How MICROBIOCIDES Will Contribute to Further Substantial Reduction of Emissions from Coatings

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INTRODUCTION

The modern world is awash with "green" initiatives in nearly every aspect of life. Politicians, businesses, celebrities, scientists, and the general public are supporting such diverse green developments as hybrid cars, wind energy, solar energy, ethanol production, the production of black lists of dangerous chemicals, and sponsoring products and processes claiming to be green. There is no argument against reasonable actions being used to avoid environmental pollution. However, taking the complexity of air quality issues as an example, it is unclear where, or by whom, priorities for emissions reduction should be set and where resources should be allocated. Far less than 1% of man-made emissions in California are coming from architectural coatings, while transportation contributes the major part. There is no disagreement about the need to develop technologies to reduce the impact of human activities on the environment, but there is a general disconnect with regards to priorities, the relative magnitudes of different environmental problems, and a concept of cost/benefit analysis in deciding what issues should be considered first.

While at first air quality programs focused on exterior issues (as well as exposure in the workplace), today, interior air quality is considered among the highest priorities. Part of this is a reflection of how much the general environment has improved over the last 30 years; part of this is a matter of what is the popular target of the moment.

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Presented at FutureCoat! 2008, sponsored by FSCT, October 15-16, 2008, in

VOCs are emitted into indoor air from building materials, furnishings, cleaning compounds, office equipment, personal care products, air fresheners, people, food, and unvented combustion processes such as tobacco smoking or cooking with gas stoves. In general, the concentration of pollutants in indoor air can be reduced most rapidly by air exchange with outdoor air, provided the pollutant is actually being emitted by indoor sources.

In this context, the extension of the VOC definition to include all organic molecules having a sufficient vapor pressure to become airborne in sufficient amounts to provoke a concern for human well being (i.e., is measurable) is often used. Also, it is important to understand that volatile organic compounds can be generated by the reaction of coating ingredients with air oxygen and not just by the ingredients. Well-known examples are oxidative drying systems, which emit low molecular weight aldehydes for long periods of time—long after all solvents are completely evaporated. Although VOC reduction in architectural coatings should be considered as a positive step, a more holistic approach to careful consumption of energy and resources and to reduce emissions over the entire life cycle of a product should guide the next steps.

Functionalities imparted by adding antimicrobial substances to paints assist with, and have a positive impact on, waste reduction and the reduction of emissions. One example is that cleaner exterior surfaces over longer periods of time and the subsequent extension of renovation cycles reduces pollution overall. Antimicrobials provide the security to avoid moldy surfaces in damp rooms, and this has a positive impact far beyond any savings of VOC gained by choosing a low-VOC antimicrobial. Effective antimicrobial additives allow for the reduction of coalescents and the use of raw materials from renewable resources in paint production. However, doing so makes the coating more susceptible to microbial degradation than the full synthetic counterparts.

Preservatives are integral components of modern coatings. Advances in binder technology and the introduction of new performance additives have provided formulators with the tools to develop low-VOC paint formulations without sacrificing coating performance. While the new binders optimize physical and performance properties, their influence on the microbiology of paint preservation is frequently not evaluated or considered.

U.S. regulation of microbiocides differs significantly from Europe, which is in a transition period with the Biocidal Product Directive (BPD—1998/08/EC). Consolidation within the world's paint industry and the necessity of extensive eco-toxicity and toxicity data generation in Europe has triggered the search for optimized paint film microbiocides applicable in different coating systems and climate zones in Asia, Europe, and the Americas.

This article describes some opportunities for further VOC reduction in the coatings industry by proper selection and use of preservatives. The following principles will be discussed with examples from practice:

1. Replace organic solvents in preservative formulations.
2. Reduce emissions when the preservative is produced, stored, and transported.
3. Reduction of waste in coatings production.
4. Further reduction of VOC of paints.
5. Reduced emissions from the coatings in service.

