Biocides under Pressure


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On 6 and 7 February, 98 biocide experts from 16 countries met in Berlin to discuss innovations regarding antimicrobial agents for in-can and film conservation - in view of the implications of the new EU Biocidal Products Directive. The intensive discussions during the conference made quite clear: There are highly innovative developments, however, the high costs of notification make new active substances on the market very unlikely. And for biocide mixtures, “synergy” is a buzz word having also negative implications.

Blends may indeed face a difficult suituation. On the one hand, they are needed more than ever, because waterborne coating systems offer microorganisms everything they could wish for. If they are not controlled, they can cause a considerable damage - in the can, in the coatings production process, or in the coated product after application. However, under the new European Biocidal Products Directive (BPD), the use of biocides is strictly regulated. Several speakers at the ECC “Novel Biocide Technology” in Berlin addressed the implications of the BPD - above all John Duddridge (Rohm and Haas), who delivered the opening presentation at the conference, as a renowned expert on this topic. Duddridge explained the definitions, procedures and relevant time frames of the BPD and other relevant directives, and also discussed the data requirements necessary for the product notification.

5-8 Mio EUR per active substance

The BPD evaluates biocidal products based on risk assessments rather than hazard assessments. Hazard corresponds to toxicology data in terms of effect/dose, but risk includes both hazard and exposure, i.e. an analysis of the time-dependent concentrations of the substances in the environment. To collect corresponding data is time-consuming. Test results often require 23 days.

New uses for old substances

Despite the cost-dilemma, the compulsion towards innovative biocide systems remains. Thus, the first day of the ECC “Novel Biocide Technology” mainly addressed new ideas for the use of old active biocides.

David Roper (BASF Biocides) presented BIT/Bronopol-blends as well as a new KHDO-variant (Potassium N-cyclohexyldiazoniumdioxide), which predominantly excel as strong fungicides. Scott Betts (Thor Specialties) reported on MIT/BIT-combinations against antibiotics, because biocides generally attack a multitude of targets within the bacterial cell, and because resistances of bacteria against biocides is far less likely than antibiotics: Will the use of biocides (particularly upon prolonged underdosage) bring about more dangerous, mutant bacteria, which possibly will also be resistant to antibiotics? This might of course be a severe health problem, but it would also force the development of new active substances. But Cornish was able to show that such resistances of bacteria against biocides is far less likely than against antibiotics, because biocides generally attack a multitude of targets within the bacterial cell, and because their mechanism of action usually “brutally” affects the cell’s physiology. Mutations leading to resistance are thus hardly imaginable - and, more important, the studies demonstrate, that upon critical examination almost all spoilage incidents could be attributed to other causes than mutagenic bacterial tolerances.

Bacterial resistance to biocides is unlikely

Alex Cornish (Avecia Biocides) reported on studies that closely examined cases of alleged resistance of microorganisms against common biocides (BIT, MIT, CMIT, isothiazolones), which show almost a lower age incidence than for bacterial tolerance compared to CIT, based on their different mechanism of action. According to Betts, CIT, which has been in use for a long time, is likely to be phased out of the market under the BPD. Blaise Henry (Dow Chemical) discussed studies on DBNPA, a “quick-kill”-biocide, that again has been known for a long time, but which has not been used in coatings formulations yet. He pointed out, that it can very well be used as an effective disinfectant, which is also environmentally friendly, because it decomposes rapidly, after unfolding its effects. Kornelia Treskonova (ISP Specialties) reported on MIT/BIT-combinations of formaldehyde releasers (IPBC/CTL), also featuring an improved efficacy. Addressing a similar topic, Holger Zitt (Bode Chemie) featured new blends of isothiazolones (CFM, MI) with formaldehyde releasers (TMAD), showing both good efficacy and a very low smell - which is unusual for formaldehyde release biocides, and also makes them VOC-compliant.

