

Preservative Innovate to Protect

aint and coating formulations offer ideal substrates for the growth of bacteria, mold, mildew, and fungi. Preservation of paints and coatings—both in-can and as applied films, remains critical for maintaining the appearance and performance of these materials. Manufacturers of preservatives for this market expect to see continued demand for their products in paints and coatings despite ever-increasing regulatory burdens and competition from low cost producers. Key players are developing innovative blends and formulations of existing actives that will meet the ever-changing needs of paint and coatings formulators.

The total U.S. market for biocides was estimated to be \$1.6 billion in 2003, according to Business Communications Company, Inc. (BCC), and was expected to grow at an average annual rate of 3.2%, reaching \$1.87 billion by 2008. For paints and coatings, biocides are the fourth largest type of additive after thickeners, plasticizers, and corrosion inhibitors. Consumption of biocides in paints totaled \$60 million in 2002 and is predicted by BCC to increase by the same annual growth rate of 3.2% per year to \$70.4 million in 2007. Some industry players estimate the market will climb as high as \$100 million by 2007.

The largest application for biocides in the paint and coatings market is for protection of the appearance of dry paint films. Approximately 56% of biocides by volume are sold for this purpose, according to Steven Nerlfi of Kusumgar, Nerlfi & Growney, a market research firm. The other 44% is used for in-can preservation. These dry film biocides are typically used at a level of 1% or less by weight and act to inhibit the growth of molds, mildew, fungi, and algae that can destroy the material in the can, discolor and damage paint films, possibly contribute to "sick building syn-

by Cynthia Challener

Market Growth

drome," and cause off-odors. In-can preservatives are used to protect the paint from microbial contamination until it is applied.

While the protection of paints and coatings will remain a necessity, manufacturers of the active ingredients must contend with several major issues currently facing the industry. Consolidation within this traditionally fragmented market has begun to occur and will ultimately result in many fewer players. Increasing regulatory burdens, including reduced levels of volatile organic compounds (VOCs) in paints and the European Biocidal Product Directive (BPD), are having a significant impact and will continue to do so for the foreseeable future. Growing consumer awareness of "sick building syndrome" and the role that preservatives can play in preventing this problem will also affect the market.

Consolidation of preservative manufacturers has been occurring slowly over the past few years. Rohm and Haas acquired Swiss biocide producer Acima in early 2000. Troy Corporation purchased the North American operations of the German producer Shulkë-Mayr in 1997 and the German biocide producer Riedel de-Haen in 1998. Dow's acquisition of ANGUS Chemical in 1999, followed by its merger with Union Carbide in 2001, also affected the biocides

playing field. In December of 2002, Bayer acquired from Ondeo Nalco the chemistry associated with two biocides—thiabendazole (TBZ) and dibromodicyanobutane (DBDCB). Solvay sold its biocides business to UCB Group in 2003. In March of 2004, Arch Chemicals announced that it was acquiring the biocides business of Avecia, and International Specialty Products (ISP) purchased the German preservative formulator Biochema Schwaben.

Arch Chemicals will be gaining Avecia's Pool & Spa and a Protection & Hygiene biocides businesses in the approximately \$215 million cash and stock deal, which is expected to be completed near the end of the first quarter. The acquisition strengthens Arch's portfolio and complements its existing capabilities in water treatment and industrial biocides, according to Arch Chemicals' chairman, president and CEO, Michael E. Campbell. The Protection & Hygiene business sales are largely concentrated in North America and western Europe and add products for industrial markets including mineral slurries, polymer emulsions, and in-can coatings preservation. Avecia will use the net proceeds from the sale to pay down debt.

With its acquisition of Biochema Schwaben, ISP gains access to extensive expertise in formulating preservatives and biocides for industrial and personal care applications, plus a wide range of products targeted at the printing, paints and coatings, polymer emulsions, skin care, and hair care markets. "Biochema is a strategic, high value acquisition for ISP's biocide franchise, which helps us expand our geographical footprint and our product range," notes president and CEO Sunil Kumar.