REPLACE ORGANIC SOLVENTS IN PRESERVATIVE FORMULATIONS

Recent developmental work has focused on coatings preservatives that provide no contribution to VOC. Solventborne formulations of film preservatives, which needed to be very low water-soluble by design, like Polyphase P20T, were replaced by water-based suspension concentrates. While the first generation of suspension concentrates still contained some minor quantities of VOC,[1] most recent formulations have eliminated even the minor VOC contribution of surfactants and additives used to formulate the preservatives. Today, a complete range of zero-VOC in-can and film preservatives is offered.

REDUCE EMISSIONS WHILE PRESERVATIVES ARE PRODUCED, STORED, AND TRANSPORTED

The example of recent 1,2-benzisothiazolin-3-one (BIT) formulation technology development demonstrates the efforts to reduce the VOC contribution of this important and ubiquitous preservative. While the first generation products were alkaline solutions in dipropylene glycol or propylene glycol with a respectively significant VOC contribution, the second generation offered products such as Mergal K10N, a VOC-free water based formulation introduced more than 10 years ago. At that point, further development and overall reduction of emissions could be achieved by not only considering the physical form of the product, but by reevaluating the total value chain of the active's production, use, and transportation. Developing extremely high concentrated, pH-neutral, zero-VOC BIT suspension concentrates reduces not only the impact of transport and storage by a factor 4.5, but also requires less production of packaging and less recycling of the packaging material.

REDUCE WASTE IN COATINGS PRODUCTION

Modern zero-VOC in-can preservatives need greater assistance from improved plant hygiene practices during paint production than do the older preservative chemistries. Also, while traditional paints were much more forgiving to mistakes in production hygiene, low-VOC paints cannot be successfully produced without a proper hygiene plan. Thus, "weaker" products pitted against greater biological insult potential require that a wide variety of measures have to be taken to avoid any microbial burden from unclean production equipment, raw materials, water, and recycled materials. Sometimes the most effective plant hygiene measures are counter-intuitive. For example, overlaying storage tanks with a formaldehyde reaction product, which is known to contribute per se to the VOC in paint, actually could be a way to develop, produce, and sell paints at an even lower VOC level. In this example, a cylindrical storage tank with 10 tons of paint might be considered. Assuming a two square meter surface area and a liquid layer of 0.5 cm thickness of a solution of 0.5% of a preservative consisting to 70% of VOC would add just 0.00035% VOC (3.5 ppm) to the bulk. This small, immeasurable contribution to the bulk paint would translate to the correct level of a preservative at the location needed to protect the head space of the storage tank. As a result, the final preservative program at the end of production could be both low VOC and effective in controlling contamination. This example might also demonstrate that the simple rejection of any raw material with a contribution of VOC is not always the most appropriate path to the lowest environmental impact.

As another example, increasing the fraction of recycled wash water reused means a reduction of the environmental impact from water discharge. This is only possible by proper preservation of recycled water with an effective, quick acting preservative that might not be VOC-free itself. Still, the end result is that VOC of the "total production and distribution system" could be lower than if this counter-intuitive action were not taken.

FURTHER REDUCTION OF VOC OF PAINTS

It is well established that the reduction of VOCs from raw materials also renders paint formulations more susceptible to microbial growth. For example, binders with lower levels of residual monomers are more easily colonized by bacteria. In addition to the altered vulnerability to microbial attack, this modification influences the physical-chemical behavior of preservatives in the multiphase coating material. A lot of work was undertaken to reformulate architectural coatings over the last couple years. For acceptable in-can preservatives that meet low VOC and other environmental criteria, the list is reduced tremendously and, in fact, has left the industry with 1,2-benzisothiazolin-3 one (BIT) as the major active substance. To cover the weakness of this preservative against the important family of gram-negative bacteria, the *Pseudomonas* species, it was successfully proposed to combine the BIT treatment with the co-application of a short-term active bactericide, like 5-Chloro-2-methylisothiazolin-3-one (CIT) and bronopol. The result is effective preservation and low VOC contribution, but not the lowest VOC that might be obtained if effectiveness were sacrificed.

