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Steady growth predicted for biocides

Protecting plastics and preventing stain and odour growth have been the main requirements of an antimicrobial. However, consumer perception that products containing biocides can prevent the spread of diseases is also driving growth and prompting new developments with manufacturers. Jennifer Markarian reports.

Global consumption of formulated biocides for plastics was 15.4 million kg (34 million pounds) in 2005, with about one-third going to Europe and one-third to North America, estimates U.S.-based Townsend Polymer Services & Information (Townsend) based on their 2005 study, Plastic Additives VI (see Figure 1). European and North American markets are predicted to grow at 3-4% AAGR through 2009. While consumption in China is less than 10% of the biocide market now, it is predicted to grow at 15% AAGR. Growth is driven globally by both the need for biocides to protect the polymer and prevent stain and odour growth, and by consumer perception that products containing biocides can help prevent disease spread, say industry experts.

PVC consumes about two-thirds of formulated biocides, estimates Townsend. Biocides prevent microorganisms from feeding on the organic plasticizer in flexible PVC formulations. Biocides stop odour, prevent colour change and help maintain polymer properties. The primary active ingredients used in PVC are oxybisphenoxarsine (O BPA), 2-n-octyl-4-isothiazolin-3-one (OIT), and dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT). Biocide use is expanding beyond PVC into polyolefins, polyurethane foams, silicones and engineering thermoplastics. While polymers other than flexible PVC may not contain high plasticizer levels, microorganisms can still produce undesirable stains or odours by feeding on surface organic material. Polyolefins consume about 20% of biocides and polyurethane (PU) foam consumes under 10% of biocides, estimates Townsend. A variety of active ingredients are used in non-PVC polymers.

Applications

Biocides are seeing steady use in the major, traditional applications for flexible PVC such as flooring, wall coverings, pool liners, roof membranes, tents and

| Supplier          | Trade name(s) | Products                           |
|-------------------|---------------|------------------------------------|
| Agion             | Intercide     | O BPA, IPBC, ZNP                   |
| Akzo Nobel        | Omacide       | Zinc pyrithione                    |
| Arch Chemicals    | Vanquish      | DCOIT, BBIT                        |
| Asahi Denka       | Royalguard    | O organic                          |
| Ciba Specialty Chemicals | Irgaguard | Silver-based                        |
| DuPont            | Micro-Chek    | Silver/zinc/copper-based           |
| Ferro             | Fungitrol     | DCOIT, OIT                         |
| Lanxess           | Preventol     | O organic Fungicides               |
| Microban          | Microban      | DCOIT, OIT                         |
| Milliken          | Alphasan      | TCPP                               |
| Rohm & Haas       | Vinyzene      | Silver-based                        |
| Sanitized AG      | Sanitized     | Silver-based                        |
| Shinnan           | Zeomic        | Silver-based                        |
| Thomson Research  | Ultra-Fresh    | TBT and organic based              |
| Toagosei          | Novaron       | Silver-based                        |
| Troy Chemical     | Polyphase     | IPBC based                          |
|                   | Micropel      | O BPA, DCOIT, OIT, IBPC            |
tarpaulins. In addition, there is an increased interest in biocides for preventing bacterial growth on the surface of polymer surfaces, comments Richard Simpson, product manager at Akcros Chemicals. Akcros introduced BT X200, a combination of Bethoguard, epoxidized soyabean oil and antibacterial additive, for preventing fungal and bacterial growth on PVC wall and floor coverings.

There is a trend towards treating more materials of construction to prevent mould and mildew growth in PVC, PU and other resins, says Don Shaw, vice-president of development at Troy Corporation. Another trend is biocidal treatment of additional parts of appliances, durable goods, and automotive parts such as steering wheels and shift knobs. Biocides in polyolefins are growing in kitchen, bathroom, and institutional and restaurant uses, notes Ron Babinsky, business manager at Townsend. Food processing applications such as countertops, cutting boards, and PVC curtains used as room separators in grocery and butcher shops are growing areas for biocide use.

"Cross-contamination, which is the transfer of microbes from one area to another, is becoming a concern in food processing industries," explains Melinda Reyes, global marketing head for antimicrobials for plastics at Ciba Specialty Chemicals. The fast growing wood-plastic composites (WPC) market is also a high growth area for biocides.

"Consumers expect mould and mildew protection as part of the WPC 'low-maintenance' requirement," explains Chris Springer, market manager for biocides at Rohm and Haas. Rohm and Haas recently introduced two new Vinyzene D COIT-based formulations, a solid and a higher concentration liquid, which are designed to provide efficacy against surface fungi in WPCs.

**Biocide regulations**

Worldwide, environmental regulations are playing a significant role in the biocide market. "All biocides will be facing additional scrutiny in the next few years. Suppliers need to be experts in what data is required," warns Mr. Springer. Biocide registration with regulatory agencies globally is an important factor in market success, agrees Tom Wilkerson, global segment manager for biocides at Arch Chemicals.

