New Coating Technology to Inhibit Toxic, Black Mold Growth

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ABSTRACT

A new nanotechnology-enabled process utilizing UV-curable coatings was developed to impart resistance to the growth of Stachybotrys chartarum toxic black mold on wallboard. If wallboard has been in a flooded area, even with only several inches of immersion, water will seep into the interior of the wallboard to the paper covering, supporting growth of mold. A coating is applied to ordinary wallboard inhibiting this process. The underlying technology was derived from a novel approach to selection of polymerizable monomers together with specific nanomaterial additives in a product that uses no water or organic solvents. Thus, the liquid coating is a "100 percent solids" with viscosity that allows application with conventional systems. UV-curing takes place in under a minute in an ambient temperature process that permits use on heat sensitive materials. Examples of the nanotechnologyenabled chemistry and consequent properties are described that reduced moisture transmission on filter paper up to 200 times compared to uncoated paper substrates, approaching the performance of polyethyleneterephthalate (PETP). The use of barriers formed by these coatings has been shown to inhibit the formation of toxic Stachybotrys chartarum black mold on wallboard, without the addition of anti-fungals and their attendant complications.

1 FORMULATION

Traditionally, formulation of coatings, including UV (ultra-violet) light curable coatings, has involved the use of large molecules. Paints normally use a high molecular weight resin. Functional groups are attached to the resin, yielding desired properties such as chemical resistance. Such resins are generally high viscosity and sticky. A carrier such as an organic solvent or water is added, along with pigments and additives, to produce a coating which may be easily sprayed or brushed. In most cases UV curable coatings have been built around somewhat smaller, but still large and sticky molecules, called oligomers. Solvents and water have still been used. For 100% solids UV curable coatings, monomers have been used as reactive diluents in place of solvents or water. These diluents become part of the coating rather than being driven off or evaporating, leading to much lower emissions. However, as a rule, oligomers rather than the diluents have been the focus of prior formulation to produce the desired performance characteristics.

The coating technology described in this paper proceeds along a route which shifts the formulation emphasis from the performance characteristics obtained from large molecules to those obtained from small ones. Monomers with relatively small molecular weights are chosen according to desired structure to produce desired results in the final coating. Monomers can be combined to produce almost infinite variety of performance profiles. They may be chosen to attract water or to repel it. They may provide hardness, flexibility, good weathering, adhesion or stripability. Monomers with various shapes may fit together to form a fence against water or air. In the case of the coatings addressed by this paper, monomers are chosen to form a barrier against penetration by water. No large molecules, solvents, or water are used.

In addition to the judicious choice of monomers, other factors are required to produce the desired characteristics. The use of particles of appropriate sizes is necessary. These coatings utilize particles in the nanometer range. These particles may impregnate a substrate such as paper, rather than just lying on the surface, adding an extra dimension to the barrier characteristics. Particles in the micron range may be used in some variations to modify the barrier effect relative to permeability or other properties such as corrosion resistance.

Other elements in the formulation of these coatings involve the choice of the correct photoinitiator. A photoinitiator is a component that absorbs light and allows the energy to be used to link the elements of the coating together. A preferred photoinitiator must absorb light in the most intense frequencies emitted by the lamps utilized in the curing system. It must also absorb light in frequencies that are not blocked by pigments and other added particles. In addition, a photoinitiator should avoid yellowing, lending a pleasing appearance to the finished product.

An alternative to the use of UV radiation and the addition of photoinitiators is the use of electron beam (EB) curing. Until recently, the cost of EB curing has been prohibitive and the shielding requirements have been difficult. With current technology, smaller, cheaper, systems are available – creating an additional option for manufacturers.

2 ENERGY EFFICIENCY

Curing by the use of either UV or EB radiation is extremely efficient. Curing takes place in seconds. Traditional coatings may take 20 to 40 minutes to cure in gas fired ovens. UV energy is used only to produce a cure, not to heat whatever the coatings are sprayed on. The footprint of these systems is very small compared to thermal cure processes. The combination of enhanced speed of production, targeted curing, and lower overhead from a reduced footprint can yield energy savings up to 75%.

