Formulating Coatings with Silver-based Antimicrobials: A Systematic Approach

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Silver-based antimicrobials have increased in popularity due to their high efficacy against bacteria and low ecotoxicity. There is growing interest in using them for antimicrobial coatings. However, formulation of these products into traditional coating systems can present some unique challenges, including film discoloration, loss of gloss, poor rheology, and shelf stability. This article presents a systematic study of the incorporation of silver-based antimicrobials into starting point formulations of different industrial and decorative coatings, with a focus on optimizing dispersion, storage stability, and film clarity of the coating formulation. Antimicrobial efficacy against bacteria of common interest are also presented for the optimized coating formulations.

INTRODUCTION

Antimicrobials are chemical substances which kill or inhibit growth of microorganisms such as bacteria, fungi, and algae. These microbes feed on organic material and under conditions of high humidity can be deleterious to organic films and substrates. Antimicrobial compounds can be incorporated into paints and coatings with the intended effect of increasing their durability and effective service life, and are increasingly in demand where sterile environments are required such as in the medical profession.[1]

Paint is composed of resin (binder), pigments and fillers, solvents, and additives. Additives include surfactants, dispersants, rheological modifiers, light stabilizers, and biocides. Because in both the liquid (especially water-based systems) and cured states paint can be susceptible to attack by microorganisms, there is a need for both in-can stabilizers, which protect liquid coatings from biodegradation, as well as materials which protect cured films in the industry.

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DESIRABLE ANTIMICROBIAL PROPERTIES

Ideally, antimicrobial materials will show efficacy against a wide variety of microorganisms, be relatively environmentally safe, be colorless and odorless, and be inert with respect to ultraviolet and visible radiation. Also, it is advantageous to formulate with antimicrobial materials which are stable across a wide range of pH and which can be processed at very high temperatures. Finally, the antimicrobial should show efficacy at relatively low levels within a coating matrix.

MARKET AND MARKET TRENDS

The total global market for biocides for 2006 is expected to be approximately $400 million U.S. dollars. The highest consumption of antimicrobial by application is in the architectural market, including interior and exterior coatings which are designed to provide protection from growth of molds and mildews. The second largest market for antimicrobials is marine antifoulants, which help prevent marine life from attaching to ship hulls and the bottoms of boats.[2]

Other markets which are expected to see growth for antimicrobial coatings include hospitals, nursing homes, daycares, and medical applications where high standards of hygiene are required. A variety of target application areas have been recently developed and explored; for example, powder coating applications for the food processing industry. Other developing applications include ventilation ducting, public transport facilities (planes, buses, etc.), bathroom amenities, and flooring.

SILVER-BASED ANTIMICROBIALS

Silver has been used for centuries as an antiseptic, and is not known to be toxic to humans in low concentrations. In addition to its low toxicity, silver has several beneficial properties which make it an excellent candidate for use as an antimicrobial material. It is thermally stable, shows broad spectral activity against many target organisms, and is stable against UV/Visible radiation. These properties give silver a marked advantage over many organic antimicrobials, which can be toxic and degrade at elevated temperatures as well as degrade in the presence of UV/Visible radiation. The silver-based antimicrobial studied in this article will be denoted as SAM1. This material has an average particle size of approximately 5 microns, and contains 1% active silver and 3.3% zinc in a glass-zeolite supporting matrix. The physical form of this product is a white powder. Combinations of silver and zinc have been shown in some cases to lead to synergistic effects.[3]

FORMULATING CONSIDERATIONS

Initial screening of SAM1 raised some issues which were resolved through systematic formulating consisting of evaluating the shear forces necessary to properly disperse the filler in the coating matrices, as well as optimizing dispersant choice and, finally, assessment of surfactants to ensure flow and leveling of the coating formulations. It was determined that acrylic acid polymer dispersants were excellent for stabilizing the antimicrobial in water-based formulations and the acidic polyester/polyamides for solvent-based formulations. Sufficient shear to disperse this material can be imparted through the use of an HSD (High Speed Disperser) such as a Dispermat CN10 equipped with a Cowles blade at ≥3000 rpms for 15 min.

