UV-Curable Coatings with Nanotechnology-enabled Barrier Properties

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Formulation

When developing formulations for use with nanometer-sized particles, old-style, oligomer based formulations may not be the best place to start. Dispersions of nano-particles in monomers tend to be more stable than those utilizing higher molecular weight molecules. Monomer (nano-particle) dispersions may be added at considerable percentages. The higher the level at which such dispersions may be incorporated, the higher the particle loading and the greater the effect. For paper and plastics, it is quite possible to formulate with no oligomer(s) at all, allowing for maximal incorporation of nanoparticle dispersions in monomers. This also yields low viscosity, easily spray-able coatings. For metals, an oligomer content of approximately 25% can be quite effective and still incorporate sufficient amounts of dispersion(s).

Before the incorporation of nano-particles, a formulation should have suitable performance properties without them. Thus attributes such as adhesion and weatherability must be well established independent of the effects of nano-particles. The ideal formula will have superior performance in as many areas as possible before being modified.

Dispersions of nano-particles may be substituted for monomers in a formula, making allowances for the degree of particle loading. Thus if a monomer is normally present at 30% by weight, 60% by weight of a dispersion with 50% loading may be added. Formulations created in this manner will have a significantly higher weight per gallon. Thus, careful attention must be paid to this factor when weight per unit area is considered.

As with most situations, the devil is in the details. There are many factors that interfere with the use of nano-particles. Many surfactants, especially those with silicones, will cause precipitation. The presence of water and other solvents may cause agglomeration. The best formulations will be 100% solids, yet low viscosity. If high viscosity is required, one of us, (Ramsey), has developed agents that will produce thixotropic versions of these coatings without the use of high molecular weight materials. As few additives as possible may be used and every additive must be tested for destabilizing effects. While the use of nano-particles may provide unique combinations of film properties, it can certainly create some of its own problems.

Barrier Properties

Unique barrier properties may be created by the use of nano-particles in a formulation containing monomers with a variety of shapes, functional groups and polarities. An assortment of these ring shapes, aliphatic and aromatic, may be combined to fill space in interesting ways. Space filling by nano-particles also appears to be a key contributor. In some cases, especially when optical clarity is not required, micron sized and sub-micron sized particles may be used as well. The dosage (weight or thickness) of application of coatings may also be varied to produce a range of barrier effects.

Products using the preceding formulation concept for creating a barrier in paper show many of these effects. Several different ring structures have been incorporated. For example, a more polar, hydrophilic component promotes writability. Some forms of this coating also contain larger pigment particles. The following data shows the effects that may be produced by different dosages. The paper substrate used was qualitative laboratory filter paper. Samples were produced by draw down.

The following report is from an outside laboratory. [1]

Table I

- 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.

Utrustning: Mocon Permatran -W Twin and W3/31

Temperature: 38°C
Sample area: 50 cm^2
Relative humidity: 90%
Dry side: 0%

Sample: Coated filter paper	Gurley: Time to pass 100 ml of air through the sample	Air permeance	Mocon Ox_Tran twin Oxygen transmission	Mocon Permatran-W Twin Water transmission
	seconds	*cm^3/m^2 d atm*	*cm^3/m^2 d atm*	*g/m^2 d*
1	Too dense	-	943.8	177.7
2	12 s	7669		
3	19 s	4848		
4	45 s	2026		
5	Too dense	-	232.8	302.4
Sample: Filter paper				
6	3 s	30677		
7	2 s	46015		
8	2 s	46015		
9	2 s	46015		

The test source as provided the following comments regarding these data:

- The air permeance is lowered by this coating from 6 up to 200 times.
- 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 optimised coating conditions.
- 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 optimised coating conditions.
- It would very interesting to continue the work and perform coating using a laboratory bench coater and after this measure the transmission for oxygen and water vapour.

The performance indicated and related comments were very encouraging given the fact that these were samples of a non-optimized coating on a very porous substrate.

Mold Resistance

Water is necessary to support the growth of mold. When walls become damp, mold can flourish. If gypsum wallboard is flooded, even by a few inches of water, moisture may leach out of the gypsum into the paper that covers the wallboard and mold can take hold. When investigating the resistance of our coating to such events, we took a very practical approach. While such testing is described in ASTM D 3273, only three species are used, Aureobasidium pullulans, Aspergillus niger and Penecillium. This test protocol is also designed primarily for Ponderosa Pine, although its usage has been expanded to other substrates.

We began with a practical test. Mildew was scraped from a wall running along an indoor drainage trench. Samples were prepared using coated paper against a control of uncoated paper from the same ream. A malt agar growth medium was used to support mold growth. As can be seen from the accompanying photographs, mold grew well on the control, but not on the coated paper. Photographs are after three days and again after 13 days.

