

## COVER STORY

---

**November 3, 2003**

Volume 81, Number 44

Chemical & Engineering News CENEAR 81 44 pp. 29-30

ISSN 0009-2347

---

### FOUL WEATHER FRIENDS

Biocides prove their worth where coatings must survive under adverse conditions



**GREEN AND MEAN** Wood coating protected by Troy's iodopropynylbutylcarbamate-based biocides (right) does not show the abundant algal growth found on wood coating with conventional dry film preservative (left).  
TROY CORP. PHOTO

**MARC S. REISCH, C&EN NORTHEAST NEWS BUREAU**

Paint could be really foul stuff were it not for the biocides that preserve paints in a can or that help safeguard dry paint films.

Problems with biocides have gotten some paint makers in trouble. Late last year, [Masco](#), maker of [Behr paints](#), settled a lawsuit involving claims of excessive mildew on wood surfaces coated with the company's paints. The company took a \$200 million charge to account for the settlement.

Mold, mildew, and fungi discolor and destroy paint films. The organisms can do their dirty work because paint binders and additive components are generally organic and provide nutrients for microorganisms, according to Douglas K. Simpson, industrial biocides business manager for [Arch Chemicals](#). Provide sufficient humidity and a neutral to acidic environment, and the microorganisms can thrive, he says.

The molds and bacteria that form on dried paint surfaces indoors can contribute to sick-building syndrome--an environment where indoor air quality is further compromised by cleaning chemicals, volatile organic chemicals (VOCs) emitted by furnishings, and ozone emitted from fax and copy machines. For the truly health-conscious, coatings are now available to treat metal surfaces in a home to prevent the spread of bacteria, fungi, and mold.

Although biocides are generally used at a level of 1% or less by weight, U.S. paint makers add some 32 million lb, or \$110 million worth, of them annually to the paints they ship to users, says consultant Steven Nerlfi of market research firm Kusumgar, Nerlfi & Growney. Most of the opportunity for biocide suppliers is in preserving dry paint films. About 56% of biocides by volume are sold to keep paint films wholesome looking. Another 27% preserve liquid latex paints--solvent-based paints generally don't require in-can preservation. Antifoulants to preserve marine paints make up the remaining 17% of biocides sold.

Simpson says biocidal films are typically used in exterior coatings to help preserve the paint's appearance. Used in paint meant for interior surfaces, biocides inhibit the growth of mold along with the stains and the odors associated with mold. Increasingly, paint makers outside the U.S.--particularly in Asia--are using biocides not just to preserve paint films but also to control bacteria on painted surfaces in hospitals, schools, hotels, and other facilities, Simpson says. In the U.S., claims implying a health benefit require paint makers to register with the [Environmental Protection Agency](#).

Any U.S. makers could get assistance for such a claim from Arch, maker of zinc pyrithione, sold under the [Zinc Omadine](#) trade name, Simpson says. Included in shampoos as an antidandruff agent for about 30 years, zinc pyrithione has been used to inhibit bacterial, fungal, and algal growth on dry latex-based paint films for the past five years.

**IN PAINT FILMS**, the pyrithione is the active moiety, Simpson says, and it works by inhibiting the passage of food through cell walls, thus forcing cells to starve to death. Arch is the only U.S. maker with EPA approval to sell this ingredient in the U.S. for use in paints. Zinc pyrithione and Arch's copper pyrithione can be formulated into below-the-waterline marine paints to prevent fouling, Simpson says.



**STRONGER THAN DIRT** Arch Chemicals' Omadine biocides were used on both the interior and exterior of the Grand Hotel in Ho Chi Minh City, Vietnam.  
**ARCH CHEMICALS PHOTO**

For true germophobes, a silver zeolite is available for use in paints and for incorporation in industrial, consumer, and medical products to wipe out bacteria, mold, and fungus. Ravi M.

Bhatkal, vice president of strategy for AgION Technologies, says the company, started in 1997, licensed Japanese technology and has built on it since. Low-level release of silver ions from the zeolite carrier disrupts respiration in microbes and kills them, Bhatkal says.

**AK Coatings**, a subsidiary of AK Steel, has a license to use the AgION additive in antimicrobial coatings for steel used in food equipment, appliances, and medical equipment. Two years ago, DuPont licensed the additive for use in powder coatings for medical, industrial, and residential products.

The national security potential for the additive helped AgION raise \$10.5 million in January from Paladin Capital Group's Homeland Security & Partners' Funds. Advisers to the investment group include former CIA director R. James Woolsey and former National Security Agency official Lt. Gen. Kenneth Minihan. Paladin thinks the firm's coatings could protect against terrorist-initiated bacterial attacks.

Consumers today are concerned about mold and mildew in their homes, especially in light of "media reports about homes that have become uninhabitable because of mold infestation," says David E. Faherty, Troy Corp. vice president of sales and marketing. "Newer buildings are well insulated and have less air exchange, resulting in the potential for increased growth of

mildew, especially in bathrooms and kitchens," he explains.