MECHANISM OF ACTION

The mechanism by which SAM1 eliminates growth of microbes begins with the controlled release of silver

Figure 1— Viscosity change vs. time for starting point formulations.

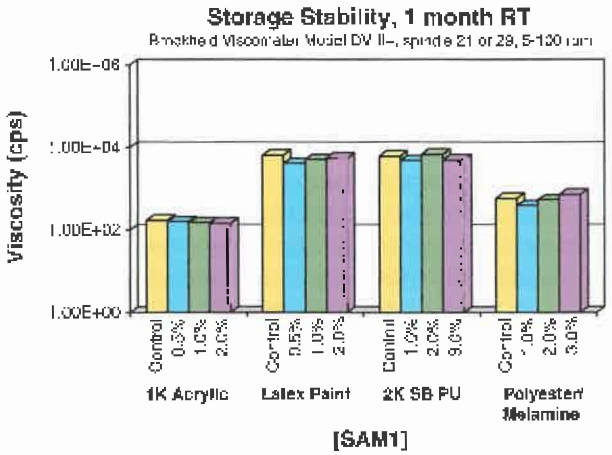


Figure 2—Gloss vs. antimicrobial concentration for starting point formulations.

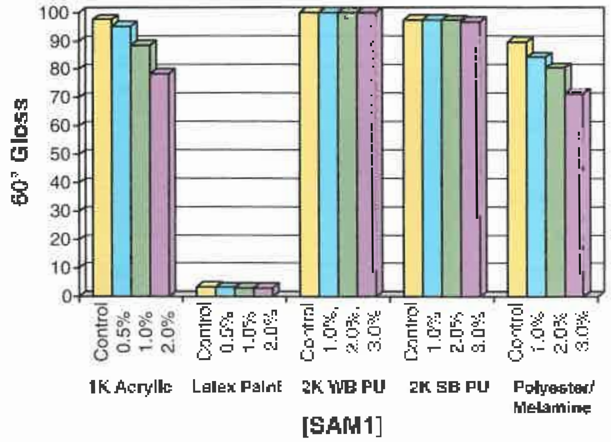


Figure 3—Bioefficacy results for interior latex paint.

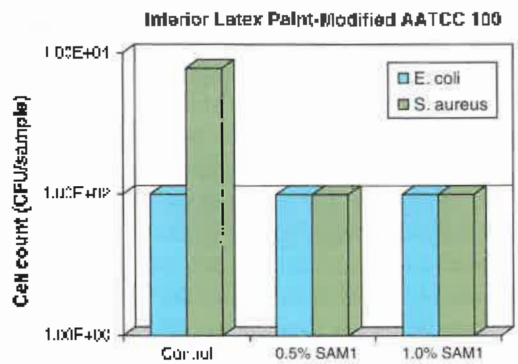


Figure 4—Bioefficacy results for 2K water-based polyurethane.

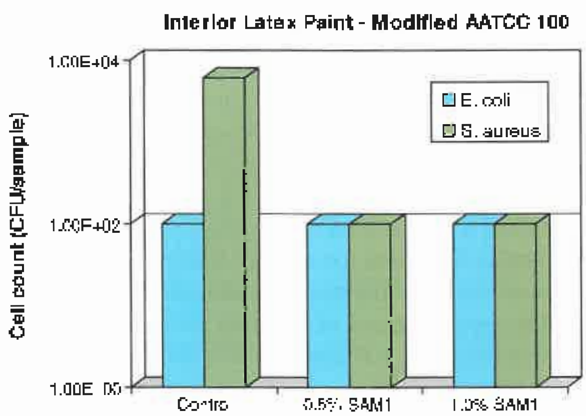


Figure 5—Bioefficacy results for water-based acrylic clearcoat.