Figure I

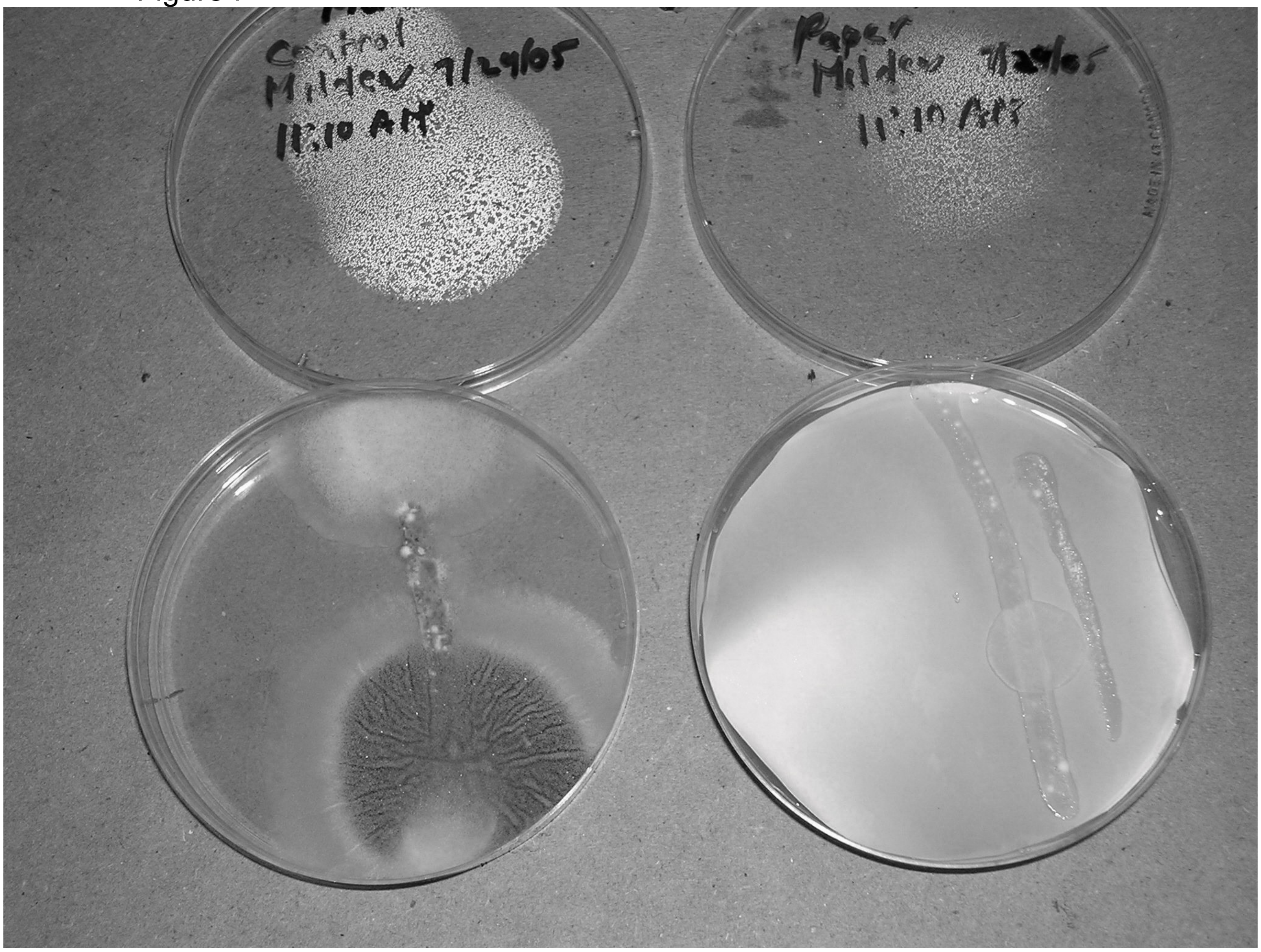
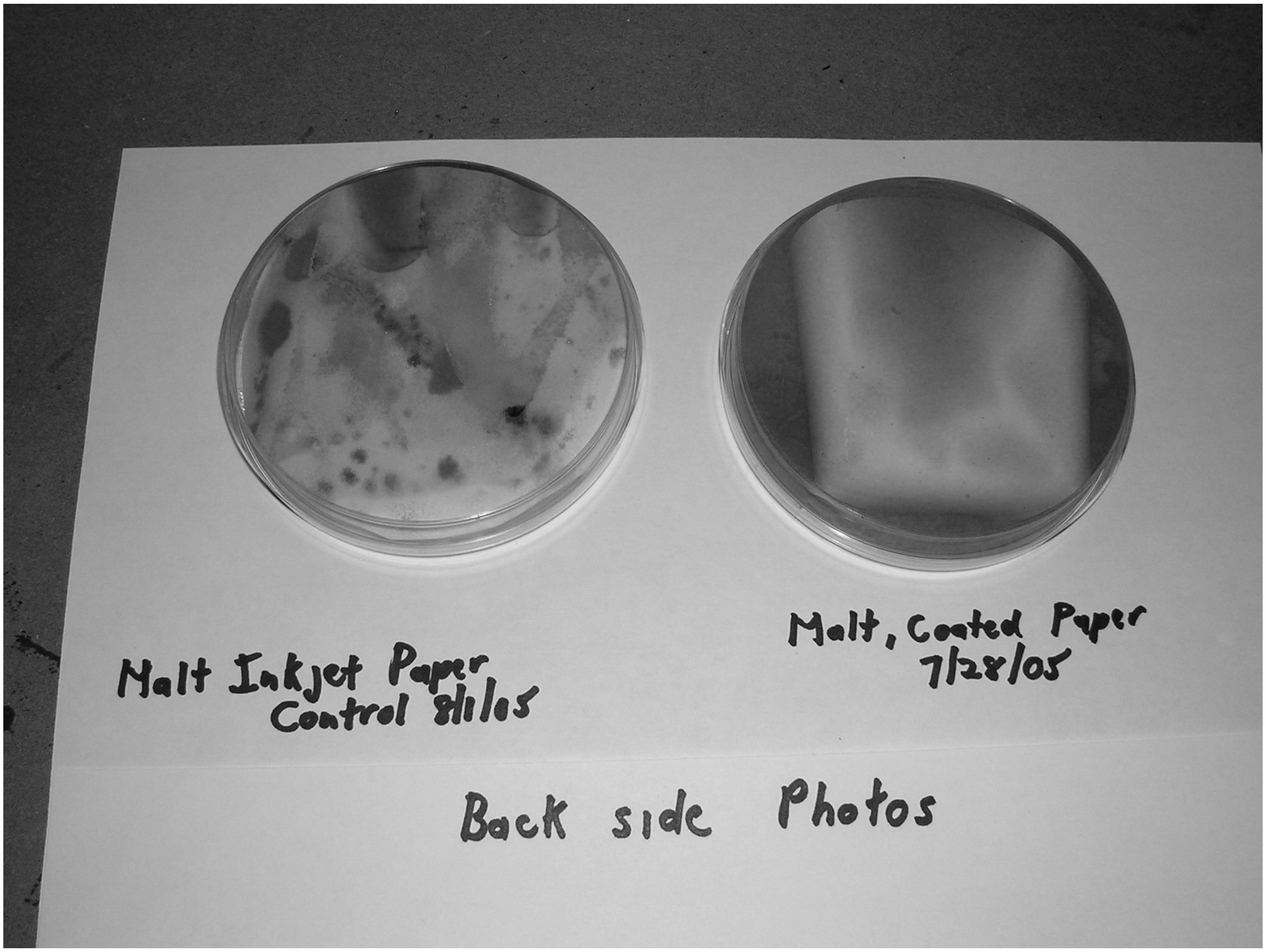


