Improving Indoor Air Quality with Functional Coatings

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REPRINTED FROM COATINGSTECH
VOLUME 11, NO. 4, APRIL 2014
WITH PERMISSION FROM
AMERICAN COATINGS ASSOCIATION

Maintaining indoor air quality (IAQ) is a growing concern in the United States as people spend more time indoors and new insulation/air sealing methods are used to improve energy efficiency. Tightening the building envelope is an effective and popular upgrade that lowers heating and cooling costs by up to 20%.[1] These savings are generated by restricting air exchange and heat transfer, which can have unintended consequences on indoor air quality, including a build-up of formaldehyde emissions emanating from common household items. Exposure to formaldehyde is known to cause eye, nose, and throat irritation; wheezing and coughing; fatigue; skin rash; and severe allergic reactions. Improving indoor air quality is a complex issue often requiring multiple strategies. Functional paints and coatings can play a role by abating undesired volatiles, such as formaldehyde, from various sources within a room. This article will review indoor air pollutants, their sources, testing methodologies, and the reduction of formaldehyde levels through the use of functional coating technology.

INDOOR AIR QUALITY: A BRIEF HISTORY

Indoor air quality is an area of emerging importance for a number of reasons, including increased awareness among builders and architects of the need to consider the comfort, health, and wellness of occupants in buildings. In the 1970s the term "sick building syndrome" (SBS) came into use to describe cases of acute health and comfort effects anecdotally linked to time spent in specific buildings, but in which no specific illness or cause could be identified. Symptoms associated with SBS have included respiratory complaints, irritation, and fatigue. In the three decades that have followed, indoor air quality has become a complex multidisciplinary field, with extensive research into several subareas of specialization, such as building science, ventilation monitoring, health exposure assessment and epidemiology, emissions and abatement technologies, risk assessment, and public policy. Today, experts in the field acknowledge that sources of low-level air pollution in homes, schools, and offices can cause

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This paper is based on the presentation made at the American Coatings Conference, held in Atlanta, GA, on April 7–9, 2014.

occupants health problems, with symptoms ranging from sore eyes and burning in the nose and throat to headaches and fatigue. Other indoor air pollutants are believed to cause and/or worsen allergy symptoms, as well as respiratory illnesses such as asthma, heart disease, and other serious long-term conditions. As reported by Sendell et al., additional study is needed to establish more specific relationships between indoor air pollutants and illnesses resulting from exposure.[2] In general, however, a 2008 Air Quality Science report observes that children, older adults, and people with chronic illnesses or suppressed immune systems are particularly sensitive to the adverse effects of poor indoor air quality.[3]

FACTORS DRIVING IAQ

The U.S. Environmental Protection Agency (EPA) Science Advisory Board ranks indoor air pollution as one of the top five environmental risks to public health in the United States.[4] Two global trends have been cited as major contributing factors. The first is a population shift from rural to urban settings, along with an associated increase in the amount of time that people spend indoors. Based on a two-year survey sponsored by the U.S. EPA, it is estimated that the average American spends 87% of his or her time in enclosed buildings.[5] A contributing megatrend is the pressing need for energy efficiency. According to the U.S. Department of Energy, residential and commercial buildings consume approximately 40 quadrillion British thermal units (QBTUs) of total energy at a cost of approximately $415 billion annually.[6] This generates almost two times more greenhouse emissions (as measured by CO_2 equivalent) than cars, trucks, and SUVs combined.[7] Fueled by these and similar statistics, energy efficiency has become a focal point of voluntary rating systems such as LEED, as well as building guidelines mandated by the American Society for Heating and Ventilation Engineers (ASHRAE), the International Green Construction Code (IgCC), and others. Many call for improving energy efficiency through the use of continuous insulation and air-sealing methods that tighten the building envelope, thereby reducing heat transfer. A study by Mudarri for the EPA reports that the emphasis on energy efficiency in the main building codes used in the United States (IECC 2009, IRC 2006, ASHRAE 62.2, EPA IndoorAirPlus, DOE Builders Challenge, and USGBC LEED) increases "occupant risk of exposures to indoor generated contaminants."[8] It is estimated that these building trends have contributed to a two- to five-fold increase in pollutant levels found in indoor air as compared to outdoor air.[9]