3 ADDITIONAL CLEANTECH CONSIDERATIONS

Since these coatings use no organic carriers, emissions are close to zero. In addition, in the absence of carriers, which may evaporate, overspray from coatings may be caught and reclaimed, with very little product going to a waste stream. The coatings contain no heavy metals or other materials regulated as hazardous components. Hazardous waste is also reduced as booth filters and other objects with unwanted coating may be cured and disposed of as ordinary waste.

4 BARRIER PROPERTIES

Barrier properties for one of these coatings were measured by an outside laboratory.¹ The testing and results are described below. Testing was performed on qualitative filter paper that was hand coated by drawdown bar. Uncoated filter paper from the same package was used as a control.

Transmission measurements.

High transmission of air was measured by a Gurley apparatus.

Low transmission of air was measured by Mocon apparatus.

Method: ASTM D 3985-02

Standard test method for oxygen transmission rate through plastic film and sheeting using a coulometric sensor.

Temperature: 23°C Relative humidity: 0%

Equipment: Mocon Ox-Tran Twin

Water vapor transmission was measured for the samples showing lowest oxygen transmission

Method: ASTM F 1249-90 Standard test method for water vapor transmission rate through plastic film and sheeting using a modulated infrared sensor.

Equipment: Mocon Permatran -W Twin and W3/31

Temperature: $38^{\circ}C \pm 0,5^{\circ}$ Sample area: 50 cm²

Relative humidity: 90% Dry side: 0% Figure 1

Transmission Results

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Coated samples	Gurley Time to pass 100 ml air (sec)	Gurley Air permeance $(cm^3/m^2 d atm)$	Macon Oxygen (cm ³ /m ² d atm)	Macon Water (g/m2 d)
1	Too dense	n/a	943.8	177.7
2	12	7669		
3	19	4848		
4	45	2026		
5	Too dense	n/a	232.8	302.4
Uncoated sample	es			
3 samples	2	46015		

The following comments were made by the test source¹.

<u>Comment 1.</u> The air permeance is lowered by this coating from 6 up to 200 times.

<u>Comment 2.</u> The oxygen transmission values for sample No. 1 and No. 5 are between high density polyethylene HDPE and polyethyleneterephthalate, PETP. This could be improved by a more even coating thickness and more optimized coating conditions.

<u>Comment 3.</u> The water vapor transmission is very low for the coated filter papers No1. and No.2. This could be improved by a more even coating thickness and more optimized coating conditions.

While these results were obtained on filter paper, these coatings may be applied to a variety of substrates. Barrier properties are greatly controlled by the dosage of coating applied.

5 MOLD RESISTANCE

5.1 In House Testing

Initial testing for mold resistance was first performed in-house. Mildew was scraped from a damp interior wall. The mildew was cultured using malt agar. Cultured and raw samples were used to inoculate samples of coated and uncoated paper in Petri dishes with malt agar.

A raw sample on a control (left) and coated sample (right) are shown below.

Figure 2: Cultures of Raw Sample



The mold which grew from our culture was extremely aggressive. As can be seen from the following photograph, a coating was effective at slowing it down, but did not stop it entirely. It served as a more challenging test than the mildew naturally occurring on the wall. The master culture is shown in the following photograph.



Figure 3: Growth derived from Master Culture

The coatings were particularly effective in preventing mold from penetrating through paper, as can be seen from the backside photograph which follows.



A number of formula variations were tested. Yellow and red iron based pigments were added. Titanium dioxide pigment was added. An AgION anti-microbial containing silver and copper was used. In addition two proprietary additives used to address the thixotropic (flow) characteristics of the coatings were tested.

All versions of the coating exhibited inhibitory effects. While the AgION anti-microbial did not appear to significantly alter results, additions of red and yellow pigments were helpful in mold inhibition. Thixotropic agents were helpful as well.