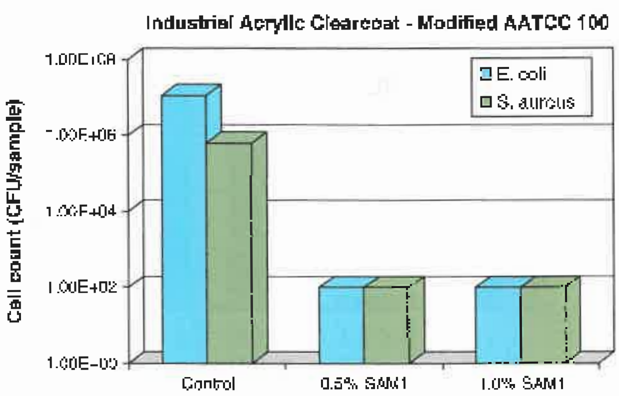


Figure 6—Bioefficacy results for 2K solvent-based polyurethane.

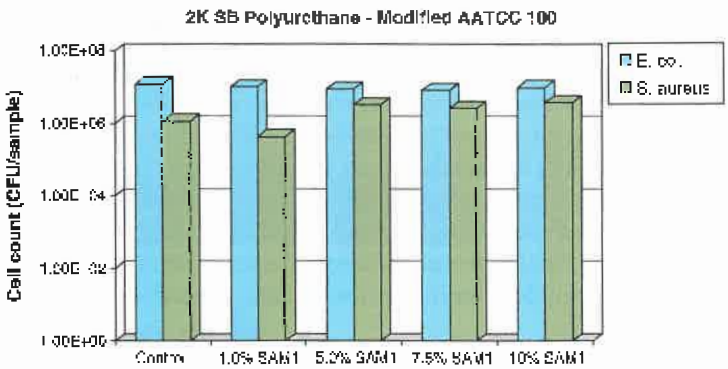
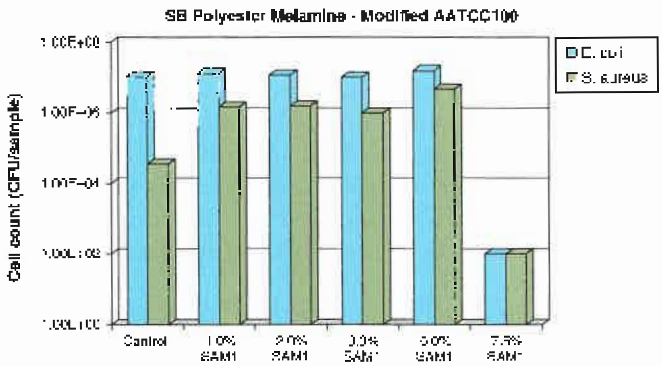


Figure 7— Bioefficacy results for solvent-based polyester melamine.



ions under ambient moisture. Silver ions liberated by moisture come into contact with target organisms and interact with multiple binding sites. As silver ions are transferred into the cells of target organisms, metabolic and respiratory functions of the cell cease, and, consequently, the target organism cells are destroyed.

BIOEFFICACY TESTING PROTOCOL

Antimicrobial efficacy is tested according to a modified version of AATCC Test Method 100-1998 (Assessment of Antibacterial Finishes on Textile Materials). The protocol for this test method involves inoculation of the organic coating with the appropriate test strains (in this case, with *Staphylococcus aureus* and *Escherichia coli*), then incubation for 24 hr at 37°C at 90% relative humidity.

After this time has elapsed, the surviving bacteria are washed off and dilution series are plated out onto agar plates with a spiral plater and incubated an additional

Figure 8—DSC spectra for water-based acrylic clearcoat.

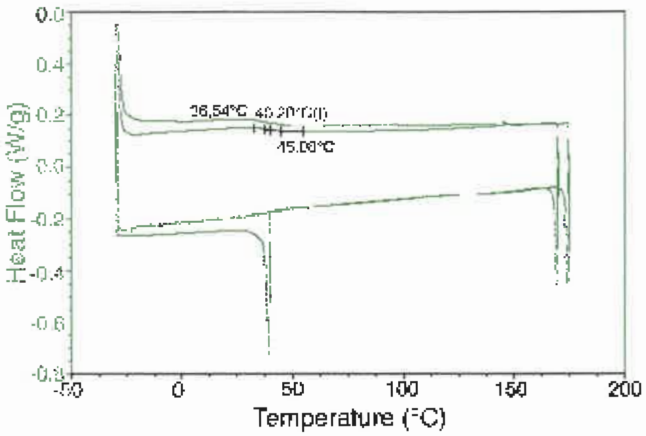


Figure 9—DSC spectra for interior latex paint.