Table 1—Formaldehyde Exposure Limits Established by Various Organizations

Organization or Standard	Application	Exposure Limit
California Office of Environmental Health Hazard Assessment (OEHHA)	General air/indoor air	0.007 ppm (7.3 ppb)
CHPS 01350 and LEED Specification	Product emissions	0.007 ppm (7.3 ppb)
National Institute of Occupational Safety and Health (NIOSH)	Occupational/ indoor air	0.016 ppm (16 ppb)
American Conference of Industrial Hygienists (ACGIH)	Occupational air	0.3 ppm (300 ppb)
GREENGUARD Environmental Institute (now part of Underwriters Laboratory)	Building materials, finishes, and furnishings	0.05 ppm (50ppb) Standard and 0.0073 ppm (7.3 ppb) for Gold
California Proposition 65 (Prop 65)	General air	40 µg /day
CDC's Agency for Toxic Substances and Disease Registry (ATSDR)	General air	Acute: 0.04 ppm (40 ppb); Intermediate: 0.03 ppm (30 ppb); Chronic: 0.008 ppm (8 ppb)
U.S. Environmental Protection Agency (U.S. EPA - IRIS)	General air/indoor air	0.8 $\mu g/m^3$
The World Health Organization (WHO)	Indoor air	0.08 ppm (81 ppb)
FEMA	Indoor air (specifically emergency housing)	0.016 ppm (16 ppb)
Germany's AgBB and the French Decree	Building materials, finishes, and furnishings	0.120 ppm (120 ppb)

TARGETING FORMALDEHYDE

Formaldehyde came to the public's attention as an indoor air pollutant in the wake of Hurricane Katrina, when displaced residents developed health issues linked to high levels of formaldehyde exposure in FEMA trailers. Used for more than a century to manufacture building materials and household items,[10] formaldehyde is found in the resins used to make composite wood products, including particle board for sub-flooring, shelving, cabinetry, and furniture; plywood paneling for wall coverings, cabinets, and furniture; and medium density fiberboard (MDF) used in drawer fronts and bottoms, cabinets, molding, and furniture tops. Because they offer a wide range of beneficial properties at low cost, formaldehyde-based resins are almost universally used in these products; however, some of these resins can break down, leading to elevated formaldehyde emissions.[11] Other sources of formaldehyde in homes and buildings include combustion, textiles, insulation, cleaning products, and wood itself. It has been determined that even human breath contains 3–5 ppbV per exhale.[11] Exposure to formaldehyde is known to cause eye, nose, and throat irritation; wheezing and coughing; fatigue; skin rash; and severe allergic reactions. In 2004, the International Agency for Research on Cancer (IARC) reclassified formaldehyde from a *probable* human carcinogen to a *known* human carcinogen. The U.S. Department of Health and Human Services National Toxicology Program followed suit in 2011, and in 2013 the EPA issued a proposed wood composite regulation to limit formaldehyde emissions.

Table 1 presents formaldehyde exposure level limits established by various regulation and certification

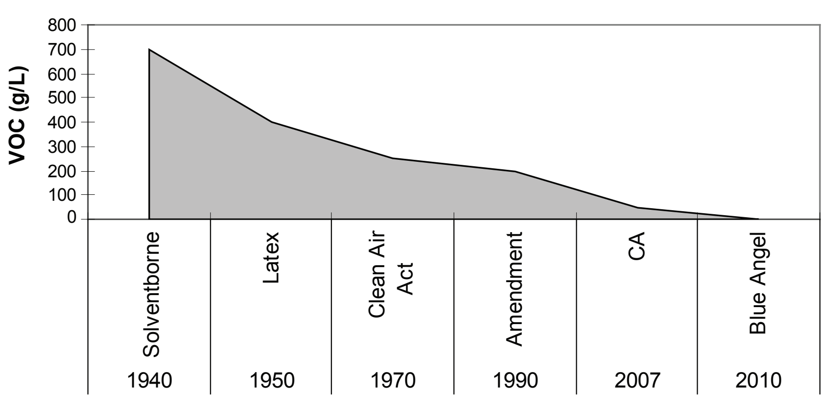


Figure 1—History of VOC content of paints.