Further consolidation is expected, as manufacturers deal with the increasing costs of developing and introducing new preservatives in highly regulated regions while fighting low-cost producers from other areas of the world. "In fact, global consolidation of the market makes it easier for preservative chemistry regulations to be implemented. This could lead to less and less chemistries receiving re-registration in the future," says Kevin Ajoku, marketing manager for Bayer Chemicals Industrial Preservation group. Major differences between regions in terms of regulatory requirements and cost/performance expectations are also an issue for preservative suppliers, according to David Sutton, North American marketing manager for coatings and latex biocides with Rohm and Haas.

In the U.S., paint and coating manufacturers must meet increasingly stringent requirements for low VOC products. Preservative suppliers, as a result, must provide formulations with minimal VOCs that still maintain the efficacy and cost effectiveness of their traditional offerings. "One of the key issues for biocide manufacturers is the need for low VOC biocide formulations to support new paints that must meet regulatory requirements for lower VOCs," says Douglas K. Simpson, Ph.D., business manager of industrial biocides for Arch Chemicals. "While formulating to meet new VOC regulations, paint manufacturers are unwilling to sacrifice performance in the biocides they select, creating a challenge for

www.coatingstech.org May 2004

Leading Suppliers of Preservatives for Paints and Coatings

Acti-Chem Specialties (Thor Group)

Arch Chemicals (acquiring Avecia biocides business)

BASF

Bayer Chemicals Corporation

Buckman Laboratories

The Dow Chemical Company

International Specialty Products (ISP)

Rohm and Haas Company

RT Vanderbilt Company, Inc.

Troy Corporation

suppliers to offer improved performance and compliance in their new products" says David Faherty, vice president of marketing with Troy Corporation.

There are other regulatory costs for biocides in the U.S. now. Recent legislation requires application fees for new biocides. "These costs, introduced by the EPA, do not take into account volumes of products, so it will be more difficult to bring out a biocide for a niche market as these rules appear to have been written with the agricultural sector in mind," says Jerry Tracey, technical director with Acti-Chem Specialties. "These new regulations may have an inhibitory effect on new molecules being introduced to the market in both the short and long-term. A fairer system would be to base the existing maintenance fee on actual volumes sold and to scrap the application fee."

In Europe, the BPD has already begun to impact the market. According to some industry experts, the cost of registering a new active in Europe has been estimated to be about Euro 5 million. The costs associated with funding extensive R&D programs and investing in new plants and processes will be additional investments. "Most companies therefore expect to see an increased focus on existing actives and a decreasing total number of actives over time," says Bernie Franc, NAFTA biocides business manager for BASF Corporation. In such a climate, there will be a move toward more global partnerships between paint and coatings suppliers and biocide producers, according to Jerry Konst, marketing manager with Dow Biocides. "Paint and coatings manufacturers will need to have a partner with a global reach and resources that can help them develop solutions to their preservative problems," he explains.

Arch's Simpson notes that some longstanding biocides like carbendazim and diuron may disappear in Europe shortly. He expects that paint producers will reformulate their systems to eliminate the use of biocide blends that incorporate these two actives. Mr. Faherty notes, however, that consumption of these key actives has increased in all markets outside of Europe due to the well known efficacy of these actives and the reluctance of other regulatory bodies to share the view of European regulators. Last year, carbendazim successfully completed an FQPA re-evaluation in the U.S. with no restrictions on end use. Other actives scheduled for an FQPA re-evaluation as part of U.S. EPA re-registration in 2004 are BIT, zinc pyrithione, and sodium pyrithione.

There is also concern that new actives will not be reviewed in Europe for the next 10 years as existing products go through the evaluation process required by the BPD. "There is a real danger that this reduction in choice may lead to an increased probability of difficult to control (tolerant/resistant) organisms being generated," continues Mr. Franc. "In fact, there is evidence that this is already happening in some industry sectors where regulatory demands mean that biocide choice is restricted." These regulatory factors along with lower costs are resulting in a trend to move paint manufacturing to areas outside the European Union, according to Daryl Smith, president and chief executive officer of Troy Corporation.

In Asia, the Chinese ban on formaldehyde has also raised concerns for in-can preservatives whose mechanism of action relies on the release of formaldehyde. However, Mr. Faherty notes that demand for formaldehyde adduct biocides that meet U.S. and European standards for formaldehyde exposure continues to grow since they are effective, low cost, and meet prevailing health standards.