In the European Union, the Biocidal Product Directive (BPD) requires registration of active ingredients by the end of 2008. Once registered, biocides will undergo a testing and review process. The BPD is viewed by the industry as being significantly more restrictive than U.S. EPA [Environmental Protection Agency] regulations.

"The positive impact of the BPD is that stronger products will come to the forefront. On the other hand, the costly process to register may stifle development of new biocides," comments Tom Aroella, regulatory affairs manager at Thomson Research Associates. "New' active ingredients may come mainly from actives already used in other industrial sectors that can be modified to suit plastic applications, adds Dan Nichols, group market development manager for Thor Group Limited and author of a recent report on biocides in plastics.

In the U.S., biocides used as additives for material preservation must be registered with the EPA under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). The U.S. EPA and the Canadian PMRA [Pest Management Regulatory Agency] have scheduled reviews of registered biocides in 2006, including requests for additional toxicity data, notes Mr. Springer. Suppliers have become more aggressive in promoting use of biocides with end-users in applications that have human or food contact, therefore implying a health benefit, notes Mr. Babinsky. However, health claims are monitored closely by the EPA in the U.S. and increasingly by regulatory agencies globally, say industry experts. In the U.S., the Treated Articles Exemption of FIFRA allows a company to avoid the lengthy and expensive pesticide registration process, but they can not make explicit or implicit health benefit claims about the product and must state to customers that the biocide is solely for protection of the treated article. Suppliers take regulatory compliance very seriously, offering guidance to their customers on using appropriate claim language for the finished product. To support claims appropriately, efficacy of a biocide must be tested in the specific end-use application.

We offer the 'Saniproofed' label for use by our customers only after a rigorous testing program in the plastic article," notes Mr. Simpson. Despite marketing limitations, consumers are making the assumption that if bacteria do not grow...
on the surface, people touching the surface will have less chance of contact with germs, say industry experts.

Active ingredients

In active ingredients, OBPA has the largest global market share, with more than one third of formulated biocide volume, estimates Townsend (see Figure 2). Isothiazalone biocides such as OIT, DCOIT, and n-butyl-1,2-benzisothiazolin (BBIT) together hold another one-third or more of the market. Other organic biocides include zinc omadine, 3-iodo-2-propynyl butyl carbamate (IPBC), 2,4,4’-trichloro-2’-hydroxy-diphenyl-ether (TCPP or triclosan), tri-butyl tin (TBT), and 2,4-thiazole benzamidizol (TBZ).

OBPA and isothiazalones

The demand for OBPA-based biocides is growing modestly while growth for isothiazalones is faster paced, with newer applications favouring non-metallic chemistries, agree industry experts. OBPA has received scrutiny because it contains arsenic, but it is very cost-effective and is expected to maintain its leading position. Troy Corporation, which in 2004 acquired Micropel LLC and the company’s broad Micropel® biocide product line, has expanded the Micropel® OBPA product line to new DINP and DINP carriers in response to customer requests. While current OBPA users may hesitate to switch active ingredients due to the cost and reformulation time, OBPA may be limited in new applications or with new users, suggests Mr. Babinsky.

DCOIT and OIT isothiazalones have broad anti-fungal properties and are cost-effective, lower toxicity profile alternatives to OBPA, says Mr. Springer. DCOIT and OIT are seeing strong growth in applications such as PVC roofing membranes, pool liners, vinyl flooring, exterior signs and interior wall coverings. Growth in these markets is driven both by market growth and by conversion from OBPA to DCOIT or OIT.

In PVC roofing membranes, the trend toward ‘green’ construction increases the desire for additives that can prolong a roof’s useful life. DCOIT’s key performance benefit is better resistance to UV degradation than OBPA, explains M r. Springer. BBIT is being used in polyurethane applications such as flexible foams, gaskets, and insulation, and in PVC flooring, fabrics, and gaskets, notes M r. WIlkerson. Arch Chemicals Inc., which purchased A vecia’s biocides business in 2004, recently achieved US EPA registration for its Vanquish® biocides, including neat liquid BBIT and blends of BBIT and zinc omadine in various carriers. Akros Chemicals recently added DCOIT products in additional carriers to its Intericide® line, as well as more concentrated versions of OIT.

Other organic biocides

Zinc omadines, which have broad spectrum effectiveness against bacteria, algae, and fungi, are also being used as lower toxicity alternatives to OBPA in PVC and polyurethane foams. Other attractive properties of zinc omadine are that it has no VOCs, no odours and is not a sensitizer, says Mr. Wilkerson. Sanitized AG introduced Sanitized® PL 21-60 in a DINP carrier in 2003. Arch Chemicals recently received EPA registration for Vanquish® 100, a neat miscible liquid, and Vanquish® SL-10, a unique blend of Zinc Omadine® and BBIT designed for applications with stringent antimicrobial property requirements, including soil burial applications.

