Advances in PVC heat and light stabilization

Stabilizers play a key role in the PVC industry, where the market is driven by both regulatory and cost-performance issues. Jennifer Markarian reviews some of the latest developments in heat and light stabilization for PVC.

Both rigid and flexible PVC require an effective additive package to function, including some combination of stabilizers, lubricants, processing aids, plasticizers, and impact modifiers. Additives may interact, and an additive package should be optimized for cost-performance in a given application. Stabilizers are key components of an additive system. Heat stabilizers are used primarily to protect the polymer during processing, but also prevent longer-term heat degradation in the end-use. Light stabilizers are used primarily in flexible PVC to protect the polymer from ultraviolet light degradation. Development in stabilizers is driven by both regulatory and cost-performance issues.

The global market for heat stabilizers, with virtually all product going into PVC, was 500-540 million kg (1.1 to 1.2 billion pounds) worth between $1.7 and 1.8 billion in 2003, notes Fred Gastrock, product manager for additives at BRG Townsend, Inc., a plastics consultancy. Heat stabilizer market growth generally follows PVC market growth with an average of 2-3% globally. Lead stabilizers made up about half the volume and about one third of the value, but are predicted to have little to no growth. Tin stabilizers, with about 15% of market volume and just less than a third of the market value, are expected to see 3% volume growth. Mixed metal stabilizers, with about 25% of the volume and more than a third of the market value, should grow at about 4%. Organic stabilizers have a small piece of the market with less than $10 million in sales.

The Asia-Pacific region has the largest and fastest growing heat stabilizer market, with about 40% of global sales. Overall, the region has an AAGR of 4%; in China alone the AAGR is 10%. While a significant amount of additives used in China is imported, some additive production is beginning in China, says Mr. Gastrock. Atofina, for example, has a new facility in China producing butyl and octyl tin stabilizers. A rare-earth co-stabilizer sourced, produced and used in China makes up about 5% of the Chinese market, notes Mr. Gastrock. "The Asian PVC industry appears to be adopting additive types used in the Americas, such as tin and mixed metal stabilizers. While local markets might accept lead-based stabilizers, the Asian PVC industry is targeting exports that meet requirements for American applications, such as the growing vinyl siding and profile markets," says Mark Heldt, business manager for stabilizers at Atofina.

PVC consumed between 1.8-2.3 million kg (4-5 million pounds) of light stabilizers in 2003, which is only about 6% of the global light stabilizer market, comments Mr. Gastrock. Benzophenone ultraviolet absorbers (UVAs) are the most prevalent PVC light stabilizer, followed by benzotriazole UVAs. Light stabilizers are used primarily in flexible PVC.

Flexible PVC
Flexible PVC, used in applications such as flooring, wall covering, toys, and coated films and fabric, typically uses barium/zinc (Ba/Zn), calcium/zinc (Ca/Zn), or barium/cadmium (Ba/Cd) mixed metal stabilizers. Cadmium stabilizers are no longer used in Europe, and continue to be replaced with other mixed metals in North America. The biggest issue for flexible PVC, particularly for flooring and wall covering, continues to be volatility. New additives such as Akros' Akrostab, Crompton's Mark 9300 series, and Ferro's Therm-Chek liquid mixed metal stabilizers have very low volatile organic compound (VOC) levels, which reduces emissions at both the production plant and the end-use point. The new additives also have low levels of phenols and phenolic compounds, which are a concern in wall covering and flooring applications for improving indoor air quality. In Europe, the trend is to also eliminate nonyl-phenols, which may be regulated in the future. Printability is an issue in calendered film applications such as banner stock. Ferro has developed new stabilizer systems in which low molecular weight material does not exude to the surface and interfere with printing.
The most commonly used UV stabilizers in flexible PVC are benzophenone UV absorbers, such as Ciba® Chimassorb® 81, Crompton's MarkScreen 1413 or Cytec's Cyasorb® UV 531, and benzotriazole UV absorbers, such as Ciba® Tinuvin® P or Crompton's MarkScreen UV-7P. *There has been renewed interest in extending the performance and durability of PVC beyond what is possible with traditional UV absorbers. This interest has come primarily from producers of flexible PVC roofing membranes and producers of PVC alloys such as PVC/ABS,* notes Gerry Capocci, NAFTA market manager for construction plastic additives at Ciba Specialty Chemicals. Although conventional hindered amine light stabilizers (HALS) cannot perform well with highly acidic PVC due to their basicity, new, non-basic light stabilizers like Ciba® Tinuvin® XT 833 perform extremely well in an acidic environment. Ciba has found that Tinuvin XT 833 gives better durability than twice the concentration of a UV absorber in PVC. Tinuvin XT 833 is being used in roofing membranes, which is one of the most demanding flexible PVC applications. *"We think it is possible for Tinuvin XT 833 to replace UV absorbers in flexible PVC similarly to the way traditional HALS replaced UVAs in polyolefins several decades ago,"* predicts Mr. Capocci.