Table 2—High-Quality Flat Paint Formulation 45% PVC/37% VS

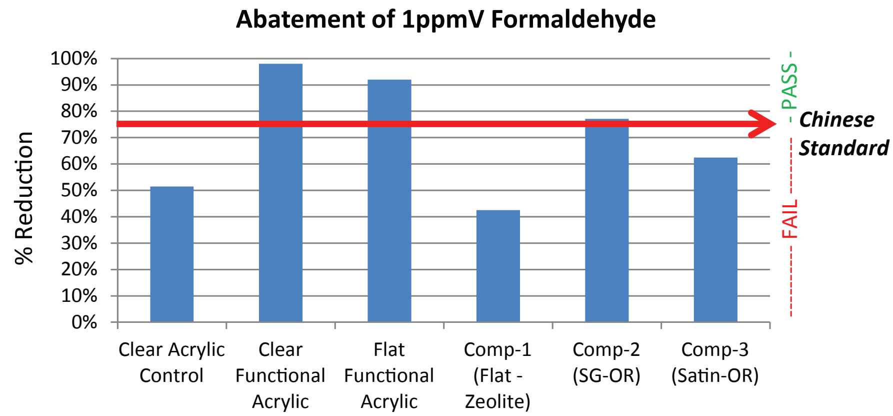
Material Name	Type	Pounds	Gallons
Grind	Stage		
Water	Water	98.79	11.84
TAMOL™ 165A	Dispersant	27.33	3.09
ECOSURF™ LF-30	Surfactant	1.98	0.24
Foamstar A-34	Defoamer	1.49	0.18
KATHON™ LX 1.5%	Biocide	1.68	0.20
Minex 4	Extender	172.87	7.93
Diafil 525	Extender	12.35	0.68
	Grind Sub-total	316.49	0.25
Premix	Stage		
FORMASHIELD™ 12	Binder	394.00	44.64
Foamstar A-34	Defoamer	0.99	0.12
Kronos 4311 DD	Titanium Dioxide	257.83	13.22
	Premix Sub-total	652.81	0.16
Add Grind to Premix			
Let-Down	Stage		
ROPAQUE™ Ultra E	Opaque Polymer	37.65	4.40
Foamstar A-34	Defoamer	1.49	0.18
AMP-95™	Base	0.75	0.10
ACRYSOL™ RM-400	Thickener	10.50	1.22
ACRYSOL RM-3000	Thickener	31.71	3.64
Water	Water	69.36	8.31
	Totals	**1120.77**	**100.00**

bodies. Not surprisingly, the most stringent formaldehyde restriction comes from the California Office of Environmental Health Hazard Assessment, which sets the threshold for chronic relative exposure limit at 7 ppb (volume) per person per year. This level also has been adopted by California's Collaborative High Performance School (CHPS) Standard 01350 as the upper level limit for formaldehyde off-gassing from building products and materials as measured in emission chambers. Certification programs like LEED and GREENGUARD Children and Schools also have adopted this limit level.

COATINGS AND IAQ

Architectural coatings were historically made with solvents that would evaporate upon drying and release volatile organic compounds. Through a combination of regulation and technology, the paint industry has successfully reduced the VOC content of paint without reducing paint performance. *Figure* 1 presents the steady decline since the introduction of waterborne paint in the 1950s. Today there are more than 200 paints on the market that can be described as low- or ultra-low-VOC. Intensifying the focus on indoor air quality, recent versions of LEED v4 and ASHRAE 189.1 have sections on Indoor Environmental Quality (IEQ) that, among other things, promote the use of low-emission products. For paint, California's CHPS standard 01350 is gaining acceptance and momentum for defining test protocols and threshold levels for paint emissions. This testing method inputs "clean air" into a sealed chamber with product samples and measures volatiles in the output air by established analytical methods for four days, after having equilibrated for 10 days. This protocol is referenced by Underwriters Laboratories' GreenGuard Gold, Master Painter Institute's Extreme Green Standard, and LEED v4; however, there are variations throughout other global regions. For example, France's French Decree, Germany's AgBB, and Northern Europe's NordTests all similarly measure dynamic airflow through chambers, but these focus on ISO-16000 methodologies using different measurement periods (e.g., 3 and 28 days) and thresholds, as presented in *Table* 1. For measuring actual abatement of undesired volatiles, ISO-16000-23 and -24 monitor the reduction from a steady state of a pollutant-spiked air flow through a chamber containing the sample. However, they make no mention of what values are or might be considered acceptable. An exception is the Chinese Building Material Industrial Standard, JCT-1074-2008, which specifies that 75% of the 1 ppmV (volume) formaldehyde-spiked air flowing through the test chamber must be abated within 24 hours.