Troy Corporation has introduced new IPBC-based fungicides with broad spectrum activity and safe environmental profiles. M icropel 612 is designed for polyolefins and styrenics, and M icropel A285 is a nonmetallic liquid for flexible PVC.

M icropel T685 provides both bacterial and fungal protection for polyolefins, styrenics and other polymers requiring high temperature stability antimicrobials. The Th or Group introduced an Acticide® PI range of products based on IPBC as well as Acticide® PZ based on zinc pyrithione.

Tri-butyl tin (TBT) has experienced some backlash from publicity over the ban of TBT in marine anti-fouling paint, but continues to be used as an antimicrobial in all regions other than Europe, says Tom Aroelia, regulatory affairs manager at Thomson Research Associates, a supplier of TBT, silver antimicrobials, OIT and zinc omadine.
Inorganic biocides

Inorganic biocides are primarily silver ions, although other metals such as copper and zinc can be used. The metal ion active ingredient is contained in an inert matrix of ceramic, glass or zeolite. The metal ions are released at a controlled rate to provide long-term protection.

Major suppliers of inorganic silver biocides include AgION, Ciba Specialty Chemicals, Fuji Chemical, Milliken, Sanitized, Sinanen Zeomic Company and Toagosei.

Silver biocides are being used primarily to prevent bacterial growth on part surfaces. Use is affected by the consumer’s perception, which varies by culture, of where the antimicrobial benefit is needed. Silver antimicrobials are used most widely in Japan, followed by North America and Europe, says Barry Green, marketing manager at AgION.

China has the highest growth in use of silver antimicrobials because of concerns about SARS and bird flu viruses, he adds. In the U.S., silver antimicrobial use is growing in HVAC (heating, ventilation, and air conditioning) filters and ducts, says Mr. Michele Potenza, business development manager at Agion.

Antimicrobial use in home appliances, particularly refrigerators, has been growing over the past year, notes Lee Close, AlphaSan™ market manager at Milliken & Company.

A study from the Institute of Hygiene and Public Health at the University of Bonn shows that refrigerator inner surfaces treated with silver antimicrobial have significantly reduced listeria levels, reports Mr. Arla Brandon, Sanitized specialist at Clariant Corporation, the global distributor for Sanitized antimicrobials, whose Sanitized® Silver was used in the study. Of the top nine refrigerator producers in Europe, seven have antimicrobial-containing products, notes Mr. Close.

Asian manufacturers are using antimicrobials in refrigerators, and North American refrigerator manufacturers are beginning evaluations, he adds. Water contact applications, such as water coolers, ice makers, filters, valves, tubing, and fittings, have high growth potential for antimicrobial use, agree industry experts.

In these applications, bacteria can build up a bio-film, which can either deteriorate the polymer or slough off and affect water quality appearance. For example, Milliken & Company’s AlphaSan® silver antimicrobial is used to reduce biofilm in PVC piping for American Standard’s StayClean™ Whirlpool System.

“We expect higher visibility for antimicrobials in these markets in coming years. People are quick to accept the idea of making the surface easier to clean and keeping the surface clean longer,” says Mr. Close.

Over the next few years, silver biocides are expected to grow in medical applications, where they reduce bacteria levels on the surface of plastic parts. Growing global concern over hospital acquired infections has people looking for remedies, notes Mr. Green. Applications include tubing for fluid management systems, needle free valves, catheters, infusion systems, and medical films and adhesives. In the U.S., these applications are regulated by the FDA [Food and Drug Administration] rather than the EPA. Higher silver antimicrobial loadings in the product are being considered for preventing spread not only of bacteria but of viruses such as MRSA (Meticillin-Resistant Staphylococcus Aureus) and SARS (Severe Acute Respiratory Syndrome), claim suppliers.

Milliken recently introduced Alpha-San® RC 2000 with a 10% silver loading. Higher silver loadings allow use of lower levels of formulated biocide, notes Mr. Close.

Agion Technologies introduced Agion™ AC, a combination of silver and copper ions, in 2004. While silver prevents bacteria growth, copper prevents growth of mould and mildew in applications such as HVAC, notes Mr. Potenza. Ciba introduced Hygate™, a novel form of silver biocide that is incorporated as elemental silver and is ionized in use.

“Hygate has a highly porous structure that results in high surface area per unit of weight. It has a slower, more controlled release than silver incorporated as silver ions in an inert matrix. This gives it more durability,” explains M.S. Reyes. Hygate is being used commercially in Europe and in some U.S. applications, and is in the process of being registered with the U.S. EPA. Canadian based Thomson Research Associates introduced Ultra-Fresh silver-based biocides in a glass matrix for plastic applications in 2002. In 2005, Thomson Research Associates introduced nano-sized silver for topical application in textiles.

The high surface area of nanoparticles makes them highly efficient, notes Mr. Areola. Silver nanotechnology is being investigated for use in plastics.

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