**PVC in wire and cable**

In both North America and Europe, flexible PVC in wire and cable jacketing applications are beginning to move from lead-based stabilizers to mixed metal stabilizers. The European vinyl industry has a voluntary commitment called Vinyl 2010 to replace lead stabilizers with more environmentally friendly mixed metal or organic stabilizers. The goal is to be lead-free by 2015 and to have reduced lead consumption by 50% from 2000 to 2010. *"The challenge is in finding stabilizers with comparable cost-performance to lead-based stabilizers. Significant development efforts have led to mixed metal stabilizers that can offer the market a workable solution,"* says David Ankrett, business director for stabilizers at Ferro Polymer Additives.

**Rigid PVC**

Rigid PVC, used in applications such as pipe, siding, and window and door profiles, experiences higher processing temperatures and higher shear than flexible PVC and requires more effective heat stabilizers. In North America, rigid PVC typically contains tin-based heat stabilizers. Tin is expected to remain the primary stabilizer system, with mixed metal and organic stabilizers filling niches, notes Scott Chambers, North American business director for vinyl additives at Crompton Corporation and president of the U.S. Tin Stabilizer Association (TSA). Tin mercaptide stabilizers have very good heat stability but poor light stability, which can be overcome by the addition of titanium dioxide. Because of its opacity, titanium dioxide acts as an ultraviolet light (UV) blocker in addition to being used as a base for white pigment. Darker coloured siding and profiles, growing in use in the U.S., cannot use titanium dioxide. Tin maleate or tin carboxylate-based stabilizers offer better light stability but poorer heat stability. UVA light stabilizers may be used with these to give incremental improvements, notes Don Brilliant, PVC industry consultant. New light stabilizers such as Ciba® Tinuvin XT833 can have a very positive contribution to weatherability in non-tin mercaptide formulations, adds Mr. Capocci. *"New additive technology for exterior applications balances the need for good processability and durability with weatherability,"* explains Mr. Chambers. Crompton's Mark 2289, containing a tin maleate stabilizer, is designed to prevent yellowing of light colours, particularly in the desert-like conditions of the south-west U.S., for example. Crompton's Mark T634 stabilizer combined with an appropriate lubricant and UV stabilizer will minimize fading or chalking of dark colours over time in wet environments, adds Mr. Chambers. In some products, a PVC cap layer with a higher level of tin stabilizer is coextruded over a PVC base with a lower stabilizer level. An alternative solution for weathering protection is to use an inherently weatherable capstock material such as acrylic or PVC-acrylic alloys. These capstocks are currently used most with darker colours in the premium siding market. The North American-based Vinyl Siding Institute plans to raise the minimum performance standards of vinyl siding over a period of several years. This will force the industry to look at options such as cap materials and UV stabilizers to improve weatherability, says Mr. Capocci.
Europe, which does not have a significant vinyl siding market, currently uses mostly lead heat stabilizers in window and door profiles. Tin stabilizers are used in Europe only in niche applications such as clear parts. Window and door profile applications are slowly changing from lead stabilizers to Ca/Zn mixed metal stabilizers, since organic based stabilizers do not meet weathering criteria, says Peter Marschalek, marketing manager at Chemson. "Outdoor weathering tests are currently in progress with profiles containing Ca/Zn stabilizer systems. Once these new systems are shown capable of meeting Europe's ten-year weatherability guarantee, the changeover from lead to mixed metal stabilizers will probably proceed very quickly. Producers are also keeping in mind the goal of being lead-free by 2015," adds Mr. Marschalek.