VOC FROM TINTED PAINTS

In the latest publication for the environmental label Green Seal, "Environmental Standard for Paints and Coatings (GS-11)"[2] there is a requirement also to consider the colorants added at the point of sale when final paint VOC evaluation is performed. This requirement is effective as of January 1, 2010. To reduce VOC, more and more colorants are formulated with no APEO as a surfactant. This, in combination with the current consumer fashion trends toward more intense colors and deeper shades, has negative implications with respect to the microbiology of preservation of the colorants and the final paint.

To achieve the necessary brightness, depth, opacity, and fastness properties at acceptable costs, the colorants also need broad compatibility with different paint formulations. While propylene glycol as a humectant helped to preserve a tinting system and did not influence the susceptibility of the final coating, its replacement by nonvolatile components increases the susceptibility of the tint dispersion itself, as well as the final tinted coating, to microbial growth. It was long known that the tinting machines at the point of sale can develop heavy fungal growth on the semi-dried tin-

Table 1—Wet-State Preservation Challenge Test of Low-VOC Colorants

Colorant	1/7D[a]	2/7D[b]
Black	2	2
Gray	3	3
Magenta	2	2
Orange	0	2
Organic Red	0	0
Organic Yellow 1	0	0
Organic Yellow 2	0	0
Oxide Red	3	3
Oxide Yellow	1	1
Red Toner	4	4
Phthalo Blue	4	4
Phthalo Green	0	0
White	0	0

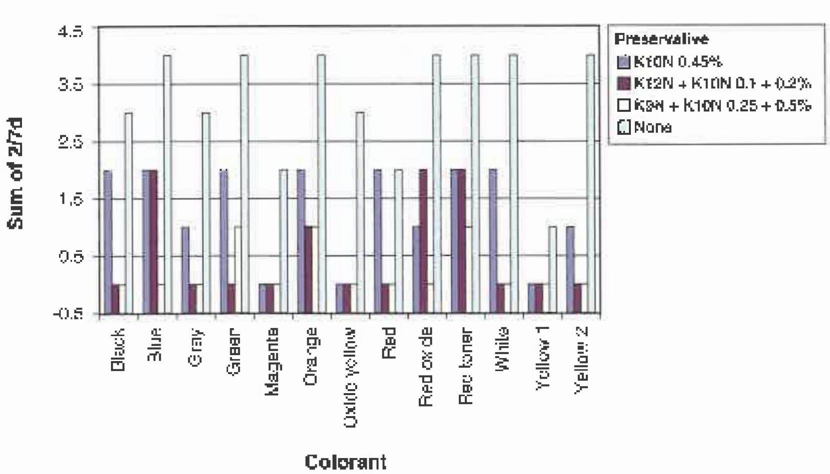
(a) 1/7D: 1st inoculation, bacteria score after seven days contact time.
(b) 2/7D: 2nd inoculation, bacteria score after seven days contact time.
Evaluation scheme: 0: no bacteria recovered, 4: more severe bacterial growth

ters. This in turn can clog the valves and make exact dosing impossible. Very low levels of special fungicides like BCM-IPBC combinations added to the colorant at approximately 100 mg/kg active substance can keep the tinting machines clear from fungal growth on the semi dried stage. However, bacterial contamination has become very difficult to control. This is because the application of amine-based in-can preservatives like HHT or oxazolidines, which provide significant "head-space-preservation," will not be possible, because trace amounts of formaldehyde are given off into the matrix. This issue is further potentiated if surfactants based on renewable resources like soy lecithine become part of the recipe. The examples in *Table* 1 and *Figure* 1 demonstrate that single BIT or CIT/MIT based in-can preservatives cannot safely preserve low-VOC colorants. It is evident that the pigments are not inert for the microbiocides used. Carbon black is, of course, one of the most difficult colorants to preserve as the pigment adsorbs huge amounts of organic molecules. Taking the solvent out of the formulation renders the adsorption phenomena even more severe. Phthalocyanines can react with electrophiles like the isothiazolinones, and deactivate them. These facts lead to the common observation that different shades have different levels of sensitivity to microbial contamination.

