Low VOC Stain Blocking Specialty Primer Coatings – A Proposal

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I. Background

California's 2007 Suggested Control Measure (SCM) calls for the VOC limit for coatings used as Specialty Primers, Sealers, and Undercoaters (SPSU) to be reduced to 100 g/L, effective January 1, 2012, from the currently allowed limit of 350 g/L. The best performing current products that meet the 350 g/L VOC limit are solvent based coatings. A number of lower VOC, water based SPSU coatings are available; however, these products typically require more than one application to effectively block water soluble staining agents on substrates of interest within this category (e.g., certain stains from fire, smoke, or water damage, other water-soluble stains, and tannin compounds in certain wood substrates).

Low VOC products that are available in the market today have resulted from the efforts of manufacturers who have responded to the anticipated direction of regulatory mandates. Their efforts have resulted in development of low VOC coating binders and additives for architectural coatings in general. However, the question, "Do products formulated with these new materials meet the challenge of single coat performance within the SPSU category?" remains unanswered. Answering this question is critical for effective implementation of the proposed VOC regulations in a timely manner.

II. Objectives of the Project

The objective of this project is to determine whether the coatings in the SPSU market today containing VOC levels less than 100 g/L perform, in single coat applications, equal to or better than higher VOC coatings within this category.

III. Proposed Approach and Tasks

The project Technical Plan comprises four major Tasks that are outlined below. Successful execution of the technical plan requires close collaboration with industry throughout the project. If funding for the project is approved, the project team will take appropriate action to immediately inform the industry about initiation of the project. This can be accomplished by news releases to trade journals and magazines, both print and electronic, and by emailing an extensive list of industry contacts maintained by Cal Poly polymers and coatings program. The PI and CI participate in many coating industry events such as technical conferences, professional society meetings, and jointly sponsored research projects. In addition, Cal Poly polymers and coatings program is visited by many coating industry personnel as training course attendees, as research collaborators, and as advisory council members to the program. We feel very confident of our ability to keep industry informed about the project and its progress through these contacts.

Task 1. Survey Currently Available SPSU Coatings and Related Literature

A considerable amount of information on currently available SPSU coatings has been already compiled by CARB. The project team will first review the product information compiled by CARB and contact manufacturers to obtain any additional information needed. Information on products introduced in recent months will also be compiled and analyzed within this task. Paint manufacturing companies to be contacted include PPG, Sherwin Williams, Behr Process, Dunn-Edwards, Kelly-Moore, ICI, Akzo Nobel, and others.

Wood is one of the substrates of interest in the proposed project. Early low VOC coating developments for wood include replacement of nitrocellulose lacquers[1]. A project sponsored by EPA in early 1990's developed low VOC waterborne epoxy coatings for wood furniture[2]. The formulations were based on epoxy resin technology developed (with funding from the California Air Resources Board's ICAT program) by Adhesives Products Co (Adco), which was later acquired by Air Products and Chemicals, the PI's previous employer. Our cursory literature survey so far did not uncover reports on new stain blocking primers for SPSU coatings. A 2003 patent assigned to Sherwin Williams describes the development of a wood coating[3], "Primerless Latex Paint with Tannin Blocking".

The key challenge is to overcome the problem of migration to the surface of water-soluble staining agents found on SPSU substrates. Compiling information on relevant staining agents -- their chemistries, solubility characteristics, and diffusion kinetics will be part of this Task.

Task 2. Substrate Characterization

We will conduct a thorough investigation of all substrates typically encountered during the application of SPSU coatings. Information on their chemistry as well as physical properties (porosity, surface tension, surface texture, etc.) will be compiled within this Task. Testing of the effect of typical staining agents on these substrates will also be conducted to learn not only

what stains are most difficult to hide, but the mechanisms of the interactions of the stains with both the substrate and the SPSU coatings. In general, the staining agents will depend on the substrate material. The primary staining agents from wood substrates are various tannin compounds which are present at high levels in redwood and cedar, and lower levels in other wood substrates. Composition of water stains on acoustical ceiling tiles would be more complex. The multilayer structure of these products typically consists of the porous tile containing pulped, recycled newspaper and other fibers plus popped perlite held together with starch based binders. In addition, several coating layers are present on both sides and the edges of the product. As a result, water stains on the face of the tile would contain a complex mixture of water soluble material. Compositions of smoke and fire related stains on drywall would be a different category.