That is all the more reason for use of broad-spectrum algaecides and fungicides in home paints, Faherty says. The firm's Polyphase line of iodopropynylbutylcarbamate-based algae- and fungi-killing film additives has lower VOC content than conventional products. The firm's in-can preservatives, based on benzoisothiazolinone (BIT), include Mergal K10N, which has zero VOCs because it is "a soluble form of BIT that does not require solvents and cosolvents to make a typical dispersion product."

**Dow Chemical's** Jerry Konst, North America biocides marketing manager, says sick-building syndrome is a real concern. The firm's Amical line, based on diiodomethyl p-tolyl sulfone, is effective against fungus and mildew. Based on iodine, this additive can cause yellowing in a paint film exposed to ultraviolet light. However, sold in paints to coat the backside of sheetrock used to build walls, it makes a cost-effective biocide, Konst says.

Dow's paint biocide line includes 13 distinct chemistries for both in-can and dry-paint film preservatives. Its most recent release is Dowicil 96, a broad-spectrum liquid bactericide based on oxazoladine chemistry to preserve emulsion paint films.

**Rohm and Haas** has a strong line of in-can and dry-paint film microbicides as well, much of it based on isothiazolin chemistry. These preservatives work by penetrating cell membranes and "inhibiting specific enzymes in the Krebs cycle," leading to cell death, says David Sutton, American coatings and latex biocides marketing manager. As formulators have reduced VOC contents in paints in recent years, water-thinned paints have required greater use of biocides, he says.

Focusing on isothiazolinone chemistry, **Avecia** provides a broad-spectrum antimicrobial for in-can paint preservation based on 1,2-benzisothiazolin-3-one. A new version of this chemistry--Proxel AQ, recently launched in Europe-- contributes no VOCs at all to a paint preparation. Alex Cornish, international marketing manager, says Avecia intends to register AQ in the U.S. soon. Avecia also sells chlorothalonil under the Densil tradename for paint film preservation.

[International Specialty Products](#), a supplier of a broad range of biocides, has also come out with a biocide with a patented no-VOC-containing carrier. [Fungitrol 720](#) is a paint film preservative based on iodopropynylbutylcarbamate. According to William Woods, biocides business development manager, this newly tweaked product acts as a fungicide with antibacterial properties, freeze/thaw stability, and no odor.

**MARINE PAINTS** are much more demanding than a typical wall paint because they must protect ships' hulls below the waterline against fouling by seaweed, barnacles, and other organisms. According to John Martin, formerly with Arthur D. Little and now a senior manager at technology consulting firm Tiax, marine paints are tricky coatings to formulate. "The biggest problem with biocides in marine coatings is that they need to work and be nontoxic in the environment," Martin says. The International Maritime Organization has banned tributyltin antifoulants in marine paints; the ban will take effect in 2008. While TBT effectively cut down on foulant growth--which can increase the drag on a ship's hull and thus increase operating costs--it is also environmentally persistent. In its place, copper-based paints are now widely used to discourage bacteria, algae, and fungi growth.

But copper alone doesn't offer as effective biocidal action as did TBT. In some instances, formulators are adding Rohm and Haas's [Sea Nine](#), an isothiazolin-based paint film biocide that is effective against barnacles and algae. Rohm and Haas's Sutton says copper needs to be used with Sea Nine to increase its spectrum of activity against marine organisms.

However, some government authorities suspect that copper may also persist in the environment, Martin says. So it may be a matter of time until copper itself undergoes the scrutiny TBT received. Of course, ship owners can choose a silicone-based coating that sheds barnacles and seaweed as it glides through the water. But the vessel has to move faster than the typical tanker to cleanse the hull. And, Martin says, "soft silicones don't last long."

One new alternative is a menthol derivative--menthol propylene glycol carbonate. Incorporated into a below-the-waterline paint at a cost comparable to that of TBT, the additive is nontoxic and cost-effective, says Jonathan R. Matias, executive director of R&D at testing firm [Poseidon Ocean Sciences](#). Matias says his firm has licensed for marine use the antifoulant it calls Frescalin to [Symrise](#), the flavor and fragrances firm formed earlier this year from the merger of Dragoco and Haarmann & Reimer. Symrise is a major manufacturer of synthetic menthol.

Matias says a researcher for his firm, a Catholic nun named Sister Evelyn who is located in India, first identified a coral extract--juncelin--that was both biodegradable and effective against barnacles on ship hulls. At \$300,000 per kg, juncelin "was only good for academic interest," Matias says. So Sister Evelyn began to screen compounds with structures similar to juncelin and settled on the menthol derivative.

The menthol acts as a nontoxic repellent, Matias says, and is already registered for use in South Korea, "where 50% of major marine construction and repair takes place." Because it is most effective against barnacle and oyster larvae, and weaker against algae and sponges, zinc or copper needs to be added, but at reduced rates compared with current systems. Matias says Poseidon is working on a similar menthol additive it calls Menthradin as an in-can mold and mildew preventative.

Whether marine, architectural, or industrial paint makers, formulators have a number of choices when they need a cost-effective, environmentally sound biocide, without detracting from appearance. Foul-ups are preventable, but none of the biocide choices are clear-cut.