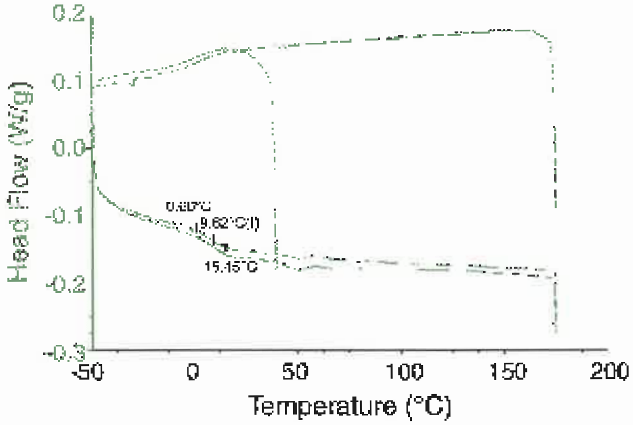


Figure 10—DSC spectra for 2K water-based polyurethane.

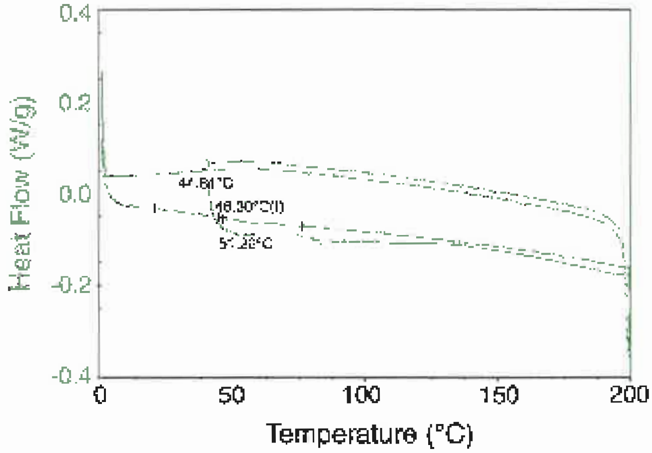


Figure 11—DSC spectra for 2K solvent-based polyurethane.

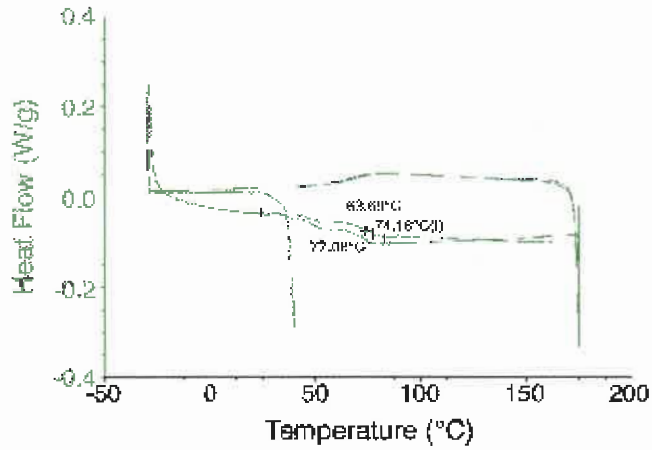
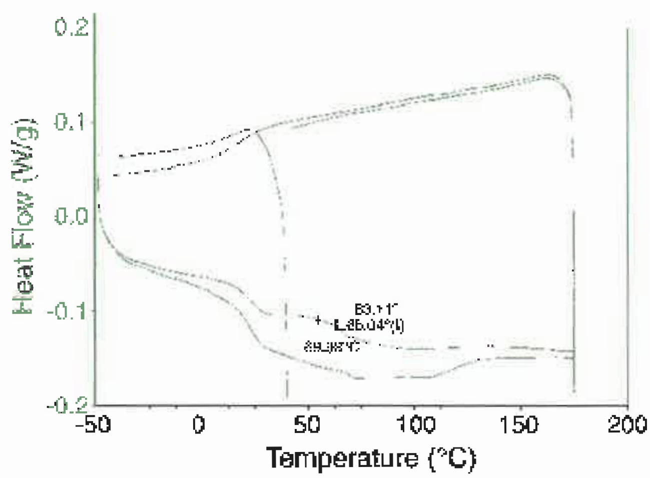


Figure 12—DSC spectra for polyester/melamine.



