Maximization of this extinction, through chemical design is the second priority for product design and can be used to help reduce the concentration required in the formulation.

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The synthesis of extensions to existing versions of triazines is also fairly general, starting from cyanuric chloride. UVA1 and UVA2 are commercial materials that were developed based on the variation of aromatic constituents around the triazine core. Electron donating groups and extended π-systems were used to vary absorption maxima and increase molar extinction, respectively.

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Florida with 1% standard HALS in all formulations. Standard triazine UVA shows superb performance at a 40 μm layer thickness at 1% concentration, as expected (Figure 3d). However, if thinner films are required, both standard benzotriazoles and triazines show degradation and delamination at 20 μm dry film thicknesses and 1.4% concentration (Figure 2a-b). Using UVA2 at only 1% concentration and 20 μm layer thickness. Figure 2c shows that the film holds well to weathering. Significant savings can be realized by using only half the coating previously required—and thin film applications previously not possible can now be achieved.

The photopereformance of UVA2 relative to known benzotriazole chemistry can be observed in Figure 3. Transmission curves of 2K clearcoats over silver metallic basecoats containing these materials were plotted versus wavelength. Again, 54-month 5° South Florida exposure shows a significant impact on a coating containing a commercial benzotriazole UV absorber. In stark contrast is the amazing photostability of UVA2, with virtually no change in transmission after 54 months of exposure to the elements. What is even more significant is that the coatings containing UVA2 are only half the thickness of the samples containing the commercial benzotriazole material (20 μm versus 40 μm). These data suggest that not only can these advanced UV absorbers be used in thin film applications, but will perform under very harsh conditions.

**RADICAL SCAVENGING**

Hindered amine light stabilizers are used in coatings and plastics formulations to eliminate radical chain degradation processes initiated by light. Together with UV absorbers, stabilization of organic materials with synergistic results can be realized. In the case of HALS is generally related to improved surface gloss and reduced chalking for more durable final articles. As amines, HALS can be basic, depending on the nitrogen substituent in the molecule. Basicity from unsubstituted and n-allyl HALS can interact with acidic components of a formulation or metal catalysts present to initiate crosslinking reactions. Acidic components can vary from urethane crosslinking catalysts to carboxylic acids, resins, dispersants, and rheology control agents. The introduction of n-alkoxy substituted additives, known as NOR HALS, opens the door to stabilization potential for new resin chemistry. In addition, introducing a NOR species delivered the active form of a HALS stabilizer, eliminating the need for the "activation" by oxidation required with unsubstituted, n-allyl, or n-acyl HALS.

More recently, it became apparent that migration of light stabilizers can occur, relocating valuable chemistry to an undesired location. For example, some NOR

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**WATER COMPATIBILITY**

Waterborne coatings formulations have traditionally contained sufficient co-solvent for incorporation of organic components for various effects. With the increase in regulations and desire to minimize the amount of VOCs released into indoor and workplace, the need has come to develop new chemistry compatible with pure water. Chromophore-containing UV absorbers and functionalized HALS consist of organic functionalities inherently incompatible with water. This paradox created the necessity for out-of-the-box thinking and a new technology to yield compatibility without any compromise of light stability.

Recent developments in polymer chemistry combined with emulsion polymerization techniques yielded a technology where traditional organic-based materials can be used in waterborne systems. Unlike historical approaches using surfactant technology and water dispersion, polymers can be used to encapsulate additives. The resulting composition contains sub-micron-size capsules consisting of at least 50% active material, available for delivery to waterborne formulations. The overall solids content of such water emulsions is typically in the range of 40%. Figure 6 shows a micrograph of a typical product containing a hydrophobic triazine UV absorber. These materials do not contain any VOC components and the technology can be used to synthesize compositions containing UV-absorbing species.
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Figure 6—Micrograph of encapsulated hydrophobic UV absorber additive in a polymer matrix in water.

Figure 7—Comparison of (a) unstabilized, (b) encapsulated additive, and (c) a milky UV absorber additive in a waterborne coating over glass after cure.

The encapsulation technology developed here uses specific polymers that allow for efficient incorporation of the hydrophobic additives into the resin without exudation or separation. This effect is illustrated in Figure 7 with the product incorporated into a waterborne coating over glass. The clarity of the resulting film is no different than systems without additives.

CONCLUSION

Technology will continue to give solutions to coatings needs, raising the bar for the industry and creating better products for consumers. New UV absorbers discussed in this article are examples of new performance alternatives that allow for better stability and new applications to exist. HALS can be confined to the areas where needed with the use of crosslinking functional groups in the molecule. Finally, an encapsulation technology can be used to combine low-VOC waterborne coatings with hydrophobic additive performance.

Developments will continue and these, as well as other technologies, will be used to create new standards for additive effects.

References


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