Cell analysis in real-time

Patrick Schwarzentuber (Onyx) addressed the analytic problem: Using standard incubator/plate-counting methods, the analysis of cell concentrations in liquid systems is very time-consuming. Test results often require 23 days. Schwarzentuber presented a technique that simultaneously measures the electrical impedance and fluorescence of the liquid, while passing a thin tube. Using appropriate colouring
of the bacteria, this allows to count and to analyse the cells within seconds. In addition, the colouring also allows to monitor the physiological status of the cells (active/inactive/dead). Pigmented coating systems can also be analysed, in this case the solid content has to be separated off by centrifugation first.

**Antimicrobial polymers**

The second day of the conference focussed on new biocidal substances: The first three lectures presented polymeric active substances, which have the advantage of being fixed within the coating matrix, and of not being consumed in use. Kim Lewis (Northeastern University Boston) featured a polymer system based on poly(4-vinyl-N-alkylpyridiniumbromide) and polyethylenimine. The polymers are fixed on the surface, and the active group penetrates the target cells and kills them while still being chained to the surface via the polymer. The result is an actively sterilizing surface. Detlef Thölmann (Degussa) discussed a slightly different concept: Polymers with aminofunctional groups on their surface are incorporated in the coating and show a permanent, effective antimicrobial activity, without releasing any agents in the environment. Andreas Holländer (Fraunhofer Institute for Applied Polymer Research, IAP) had a similar solution, and described the antimicrobial efficacy of polyammonium compounds, that are chemically coupled to various polymers (plastics), forming a merely nanometer thin layer. These coatings are highly efficient, require only very little material, and are chemically stable - due to their extremely low thickness, however, they are of course somewhat prone to damage by scratching.

**Reloadable biocidal coatings**

A different concept was put forward by Jeff Williams (Vanson Halosource): n-Halamine-based coatings act biocidal through active halogens. The halogen concentration released by the coatings is such that it effectively kills off bacteria, but is not odourous. Hydantoinyl-compounds are polymerized into a polyurethane matrix, the coating can then be loaded with chlorine simply by rinsing with a sodium hypochlorite solution. The coatings excel with a very high and long-term efficacy, which can just as easily be regenerated by another loading step.

**Powders and inorganic biocides**

Harry Brodie und Steven Green (Biocote) demonstrated the possibility to formulate biocidal powder coatings. They managed to incorporate both organic and inorganic biocides in the formulation, which survive the challenging conditions during powder coating production, and still unfold a high biocidal efficacy. Two presentations dealt with purely inorganic biocides: Jörg Hocken (Sachtleben Chemie) focussed on the use of nanoparticles of TiO₂ and ZnS. These particles are photocatalytically active - upon irradiation, hydroxyl radicals are formed in the case of TiO₂, and traces of dissolved zinc in the case of ZnS; both with a high biocidal efficacy. The nanoparticles can be used to generate easy-to-clean surfaces at the same time, effectively preventing the formation of biofilm - which generally, once formed, is extremely difficult to remove and often presents a real nuisance, particularly within production vessels and the like. Christian Goebbert (ITN Nanovation) finally reported on silver-coated TiO₂-nanoparticles, which are incorporated and fixed in the coating matrix and again show a high antimicrobial efficacy over years. Highly innovative the new polymeric and inorganic biocides may be, however, they too fall within the scope of the European Biocidal Products Directive and thus cannot avoid the regulative costs either.

Resumee of the conference: Despite many innovations it will become more difficult for both producers and users of biocides to find the perfect system - and more important at the same time. As the chairman of the first conference day, Jeff Williams perhaps asked the crucial question: “Has anyone ever calculated the cost of NOT using biocides?”

A limited number of conference proceedings is still available at a price of 435,- EUR from Vincentz Network, contact Maice Sandmann, Tel. +49 (511) 9910-273, Fax: +49 (511) 9910-279, sandmann@coatings.de

**ECC “Smart Coatings II”**

The next European Coatings Conference will take place on 16 and 17 June 2003, as always in Berlin. For the second time, the topic will then be “Smart Coatings” - raw materials, formulations and processes for coatings with novel functionalities. Details can be found at www.coatings.de/ecc