24 hr at 37°C. After incubation, visible colonies are counted and the results are given as colony forming units per sample. Generally, a 2 order of magnitude reduction in CFUs (colony forming units) due to the presence of antimicrobials is accepted as evidence of bioefficacy. Ideally, a result of <100 CFUs is considered full activity, as this is the limit of detection for this testing.

The modification of this testing from the original AATCC Test Method 100 is necessary because the original method calls for a high level of nutrient broth (protein), which in this case causes the silver to bind to the protein before it is able to come into contact with microbes. Thus, the concentration is dropped from 0.5% to 0.05% soybean-casein digest broth. Controls are run on coatings in each case that do not contain antimicrobials to assess for "blank effects," or to ensure that other components in the formulation are not responsible for destruction of target organisms evaluated in the testing.

Figure 13—Correlation between minimum silver antimicrobial concentration to obtain bioefficacy and T_g.

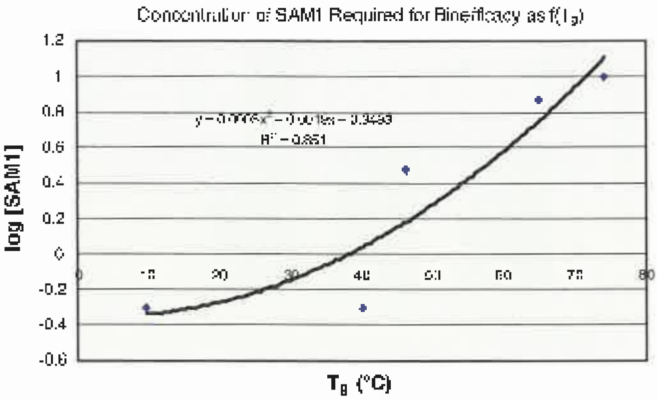
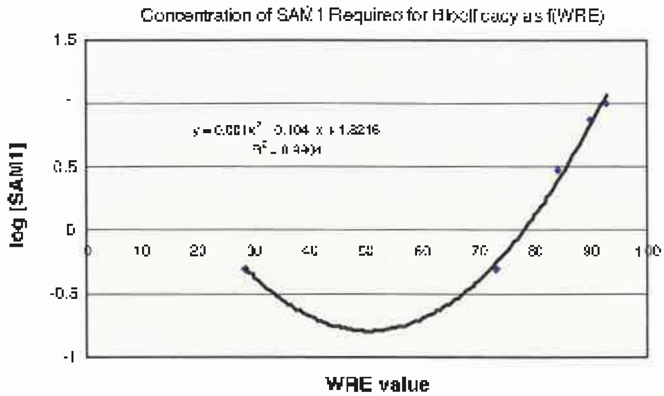


Figure 14—Correlation between minimum silver antimicrobial concentration to obtain bioefficacy and WRE value.



EFFECT OF SILVER-BASED ANTIMICROBIAL ON PHYSICAL PROPERTIES OF COATINGS

Initial formulations were tested for shelf stability under accelerated aging conditions at 50°C for two weeks. Samples were also evaluated for viscosity change after one month of storage under ambient conditions. The coatings tested included an interior latex paint, an industrial waterborne 1K acrylic clearcoat, a 2K water based polyurethane, a solvent-based polyester/melamine for coil coating, and a solvent-based 2K polyurethane. All formulations containing SAM1 either had no sedimentation or had sedimentation which could easily be redispersed with low agitation after the duration of the shelf stability testing. Viscosities were generally stable and are summarized in *Figure* 1 (note that the 2K water-based urethane is not included as the polyol in this system is known to hydrolyze and any effect from this could not be decoupled from a increase/decrease in viscosity due to the presence of an antimicrobial).[3] Sixty-degree gloss values were also measured and are plotted as a function of filler loading (*Figure* 2). It is evident that some reduction in gloss is incurred as a function of SAM1 loading.