5.2 Stachybotrys chartarum

In the wake of Hurricane Katrina and other severe flooding situations, it became evident that mold was a dangerous consequence of these events. When drywall is immersed in water, even to a depth of a few inches, the gypsum core soaks up a significant amount of water. Water from the gypsum then passes into the paper covering of the drywall. Many types of mold will grow on wet paper. To a large extent, this is a cosmetic problem, causing staining and unpleasant odors. There is, however, a mold whose appearance is actively dangerous. That mold is Stachybotrys chartarum. Biologically active compounds produced by this fungus can be a threat to human health. Poisoning by a toxin produced by S. chartarum is called stachybotryotoxicosis.², Disease produced by S. chartarum was first recognized as a series of outbreaks in horses in the Ukraine in the 1930's. In 1938 Russian doctors determined that the disease was associated with S. chartarum, then known as S. alternans.³ The term stachybotryotoxicosis was coined by these Russian doctors.

There have been many instances of the connection of S. chartarum with humans. Of particular interest was a cluster of cases of pulmonary hemorrhage and hemosiderosis in infants which appeared in Cleveland Ohio in 1993-1994. This outbreak brought S. chartarum to the headlines. The connection to S. chartarum, however, was considered inconclusive. Since then, additional evidence has been gathered as to the association of these diseases with S. chartarum.⁴

The spores of S. chartarum naturally occur in soil. When dust and dirt are carried by flood waters, the spores are carried as well. Building materials may be coated with dust or dirt, and thus be contaminated with S. chartarum spores. The fungus is most commonly found in buildings that have sustained water damage. While such damage may be from natural disaster, it may also occur from more commonplace mishaps such as broken pipes or a leaky wall or roof. Even condensation may be a culprit. Water is required to start the growth of S. chartarum as well as to sustain it. While this moisture may commonly come from the paper covering of gypsum wallboard, it may also be found on wallpaper, cellulose based ceiling tiles, carpets comprised of natural fibers, the paper covering on pipes and all other manner of paper products. It may even grow on the paper covering of fiberglass insulation. The spores can be hidden from sight in in ceilings walls or floors. Spores can also contaminate the interior of the room through flaws in building materials or be carried in heating, ventilation, or air conditioning systems. If organic materials have become trapped in ducts, S. chartarum can even grow on them, especially promoted by condensation due to poor design.⁵

There is a standard test protocol for the testing of mold resistance on drywall. ASTM D 3273 is the specification generally cited for this purpose. However, ASTM D 3273 does not test for the growth of Stachybotrys chartarum. A protocol for the testing of the growth of S. chartarum has been developed by Iwona Yike, Ph.D. at Case Western Reserve University (CASE).

Samples were submitted to Dr. Yike's laboratory for three purposes. The first purpose was to determine the general resistance of coated drywall samples to the growth of S chartarum. The second purpose was to determine if the addition of AgION Silver Copper Antimicrobial Type AC would enhance the inhibition of growth. The third purpose was the comparison of various coating formulations in the inhibition of the growth of S. chartarum. Four sets of samples were prepared on samples provided by Dr. Yike. We were informed that the drywall in the samples had been purchased at Home Depot. A set of samples was prepared using our standard white formulation for the impregnation of paper. This coating contains both nano-particles and titanium dioxide. Sets were prepared using two different catalysts used to produce thixotropic coatings. An additional set was prepared using coating with the addition of the AgIon anti-microbial.

All prepared samples as well as a set of uncoated controls were autoclaved at CASE to eliminate the chance of accidental contamination.

All samples were inoculated with Stachybotrys chartarum. Growth was allowed to develop.

Growth developed on controls. It did not develop on any coated samples.

The first purpose of this study was met. These coating formulations inhibited the growth of S. chartarum.

The result of the second purpose of this study is undetermined. Since all coatings inhibited growth, it is not possible to determine if the AgION anti-microbial was helpful.

Undetermined results are also yielded for the third purpose. Since all coatings inhibited growth, it is not possible to determine levels of inhibitory activity.

6 CONCLUSIONS

100% solids UV curable coatings containing nanoparticles can be used to coat a drywall substrate and inhibit the growth of S. chartarum. Further study is necessary to determine if variations in formulation or additives enhance this effect. It is clearly possible to inhibit the growth of S. chartarum without the use of an anti-fungal additive.

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