North American pipe typically uses tin stabilizers while European pipe has traditionally contained lead-based stabilizers. As in other applications in Europe, pipe is moving to Ca/Zn or organic stabilizers. The transition has been slow because pipe is particularly cost-competitive in Europe, notes Mr. Ankrett. Although the organic stabilizers do not give as white a polymer product as lead or tin stabilizers, this has not been an issue in Europe where pipes are typically coloured, compared to white pipes in the U.S., comments Mr. Brilliant (see Figure 3).

New stabilizer systems are being marketed for rigid PVC foam, which is growing in construction applications, comments Mr. Chambers. New stabilizer packages are also being marketed to the wood-plastic composite (WPC) market. While olefin-based WPC are well established in North America, PVC-based WPC are also beginning to grow, notes Mr. Chambers. Chemson has developed both lead and lead-free stabilizer packages for the new and growing European wood-PVC composite market. In Europe, profiles typically contain 20-30% PVC and are primarily used in building applications, notes Mr. Marschalek.

Other developments in rigid PVC stabilizers are additive packages designed for improved processing and higher profile production speeds. For example, Crompton's specialized tin stabilizer platform includes the Mark 2900 series packages to reduce plate-out in profile and pipe production and the Mark 2200 series packages that eliminate chatter in high speed, window profile production.

As the vinyl processing industry has improved process and dosing control, users would like to save costs by lowering stabilizer levels to the minimum necessary for performance. Atofina recently introduced the Thermolite 140 tin stabilizer formulation with lower tin levels targeted to meet both economic and performance requirements for siding substrates, explains Mr. Heldt.

**Testing of PVC heat and light stability**

Testing of polymer stability examines either process stability or heat and light stability of the end-use product. Process stability is typically measured in a static oven test, a dynamic torque rheometer test, or a process-simulation such as milling. These tests gauge colour development and physical properties over time as a measure of how well the additive package protects the polymer from degradation. Weathering or light stability is tested either in a laboratory weathering chamber that provides accelerated, simulated exposure or in actual outdoor exposure.
In simulated weathering, polymer test pieces are placed in a laboratory weathering chamber and exposed to light from xenon arc or fluorescent UV lamps. Xenon arc light sources produce UV, visible, and IR light; optical filters can be used to limit the spectrum. Moisture can be added through humidity control or water spray. Experts from Atlas Material Testing Technology say that xenon arc tests have better correlation with outdoor weathering tests. The most appropriate test and light source depends on the material and its failure mode, says Catherine Gadomski, international marketing manager at Q-Panel. For vinyl siding, fluorescent UV systems provide a more realistic simulation because moisture can be added through condensation on the polymer part. "Colour stability in vinyl siding has much to do with moisture levels, temperature, and UV rays. Moisture in outdoor applications comes primarily from condensation on the part," explains Ms. Gadomski. Required test protocols, including light source, vary by country and by application. For example, weathering test guidelines for PVC window profiles typically ask for extended testing periods equivalent to five years, with specific conditions such as moderate or extreme climate, notes Atlas. Five years outdoor weathering is equivalent to 4000 to 6000 hours on a xenon instrument.

While weatherometer testing is useful for comparing relative performance of various additive packages and may be sufficient for approval in some applications, other applications require outdoor weathering testing for approval. New chemistries are typically tested in two or more different environments. Hot, humid Florida and the Arizona desert are considered primary benchmarks. During a weathering experiment, polymer colour and physical property retention, either impact strength for rigid PVC or tensile properties for flexible PVC, are monitored. Chalking or whitening of the part surface can be observed in outdoor weathering tests. Chalking may occur in humid environments, and is particularly obvious on darker-coloured parts. The North American Vinyl Siding Institute (VSI) standards currently call for two years of outdoor weathering in subtropical, desert, and northern industrial climates. VSI is considering an accelerated, simulated ageing program that would grant temporary certification while outdoor testing results were pending.

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