Since many paints on the market already meet very strict VOC standards and are not considered significant sources of poor IAQ, it was theorized that these paints could be further developed as tools for improving IAQ through added reactive functionality. This would address the surface area limitations of activated carbon (AC) filters by taking advantage of the expanse of wall space found in homes and most buildings. At present, AC filters are used to reduce the concentration of undesirable volatiles in the air, but are limited by capacity. AC filters are readily depleted and require frequent replacement. Adding AC to paint has been



Control = Clear coating made with acrylic that does not have added abatement functionality; Clear Functional Acrylic = clear coating made with acrylic binder with added abatement functionality; Flat Functional Acrylic = flat paint made with acrylic binder with added abatement functionality; Comp-1 = a very expensive commercial flat paint advertised as containing zeolites that purify the atmosphere; Comp-2 = a premium commercial semi-gloss paint advertised as reducing malodor; Comp-3 = a premium commercial satin paint advertised as reducing malodor.

Figure 2—Effectiveness of various dry paint films at reducing formaldehyde in a microchamber with constant 1 ppmV spiked airflow.

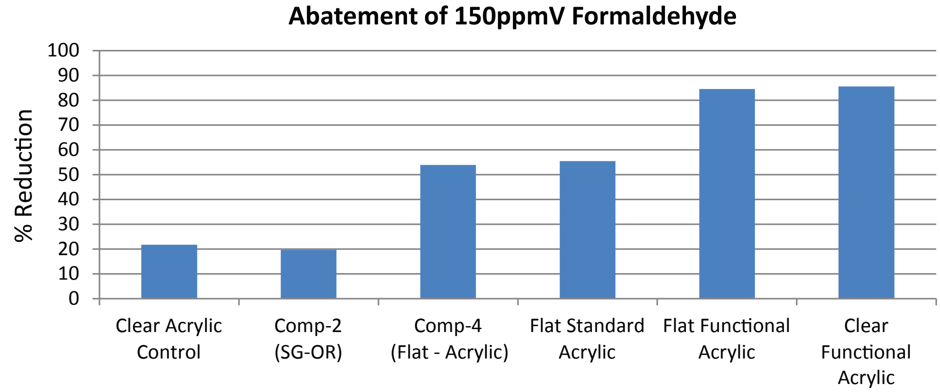
proposed as a way to increase its active surface area, but has been found to be less effective once it is incorporated into an untinted, ultra-low-VOC coating. One possible reason for this could be deactivation of the AC active sites by surfactants, defoamers, and other additives in the paint. AC addition also has been found to add an undesirable black tint to paint and, where formaldehyde is the target, has been shown to be a poor absorber of emissions.[12] These learnings demonstrate that incorporating abatement functionality into a coating involves more than just the reactivity of the additive with the target pollutant. Equally important are the interactions of the abatement functionality with other formulating compounds and the diffusivity of the target pollutant through the coating. Additionally, abatement functionality must work across a range of conditions, retain its functionality for a meaningful timeframe, and not be reversible under typical conditions.

EXPERIMENTAL

Two 100% acrylic binders were synthesized; one with added functionality to react with formaldehyde and bond it to the polymer backbone and one without this added functionality. Each binder was formulated into a clear coating to maximize the test paints' ability to abate and a flat paint to challenge the test paints' abatement capability (see *Table* 2). All test paint formulations listed are flat unless otherwise noted. The ability of the dried paint film to reduce gaseous formaldehyde was compared with three commercial controls defined in *Figure* 2.