Table 1—T_g and WRE Values vs. Antimicrobial Concentration Required for Bioefficacy

System	[SAM1]	T_g	WRE Value
Interior latex paint	0.5	9.62	28.5
WB acrylic clearcoat	0.5	40.28	73.1
2K WB polyurethane	3.0	46.3	84.1
Polyester melamine	7.5	65.04	89.9
2K SB polyurethane	>10	74.16	92.6

BIOEFFICACY TEST RESULTS

Bioefficacy testing was performed using the modified version of AATCC 100-1998 as described previously. Results are given in *Figures* 3–7. The water-based acrylic and polyurethane coatings showed bioefficacy at lower loadings of SAM1 compared to the solvent based polyurethane and polyester-melamine coatings (the 2K solvent-based polyurethane did not show efficacy at any level tested but the 10% data point is included to illustrate the relationship with properties tested). This result is consistent with the mode of action described prior, demonstrating the role of moisture in liberating silver ions from the surface of the coatings to the target organisms. This mechanism is thus enhanced for coatings with greater hydrophilicity.

CORRELATION OF T_g AND WATER REPELLENCY EFFICIENCY WITH BIOEFFICACY

Glass transition temperatures were measured for the individual starting point formulations using a Q Series Thermal Analysis Differential Scanning Calorimeter (Q100) from TA Instruments. Scans were done at 5°C/min sweep rates under nitrogen purge. Measurements of T_g were analyzed using the Universal Analysis software program and are reported (see *Figures* 8–12 for scans). There is strong evidence for direct correlation between the resin glass transition temperature and log concentration of silver based antimicrobial (SAM1) required to obtain bioefficacy against *E. coli* and *S. aureus*, with the R^2 value of the trendline in *Figure* 13 being 0.851. Thus, increasing resin T_h (or higher crosslink density) results in lower migration rates of silver ions to the target organisms, requiring higher levels of SAM1 to show bioefficacy.

Water Repellency Efficiency (WRE) was evaluated according to ASTM D5401. Southern Yellow Pine wood