Some see the increasingly global nature of registration requirements as ultimately aiding the preservative marketplace. "We believe this process will become more rather than less prescriptive as more governments start demanding similar industry standards to those in Europe and the U.S., says Mr. Tracey. "This will have the result of leveling the global playing field where all players will be required to adhere to uniformly stringent registration processes and where environmental protection laws and the resulting cost implications associated with environmentally responsible biocide manufacturing, apply to all players," he continues.

Unfortunately, while the registration process is becoming uniformly stringent on both sides of the Atlantic, the regulators are not using the same set of rules. "EU regulations are governed by the precautionary principle, which stresses inherent hazard, while the U.S. regulatory system is driven by an evaluation of actual risk," says Troy's director of regulatory affairs Donald Shaw, Ph.D. Until harmonization solves this

May 2004 JCT CoatingsTech

dichotomy, biocide suppliers will need to comply with two different sets of rules.

Troy and others are finding opportunities for preservatives with improved safety profiles. "Regulatory concerns over compliance with safe handling and worker exposure and, to a lesser extent, compliance with VOC limits have created opportunities for an increase in sales of biocides that are safe for workers producing paint and coatings and safe for their customers," says Mr. Faherty. "These new products usually contain multiple actives, meet newer, stricter environmental regulations, are just as, or more, effective than older products, and offer competitive cost-in-use," he continues. They will displace those biocides that cannot comply with new environmental regulations.

As the cost of R&D and registration of new products rises, fewer new biocide chemistries are being developed. "Regulatory and raw materials cost increases in the face of more downward price pressure from generic biocide suppliers is also an issue today," says Mr. Sutton. Mr. Simpson notes that with the very competitive environment, suppliers are being forced to limit new product R&D. "Longer term this will limit new products for the paint manufacturers," he adds. In response to this situation, companies are developing "smart application products" which are slightly modified or a combination of existing chemistries, Mr. Ajoku says.

Another issue for preservative manufacturers is the increasing demand among customers for improved "ease-of-use." More and more customers prefer to purchase pre-formulated and packaged preservatives that are easier and safer to handle, according to Bayer

Chemical's Ajoku. Paint and coating manufacturers also want the capability to formulate a few preservatives into a wide range of products. "Our customers want to be able to use a few select preservatives across their entire product line, allowing then to lower costs and reduce inventory levels," explains Chuck Carncross, vice president of Buckman Laboratories' coatings and plastics division. Preservative customers are also demanding improved technical, sales, and regulatory services from their suppliers, while expecting prices to be maintained at lower levels, according to Mr. Faherty.



Consumer awareness of hygiene issues is also impacting the use of preservatives in paints and coatings. Traditionally dry film biocides and fungicides have found widespread use in exterior paints and coatings and in interior applications where moisture is high (such as bathrooms). However, as consumers have become more familiar with "sick building syndrome" and allergies to molds have increased, paint and coating formulators have responded by developing new products for interior applications that contain preservatives.

This trend is most noticeable in the Asian market, where consumer focus on hygiene is driving demand for antimicrobial and/or antibacterial paints for interior surfaces, according to Mr. Simpson. There is also increased consumer awareness about the potential antimildew properties of interior paints in the U.S., which has led to an increase in demand for IPBC products, according to Mr. Faherty. Frank Flynn, manager of specialties and biochemicals R&D with R.T. Vanderbilt Co. adds, though, that there is still a general misunderstanding by the public about the necessity and value of preservatives that would be good for the industry to address.

Several other technical issues are also impacting suppliers of preservatives to the paint and coatings market. According to Mr. Sutton, there is more need for algal control as building materials become more inorganic-based, such as fiber and cement, and thus more susceptible to algal growth. Specialty surface coatings being introduced to the market for nontraditional substrates may require new preservative packages. "Some new coating developments have resulted in a demand for biocides with a higher tolerance for specific conditions such as higher pH and the use of other additives, which

may be aggressive to a particular biocide system," notes Mr. Tracey. Changes in production practices, such as the use of pre-dispersed products and recycled water, create a bigger microbial challenge for biocide systems as well, he adds.