Conditioning of all paints occurred at 25°C for at least 24 hours prior to being drawn down in 7- to 10-mil-thick wet films onto aluminum panels, then dried at 75°F/50% relative humidity for four days with activated carbon filtered air. All panels were weighed before and after paint application to ensure consistency across measured samples. After drying, panels were placed into dynamic airflow microchambers (modified JCT-1074-2008) and subjected to air flow at a rate of approximately 1 ml/min, leading to a very high air exchange value of 9 per hour to challenge each paint's abatement capability and offset the smaller diffusion path that occurs when scaling down from a full room to the microchamber. The formaldehyde present in the air exiting the microchambers was quantified using ISO-16000-3 methodology. A microchamber with a blank panel was used as a control to determine the loss of the system, and this value was then used to calculate a percent reduction in formaldehyde concentration. As plotted in *Figure* 2, the results of this experiment established that the functionality added to the test paint was able to increase the paint's ability to abate gaseous formaldehyde from the surrounding ambient environment.

In a second experiment, a very high level of formaldehyde (150 ppmV) was used to confirm that the test paint's functionality could be used to full capacity and was not just a surface effect that would be quickly depleted in a real-world scenario. This experiment was also designed to validate that the reaction occurs across a wide range of formaldehyde concentrations (two orders of magnitude). For this purpose, 10-liter static chambers were



Control = Clear coating made with acrylic that does not have added abatement functionality; Comp-2 = a premium commercial semi-gloss paint advertised as reducing malodor; Comp-4 = a premium competitive acrylic binder formulated into a flat paint; Flat Functional Acrylic = flat paint made with acrylic binder with added abatement functionality; Clear Functional Acrylic = clear coating made with acrylic binder with added abatement functionality.

Figure 3—Reduction of formaldehyde in chambers that contain various dried paint films and were injected with 150 ppmV.

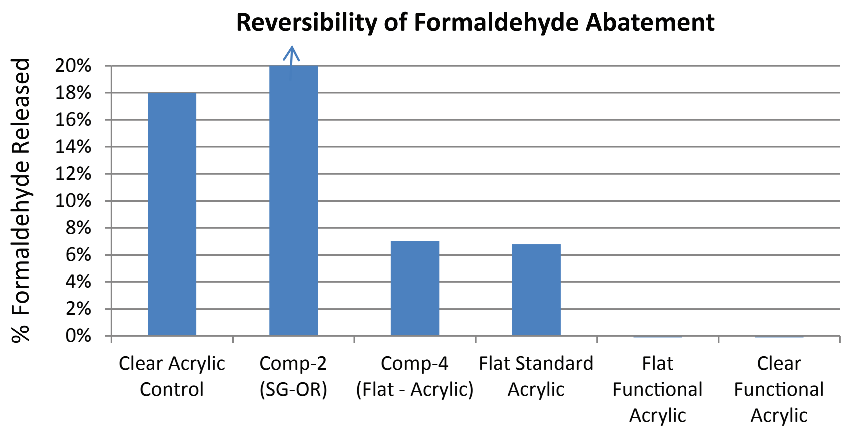


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Figure 4—Percent of formaldehyde abated during saturation which was determined to be released upon being placed into a clean environment.

used, and again percent reduction in formaldehyde concentration was calculated by comparison to a control chamber with a blank panel. As demonstrated in the results plotted in *Figure* 3, paint containing the functional acrylic binder continued to be significantly better at abating formaldehyde compared to standard acrylic paints. This confirms that the added functionality throughout the entire thickness of the applied film can contribute towards abatement, continuing to provide differentiated performance for improved reduction of formaldehyde levels.

Equally important as removing formaldehyde from ambient air is making sure that the formaldehyde is not released back into the room at some later time. This is especially true because saturation of paint with formaldehyde has been shown to cause a shift in equilibrium reactions, potentially creating an even more hazardous situation. For the results in *Figure* 4, dried paints were first saturated by injecting over 150 ppmV into each chamber in which the panels were placed. After abating for seven days, the chambers were emptied and then filled with "clean air," and allowed to equilibrate for three days before air samples were taken and formaldehyde levels were measured. The amount of formaldehyde measured in a control chamber after purging was assumed to be released from the surface of the chamber and was thus subtracted from the amount detected in the other chambers.