Table 2—Starting Point Formulations Evaluated with SAM1

Coating Type	Raw Material	Supplier	Weight (g)	Mixing
(1) Polyester/Melamine Coil Coating				(Dispermat)
Grind	Chempol® 211-4805	Cook Composites and Polymers	243.0	
	EFKA® 5010	Ciba Specialty Chemicals	34.0	
	Tronox® CR 826	Kerr McGee	400.0	
	SAM1	Ciba Specialty Chemicals	33.0	15' @ 3000 rpms
Letdown	Chempol® 211-4805	Cook Composites and Polymers	162.5	
	Cymel® 303	Cytec Industries	25.6	
	K-Kat® 5225	King Industries	6.2	
	EFKA® 5236	Ciba Specialty Chemicals	5.1	
	Aromatic 150®	Exxon Chemical Co.	192.0	
	Butyl Cellosolve®	Union Carbide	6.1	
	Butyl Carbitol®	Union Carbide	5.4	
	Mix letdown and grind, apply with 200 µm (wet DFT) wire wound drawdown rod, flash 10' ambient, cure 15' @ 180°C			
(2) SB 2K Polyurethane				
Grind (A pack)	Desmophen® 631A-75	Bayer MaterialScience	200.0	
	EFKA® 3600	Ciba Specialty Chemicals	7.0	
	EFKA® 5010	Ciba Specialty Chemicals	2.6	
	Tronox® CR826	Kerr McGee	180.0	
	PMA/Aromatic 150® (50:50)	Sigma Aldrich/Exxon Chemical Co.	60.0	
	SAM1	Ciba Specialty Chemicals	18.1	15' @3000 rpms
B pack	Desmodur® N3200	Bayer MaterialScience	135.7	
	Metacure® T-12 (10% in NMP)	Air Products and Chemicals, Inc.	0.1	
	Mix letdown, grind, and catalyst. Dilute with PMA if necessary. Spray to desired film build. Cure 15 min at 130°C.			
(3) Interior Flat Enamel				
Grind	DI H_2O		18.5	
	Igepal® CO-610	Rhodia Inc.	0.6	
	Alcolec® S	American Lecithin Co.	0.4	
	Dispex® A40	Ciba Specialty Chemicals	1.5	
	EFKA® 2550	Ciba Specialty Chemicals	0.1	
	Viscalex® HV30	Ciba Specialty Chemicals	1.6	
	Acrysol® RM825	Rohm and Haas Company	0.8	
	Ti Pure® 902	Dupont	20.4	
	Nytal® 400	R.T. Vanderbilt Co.	24.4	
	SAM1	Ciba Specialty Chemicals	1.0	10' @ 3000 rpms
Letdown	Rhoplex® AC-264	Rohm and Haas Company	24.1	
	AMP 95		0.3	
	Water		4.3	
	Propylene Glycol		3.2	
	Add letdown to grind. Brush apply or drawdown with 200 micron WFT wire wound bar. Will dry under ambient conditions.			
(4) WB Clear Acrylic Thermoset Industrial Clearcoat				
	Joncryl® 540	Johnson Polymers	100.0	
	Ektasolve® DB	Eastman Chemical Co.	5.0	
	DI H_2O		5.0	
	EFKA® 3570	Ciba Specialty Chemicals	0.5	
	EFKA® 2527	Ciba Specialty Chemicals	0.1	
	SAM1	Ciba Specialty Chemicals	1.1	
	Spray or drawdown as desired. Flash 10' @ ambient. Cure 15' @ 150°C.			*15' @ 3000 rpms*
(5) WB 2K Polyurethane				
	Adura® 100	Air Products and Chemicals, Inc.	72.0	
	DI H_2O		23.4	
	EFKA® 3570	Ciba Specialty Chemicals	0.5	
	Dispex® A40	Ciba Specialty Chemicals	0.5	
	Foamex® 805	Tego	0.1	
	SAM1	Ciba Specialty Chemicals	3.0	
	Desmodur® N3300	Bayer MaterialScience	82.8	10' @ 2000 rpms
	Metacure® T-12 (10% in NMP)	Air Products and Chemicals, Inc.	0.02	
	Mix grind, letdown, and catalyst. Dilute with DI H_2O. Apply with 200 µm drawdown bar. Will cure under ambient conditions, can heat if necessary to accelerate cure.			

blocks were coated and allowed to float for 15 min in deionized water, then inverted and allowed to float for an additional 15 min. At the end of this time period, the excess water was wiped off of the blocks and then they were evaluated for water uptake. The WRE values were calculated using the following equation:

WRE = 100[(A-B) – (C-D)]/(A-B) where:

A = weight of the uncoated specimen after water contact
B = weight of the uncoated specimen before water contact
C = weight of the coated specimen after water contact
D = weight of the coated specimen before water contact

Triplicates of each coating were evaluated. Higher numbers reflect better water repellency. *Figure* 14 shows the results of this testing, with excellent correlation between log (SAM1) and WRE values (R^2=0.99).

SUMMARY AND CONCLUSIONS

Silver-based antimicrobial SAM1 has shown efficacy in a variety of model coating systems including in water-based 2K based polyurethane, in water-based clear and pigmented acrylics, and in solvent-based polyester-melamine coating. The product can be easily dispersed into solvent- and water-based resins using a Cowles blade-type mixer under high shear without the need for additional milling processes. The main target markets for this type of product are interior and exterior architectural coatings and marine antifouling coatings. It is apparent from the data, which was a result of this work, that bioefficacy can be easily demonstrated in water-based acrylics and urethanes at levels which will be economical for the end user.

Glass transition temperature and Water Repellency Efficiency values summarized in *Table* 1 show evidence that both are proportionally related to the concentration of antimicrobial required to obtain bioefficacy in the starting point formulations evaluated. CT

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