The results of the wet state challenge test (*Figure* 1) revealed that the organic yellows and red, white, and phthalo green were well preserved with a formaldehyde adduct-based preservative. Test of the zero-VOC preservation showed that BIT added as a single active substance (Mergal K10N) was not sufficient in most of the tinters, even at the relatively high addition rate. Only organic yellow 1 was completely free of microorganisms after seven days. A combination of bronopol, CIT/MIT, and BIT provided much better protection; however, the phthaloblue, red oxide, red toner need a slightly higher concentration level than tested here. As bronopol is not stable in most of the colorants, its primary function is to reduce the level of *Pseudomonas* species from raw materials to a very low level (one controllable by the more stable BIT) before it is degraded to a non-active level. Unfortunately, low concentrations of formaldehyde are generated from degrading bronopol. The level of generated formaldehyde is, in general, much lower than the theoretical maximum value of 30% of the molecule and for most environmental labels is acceptable, except for those that incorporate an artificial no-formaldehyde content provision. As the example demonstrated, the optimum relative level of the active components has to be evaluated for every colorant separately. From the exhibit, it can be concluded that the addition rates of in-can preservatives to zero-VOC tinters might be higher than expected from the preservation of paints. Preservative label limits may not make effective preservation possible for all tinters under some currently envisioned low- or no-VOC, no-formaldehyde provisions.

However, the proper evaluation of the best in-can preservation choice provides the formulator with a tool to make no VOC colorants. Allowing some latitude in secure preservation avoids waste in production and at the point of sale. Cleaning efforts are reduced and with that the environmental footprint reduced.

Figure 1—Wet-state preservation challenge test of BIT based preservatives.



REDUCE EMISSIONS FROM COATINGS IN SERVICE

Exterior Coatings

For exterior coatings, broad spectrum, zero-VOC film preservatives formulated as suspension-concentrates in water were developed, preventing the colonization of exterior coatings even under severe climatic conditions. The recent developments at Troy eliminated even the very low levels of volatile components from the surfactants and the stabilizers. However, the main contribution of a film preservative to reduce the environmental footprint of paint and the reduction of VOC from exterior coatings is an indirect effect. It was shown that the appearance of a coating in an exterior environment is strongly correlated to microbial colonization. Microbial defacement is often the trigger for recoating and renovation. A recent generation film preservative that was tested helped to reduce the impact by keeping the walls in a proper condition. Exterior exposure tests in Florida and Oregon showed that a coating which is colonized after six months to a degree that repainting would be necessary, could stay free of defacement for more than six years by adding 0.6% Polyphase 663.

Interior Coatings

In 2004, the Institute of Medicine (IOM) of the National Academy of Sciences completed a major review of the available scientific literature pertaining to the health consequences of building dampness and mold.[3] The proportion of current U.S. asthma cases attributable to dampness and mold exposure was estimated to equal 21% with uncertainty bounds of 12–29%. Of the 21.8 million people reported to have asthma in the U.S., approximately 4.6 million (range: 2.7–6.3 million) cases were estimated to be attributable to dampness and mold exposure in the home. The associated annual cost of current asthma attributable to dampness and mold in the U.S was estimated to be $3.5 billion (range: $2.1–4.8 billion).[4]

Table 2—Zero-VOC Film Preservatives Based on IPBC-BCM Avoid Formation of MVOC from Fungal Colonized Interior Paints

Laboratory Method Comparative Teting: Latex Paint Products Using a Model 3:1 Ratio BCM:IPBC Mildewide (20%)[a]

	Percent* Mildewcide Necessary to Pass ASTM D 5590-94
Matte pastel base	0.25%
Matte base	0.25%
Flat pastel base	0.25%
Flat base	0.25%

(a) Polyphase 678.