Even though the Clear Control, Comp-2, Comp-4, and Flat Standard Acrylic paints removed significantly less formaldehyde upon being saturated, a significant amount of formaldehyde was measured in the chamber after it was purged with clean air. It is assumed that this formaldehyde was physically and reversibly absorbed into the coating. By contrast, both the Flat and Clear Functional Acrylic coatings released no significant amount of formaldehyde when compared to the blank control chamber.

The value a formaldehyde-reducing coating will have under real-life conditions will be influenced by how long it maintains abatement functionality. The functionality must not readily react with atmospheric oxygen or carbon dioxide or otherwise decompose. Further, it should be retained for a minimum of several months and, ideally, for the life of the coating. To study this, several 7-mil wet drawdowns were made on aluminum panels for each of two clear coatings: the Clear Functional Acrylic used in the previous studies and a Clear Styrene/Acrylic Control. The panels were then immediately placed in a controlled 75°F/50% RH environment. After drying for 1, 4, and 18 weeks, a set was removed and tested for its ability to reduce 1 ppmV of formaldehyde from air flowing through a microchamber (identical to *Figure* 2 data). Additional films continued to age and will be tested at a later date, but the data through 18 weeks is plotted in *Figure* 5. It clearly shows that the formaldehyde-reducing capability provided to the coating by the functional acrylic binder had no significant loss in performance over this period.

Further, it was theorized that formaldehyde-abating paint would have maximum efficacy by being painted directly over the formaldehyde-emitting source. As previously indicated, composite wood can be a significant source of interior formaldehyde emissions. Thin medium-density fiberboard was purchased at a retail home improvement store. Several 3-in. squares were cut out of the center of the MDF and the following day coated with either a Clear Functional Acrylic Paint, a commercial acrylic paint, or just distilled water as a control. After samples were dried for four days in a controlled environment, they were all placed into separate microchambers in the same manner as in the previous study, except that no formaldehyde was spiked into the airflow. The amount of formaldehyde coming out of the cells was again collected over a period of four days and analyzed in accordance with ISO-16000-3. The time-weighted averages shown in *Figure* 6 support that coating a functional paint directly onto MDF resulted in significantly reduced formaldehyde levels in the surrounding environment.

CONCLUSION

Indoor air quality is a complex issue involving interactions among pollutants (both particles and VOCs), their sources, ventilation, and human activities. Designing engineering solutions is further complicated because symptoms may arise immediately or years later. Regardless, concerns and issues about IAQ are a growing trend that lies at the intersection of two global megatrends: energy conservation and health awareness. Among pollutants, formaldehyde is the volatile of most concern because of its prevalence in buildings and homes, high toxicity, regulated exposure limit, and media coverage.

Coatings based on binders with abating functionality are well positioned to have a positive impact on IAQ. These functional coatings must

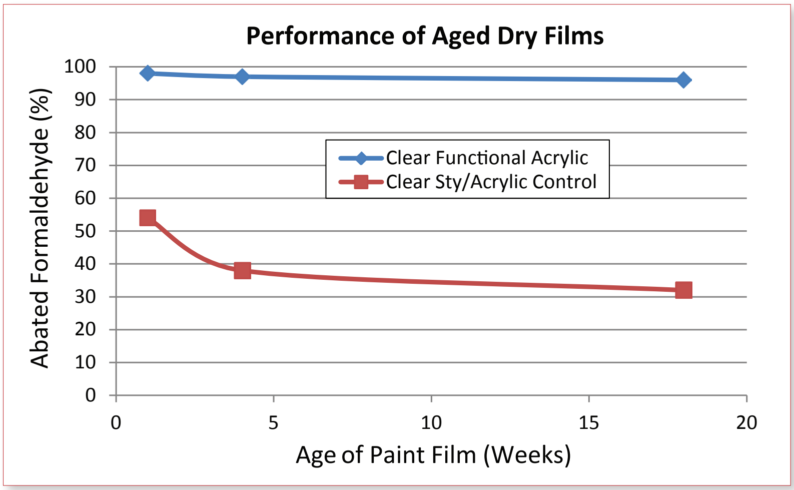

Figure 5—Effectiveness of aged dry paint films at reducing formaldehyde in a microchamber with constant 1 ppmV spiked airflow.