In the end, it comes down to offering cost effective, high performing products that provide the necessary efficacy. "Within the guidelines and regulations surrounding product development, manufacturers of preservatives must develop products and chemistries that are not only effective but also chemically compatible to maintain the integrity of the

www.coatingstech.org May 2004

formulator's finished product," explains Mr. Ajoku. Mr. Carncross adds that "new products must be cost effective, safer, and have excellent performance in order to be worth bringing to the market." Acti-Chem's Tracey concurs. "The top challenge we face is bringing to the market universally acceptable products, which fulfill regulatory and market requirements at an acceptable price, while maintaining the high levels of service our customers have come to expect."

Acti-Chem Specialties, Inc. is a member of the Thor Group and offers biocides to the U.S. paint and coatings market for preservation in both packaged materials and applied films. The company's main business is in isothiazolones, but the company also specializes in combining a wide range of biocides to enable the most effective use of the individual chemistries. Thor Group continues to expand its manufacturing facility in Speyer, Germany. In addition, a new manufacturing site representing a major investment for the group has been opened in Wincham in the UK.

Recent product introductions for Acti-Chem include Acticide® MBS, a synergistic blend of methyl- and benz- isothiazolinones launched in the U.S. for use in aqueous systems that has a broad microbiological spectrum, is temperature and pH stable, and is AOX and formaldehyde-free. Acticide® GA is a combination

of chloromethyl- and methyl-isothiazolinone (CIT/MIT) and 2-bromo-2nitro-1, 3-propanediol that has specific activity against organisms which had previously been shown to be difficult to control, particularly sulfate reducing bacteria. Acticide® OTW is a zero-VOC, water-based dispersion of octyl-isothiazolinone that can be used to preserve manufactured products from both wet state and film fungal attack. Acticide® PA is comprised of a mixture of two highly effective fungicides together with the most effective algaecide currently available and is designed for the control of both fungal and algal spoilage on exterior coatings.

Arch Chemicals provides fungicides, algaecides, and bactericides for the paint and coatings market. Applications for these preservatives include interior and exterior paints, wood stains, caulks, sealants and adhesives, and others. The company is introducing to the market new Omadine® and Omacide® iodopropynylbutylcarbamate (IPBC) products. According to Mr. Simpson,

a proprietary new low-VOC IPBC product is under evaluation by the top tier U.S. paint manufacturers to assist their formulation efforts to meet the 2005 VOC regulations.

Arch's new Zinc Omadine® ZOE Fungicide-Algaecide products have found wide application in coatings for exterior masonry surfaces due to their long-term performance and alkaline stability. These products, which are based on the leading antidandruff shampoo additive, zinc pyrithione, are also attractive for interior paint dry film protection due to their safety profile and low VOC, water-based formulations.

Avecia's product range includes the Proxel preservatives (based on 1,2-benzisothiazolin-3-one or BIT) that deliver long-term preservation in raw materials and finished paints due to the excellent alkaline stability and amine compatibility of BIT. The company also offers the Densil C series of paint film mildewcides for dry film protection.

BASF offers 2-Bromo-2-nitropropane-1,3-diol or Bronopol as an alternative for solving problems arising from tolerant organisms. The product works well on its own and is also effective when used in combination with isothiazolinone (IT) chemistries.

Bayer Chemicals offers the in-can preservative dibromodicyanobutane (DBDCB) which targets slime-form-

ing bacteria and fungi and is effective against yeast. Its thiabendazole (TBZ) product is a dry film preservative and is active against a variety of molds, mildews, and rot. The company also offers DBDCB-based combination biocide products and other fungicides and bacteriacides. According to Mr. Ajoku, the company is pursuing an EPA registration for a new active to be used in marine antifouling.

Buckman Laboratories offers biocides, fungicides, and algicides for use in interior and exterior coatings, with additional applications in wood preservatives and stains, caulks, slurries, and emulsions. Their product portfolio includes both inorganic and organic preservative chemistries such as barium metaborate (BMB), 2-(thio)cyanomethylthio)benzothiazole (TCMTB), iodopyopynlbutylcarbamate (IPBC), and chlorothalonil to name a few. Buckman recently introduced Prosan 18 for use in wood preservation. While continuing to expand its

Key Specialty Preservative Chemistries Used in Paints and Coatings

Isothiazoliones

Zinc and copper pyrithione

Dibromodicyanobutane

Iodopropynylbutylcarbamates

Thiabendazole

Bronopol

Oxazolidines

Triazines

Chlorothalonil

Folpet

Hexahydrothiazine

Dibromonitrilopropionamide

Barium metaborate

Benzothiazoles

Carbendazim

May 2004

domestic manufacturing sites in Memphis, TN, and Cadet, MO, Buckman has also opened a new facility in China.