Microbial Volatile Organic Compounds (MVOC)

Microbial volatile organic compounds (MVOC) are generated by microorganisms that thrive on construction materials. In primary metabolism, the organisms break down such materials to extract nutrients needed for building cell structures and reproduction. As byproducts, these activities create MVOC. In addition, microorganisms produce so-called secondary metabolites, whose main function appears to be a chemical weapon to compete in the environment with other organisms. These secondary metabolites may also be classified as MVOC and their formation is driven by the competition for resources in a nutrient-poor environment. Typical MVOC from fungus activity is used to detect fungal growth in buildings which is not visible (e.g., in the cavities behind drywalls). Typical MVOC include ethanol (a class 1 carcinogen according to IARC classification), 1-octen-3-ol, 2-octen-1-ol, benzyl cyanide, and terpenes like geosmin and 2-methylisoborneol. Some microorganisms simply produce ethanol by fermentation. Others, such as *Aspergillus niger*, *Aspergillus flavus*, and *Penicillium speciesi* are able to produce 1-octen-3-ol or 2-octen-1-ol. Low concentrations of this particular MVOC can be detected by their typical mushroom or musty odor. *Botrytis cinerea* can produce benzyl cyanide which emits a grassy odor. Geosmin is one of the most odor intensive molecules. 0.01 ppb is noticed as an earthy smell. The greatest occurrence of MVOC production (especially terpenes and sesquiterpenes) seems to coincide with spore formation and mycotoxin production as observed in species of *Aspergillus* and *Penicillium*. Mycotoxins differ from MVOC in that they are relatively large molecules that are not volatile, and do not easily evaporate or "off gas" into the air, but they are associated with house dust and can be transported into indoor air.

The role of mold growth in interior environments is still not fully comprehended. Less ventilation and better insulation of homes to reduce energy usage can lead to local condensation of air humidity and favorable conditions for mold growth. Damp buildings also encourage the growth of bacteria, dust mites, and cockroaches, as well as degradation of moist building materials that can also release irritant chemicals indoors. Some or all of these chemicals or biological organisms may contribute to occupant indisposition. However, the California Department of Public Health Services (CDPH) did not succeed in the implementation of the Toxic Mold Protection Act of 2001 (SB 732) until recently. This statute, enacted January 1, 2002, charged CDPH (formerly DHS) to determine the feasibility of adopting permissible exposure limits for indoor molds.[5]

It is easy to demonstrate the value of reducing any potential contribution by MVOC emissions into indoor air by adding a zero-VOC film preservative to the interior paint.

Mold growth in indoor environments and the emission of MVOCs can be prevented by addition of a low concentration of a proper zero-VOC film preservative to the finish. Other construction parts can be protected with the same combination of active substances applied in the manufacturing process. Tests should focus on the efficacy against some model fungus as evaluated in the ASTM D 3274 and ASTM D 5590 test procedures (*Table* 2).

CONCLUSION

Antimicrobial substances are a prerequisite for paint chemists to develop low-VOC coatings and the use of biodegradable ingredients, materials from renewable resources, and recycled materials. It has been shown that recent formulated antimicrobial products do not contribute to emission of VOC from coatings. Recently, even contributions from additives used to formulate the preservatives were eliminated completely. Today, the paint formulator can build in all antimicrobial functions necessary, like in-can and film preservation, with no contribution to the VOC of the coating formula.

As the task to eliminate all volatiles from the formulation of the preservative can be now considered finalized, there are still opportunities for the development of new formulated preservatives for further reduction of emissions. Significant progress could be achieved by the recent development of stable, highly concentrated, formulated additives for the in-can as well as the film preservation. The zero-VOC concentrates reduce significantly the energy input for production, transport, and storage, and therefore emissions from these processes.

As a further benefit, zero-VOC film preservatives contribute to the reduction of VOC emissions by extending the lifetime of the coating and of renovation cycles, as well as the prevention of the development of MVOCs into indoor air.

Reformulation of tinting paste is one of the current tasks in paint laboratories to fulfill the demand for low VOC coatings. Replacing the solvents in colorants creates a new environment for microbial growth, which required the development of new preservation systems. These new zero-VOC preservatives not only show efficacy in the tinter itself, but have universal compatibility to coatings and comply with forthcoming, further tightening VOC regulations. CT

References

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