Figure II



While these tests yielded very interesting information, the procedures did not address a very important matter. Neither this testing, nor that performed in ASTM D 3273[2,] addresses the growth of Stachybotrys chartarum, a mold that is both dangerous and notoriously difficult to eradicate.

In order to test the effectiveness of our coatings on the inhibition of S. chatarum, samples of our coating in its low viscosity form, two catalyzed thixotropic forms, and with the addition of 2% AgIon silver and copper antimicrobial additive on squares of drywall were prepared. These samples were submitted to Iwona Yike, Ph.D. at Case Western University where they were autoclaved along with controls, injected with S. chatarum and tested for growth. While the final report has not been issued at this writing, data transmitted verbally indicates that S. chartarum was unable to grow on any of the coated samples, although it grew on controls. Furthermore, no advantage was seen from the presence of the antimicrobial additives.

Resistance to the growth of S. chatarum is a new and important contribution that these coatings can make to the health of buildings and the people in them,[3] This mold has been implicated in a variety of illnesses[4.] Furthermore, it cannot be destroyed by bleach, necessitating the complete destruction of contaminated properties, with great impact to economic wellfare as well as physical health. We now have a potential weapon in the fight against this serious threat.

References

1. Permeability testing was performed at STFI-Packforsk. We are grateful for their help.

2. ASTM D 3273 -00 Standard Test Method for Resistance to Growth of Mold on the Surface of Interior Coatings in an   Environmental Chamber

3. Yike, I., and Dearborn, D.G. Pulmonary effects of Stachybotrys chartarum in animal studies. In: Advances in Applied Microbiology, Sick Building Syndrome, D. Strauss (ed) Elsevier Inc, p241-273, 2004

4.Miller, J.D., Rand, T.G., Jarvis, B.B. *Stachybotrys chartarum*: a really malicious mold. Med Mycol 41, 271-291, 2003