Dow Biocides provides chemistries that can be used as in-can preservatives, dry film fungicides, and cleanup biocides for the paint and coatings market. The company's most recent product introduction, Dowicil QK-20, is a multi-purpose biocide that can be used for clean-up of raw materials, recycle water clean up, and reducing overall costs of preservation through reduced in-can preservative requirements. "Dowicil QK-20 is a fast acting biocide that has been shown to offer synergistic effects when used with in-can preservatives that can reduce cost to treat by 30-40%," says Mr. Konst. Additionally, the product can help reduce re-work and waste by allowing the customer to recover contaminated raw materials and finished products. Also, Dowicil QK-20 can help with waste reduction by allowing recycled wash water to be cleaned up and re-used. Currently Dow is working on optimizing its processes and gaining ISO 9000-2001 registration for its biocide business.

ISP offers a wide range of industrial biocides for the protection of coatings and related products in the wet state from spoilage by microorganisms, and coating dry films from defacement by fungal and algal growth. The actives range from formaldehyde donors and isothiazolinones for in-can preservation to iodopropynyl-butylcarbamate, folpet, chlorothalonil, and s-triazines for the protection of dry films.

According to John McGroarty, director of global marketing, ISP's Fungitrol 700 & 800 fungicide series being launched this year will offer customers a totally new carrier system designed to provide no odor and no VOC in a unique color stable formulation. These products will have dual application in paints and coatings, as well as plasticized PVC materials. Later in the year ISP will offer two new patented synergistic dry film products that will provide both algal and fungal protection. Introduced recently to complement these products, ISP now offers a total biocides package with three new formaldehyde free sanitizers designed to treat recycled water and wastewater at the manufacturing site.

Rohm and Haas Company offers both in-can preservatives and dry film fungicides for the paint and coatings marketplace. In 2004, the company has introduced the combination mildewcide and algaecide products Rocima 63 and 65. Rocima 63 is designed to protect coatings applied to cementitious surfaces, while Rocima 65 provides broad spectrum protection for coatings applied to wood substrates. According to Mr. Sutton, Rohm and Haas is in the process of introducing Rocima 20 and 40, 20% and 40% active formulations of IPBC. A number of other products are in development as well.



R.T. Vanderbilt Company, Inc. offers bactericides and mildewcides under the tradename Vancide® that protect in-can and both waterborne and solvent-based dry film paints and coatings.

Troy Corporation offers a wide range of in-can and dry film preservatives for paint and coatings applications. Troy recently introduced Mergal K12N, bringing combined isothiazalone and Bronopol chemistry to the coatings and emulsion markets. New in-can products from Troy are Mergal® 680 and Mergal® K10N. Mergal 680 protects against difficult-to-control organisms such as *Pseudomonas* and spore-forming *Bacillus* in paints, coatings, and other applications in which other preservatives are ineffective or uneconomical. Mergal® K10N is a zero-VOC alternative to other in-can preservatives for producers and consumers who require low or no VOC emissions. Because it is an aqueous formula, this product has a higher partitioning rate of preservative into the water phase of the paint where control of bacteria is needed.

Troy also recently introduced new low-VOC, low toxicity fungicide and broad-spectrum algaecide/fungicide dry film preservatives. Polyphase 678 is a low-VOC, broad-spectrum fungicide designed for use in both exterior and interior water-based coatings and pigmented stains that is effective against more fungi than conventional mildewcides. Polyphase 662 and 663 combine more effective control against fungi, with added protection against algae. Polyphase 662 is designed for paint and other wood stains and coatings. Polyphase 663 is used for both wood and cementitious coatings.

To meet increased worldwide demand for antimicrobials, Troy recently increased production of preservatives at its manufacturing facility in Thailand and expanded technical service laboratories there to serve the Asia Pacific region. "We will continue to invest in facilities to increase our own production capacity to meet increasing world demand while carefully reviewing all external opportunities to grow our position as a supplier to the paint and coatings market," says Mr. Faherty.

www.coatingstech.org May 2004 7