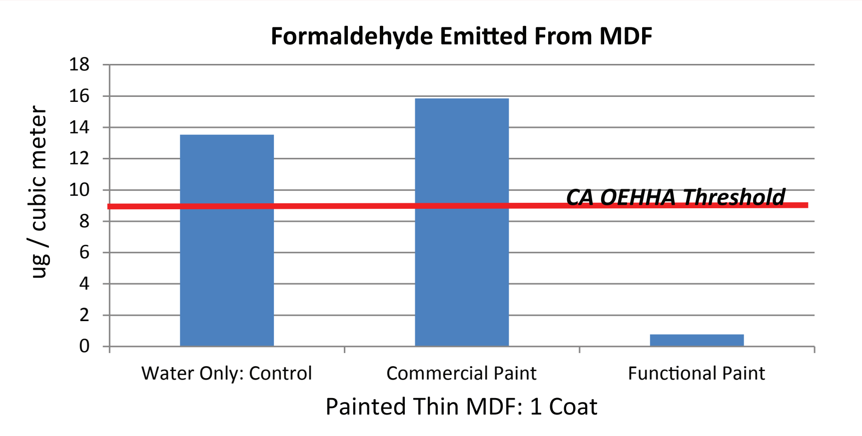

Figure 6—Formaldehyde emissions from thin MDF samples that have one coat of various paints applied. Reference red line is the California's Office of Environmental Health Hazard Assessment cRel for formaldehyde exposure.

not sacrifice the high-quality properties, both aesthetic appeal and durability, which people expect from conventional waterborne coatings. Additionally, they must target specific volatiles and not just randomly catalyze transformations, resulting in potential generation of more harmful and/or malodorous byproducts. The abated volatiles must be irreversibly locked into paint for the life of the coating and/or transformed into less harmful compounds. Lastly, addition of this added functionality must not be cost-prohibitive. Data has been presented for an all-acrylic binder that can be formulated into coatings that meet all of these criteria, facilitating the creation of a new paint category that helps to improve indoor air quality.

ACKNOWLEDGMENTS

The authors are grateful for the contributions of many Dow colleagues, especially Weijiang Yang, Larry Mink, Danny Ma, Hartmann Huang, and Dave Speece. CT

References

1. http://www.energystar.gov/index.cfm?c=home_sealing.hm_improvement_methodology.
2. Sundell, J., et al., "Ventilation Rates and Health: Multidisciplinary Review of Scientific Literature," *Indoor Air*, 21, 191-204 (2011).
3. "IAQ and Sensitive Population Groups," Air Quality Science, Inc., 2008.
4. http://www.epa.gov/region1/communities/indoorair.html.
5. Klepeis, N.E., et al., The National Human Activity Pattern Survey (NHAPS): A Resource for Assessing Exposure to Environmental Pollutants, LBNL-47713, 2001.
6. http://www.eia.gov/tools/faqs/faq.cfm?id=86&t=1.
7. http://architecture2030.org/the_problem/buildings_problem_why.
8. David Mudarri, "Building Codes and Indoor Air Quality," The Indoor Environments Division Office of Radiation and Indoor Air, U.S. Environmental Protection Agency, 2010.
9. Environmental Protection Agency, "Questions About Your Community: Indoor Air," http://www.epa.gov/region1/communities/indoorair.html, 2013.
10. Meyer, B.; *Urea-Formaldehyde Resins*, Addison–Wesley Publishing Company, Inc., Boston, MA, 1979.
11. EPA.gov.
12. Chao, et al., "The Study on Formaldehyde Emission of Composite Floor and Activated Carbon Adsorption on Formaldehyde," *Adv. Mat. Res.*, Durnten-Zurich, Switzerland, 243-249 (2011).

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