It is anticipated that sources for appropriate substrate materials for this task and Tasks 3, can be identified without too much difficulty. Our program has extensive contacts with California architectural and wood coating manufacturers, and we will seek their input in identifying substrate sources. Obtaining substrates with stains representative of smoke and other stains could present some logistical problems. It is quite likely that coating manufacturers may already have standard practices in preparing such substrates, and we can seek their recommendations. Testing and certification agencies such as Underwriters Laboratories (UL), and Master Painters Institute (MPI) are other possible sources for information in this regard. If no standards or standard practices for preparing stained substrate are found, we will develop substrate preparation methodologies.

Task 3. Benchmark testing of existing formulated commercial products

Typically, solvent based coatings perform better as stain-blocking primers than their waterborne counterparts. This is due to the fact that majority of the stains of concern are more soluble in water than they are in common solvents. The soluble staining agents can migrate to the surface of the coating through diffusion. Thorough testing of currently available fully formulated products in both solvent based and water based formulations will be conducted to determine the differences in performance between these two categories. These products will be selected from a list already compiled by CARB that are manufactured by Behr, Benjamin Moore, Devoe Paint, Dunn-Edwards, Masterchem, PPG, Sherwin Williams, and Zinsser In addition, the products to be considered for testing will include recent products uncovered in Task 1. Tests will include quantification of VOCs, stain blocking, single-coat application, plus other essential performance attributes. All tests and data analysis will be performed according to relevant ASTM methods developed by "ASTM International Technical Committee D01 on Paint and Related Coatings, Materials, and Applications". We also plan to use our Raman and infrared spectroscopy systems to characterize the areas where coatings allow stains to penetrate. In this way we hope to observe whether or not any chemical changes have taken place in the stains. This should help us identify agents in the coatings responsible for their inability to hide the stains and perhaps provide information of the mechanism of stain bleeding. Raman and infrared spectroscopy are both useful surface analysis tools for characterization of coatings and coatings defects. Both Raman and infrared are vibrational spectroscopy techniques. Since the Raman effect is a scattering process, it is ideally suited for surface analysis. Our infrared spectrometer is equipped

with an attenuated total reflection (ATR) sampling device enabling us to directly sample surfaces of substrates. These techniques are within the CI's core areas of expertise and have been used to characterize the chemistry of difficult surfaces such as ancient artifact coatings[4].

Task 4. Prepare final report

A final report will be prepared which describes in detail the results of work outlined in Tasks 1-4. Preparing the final report will be accomplished in consultation with CARB. Throughout the project, quarterly progress reports will be submitted to CARB. The first step in preparing the final report will be to submit a draft report prepared by the PI with input from the CI and the student researchers. Comments from CARB on the draft report will be addressed to finalize the project report. The results will be presented in a format suitable to CARB. Copies will be prepared in accordance with CARB guidelines.

All tasks will be performed in laboratories and offices of the Department of Chemistry and Biochemistry at Cal Poly, San Luis Obispo. Cal Poly is equipped with extensive coating preparation, testing, and analysis equipment that will be utilized throughout the experimental work related to this project. Our analytical capabilities include advanced rheometry, surface tension testing, dynamic mechanical analysis of films, thermal analysis (differential scanning calorimetry, thermo-gravimetric analysis), and a wide range of spectroscopy capabilities (NMR, IR, Raman, UV/Vis). In addition, Cal Poly is equipped with two Atomic Force Microscopy (AFM) instruments. AFM is a powerful technique that has become routine in characterization of surface topography and phase structure of materials down to a resolution of a few nanometers[5,6]. AFM, a form of Scanning Probe Microscopy, can be described as a very high resolution surface profilometry technique. In one form of operation, AFM scans an area of a few square micrometers with a nanosize probe to generate a high resolution topographical image of a surface. In another mode of operation, AFM can generate a phase contrast image indicating hard and soft areas of a surface down to less than a nanometer resolution. This technique has been used extensively to monitor the film formation behavior of latex based coatings for more than two decades[7,8].

Coating performance testing (hiding power, color, gloss, scrub resistance, etc.) is routinely conducted in our laboratories. Our coating preparation and testing laboratories as well as analytical instrumentation have been shown to CARB personnel during their visits to Cal Poly on a number of collaborative efforts.

IV. Project Management and Reports

The ultimate fiscal responsibilities associated with this project will be assumed by the Cal Poly Corporation, following the issuance of a State Standard Agreement. The Principal Investigator will submit requests for purchases, travel funds, and payroll in accordance with the methods established by the Cal Poly Corporation.

The Principal Investigator will oversee all technical aspects of the project, and will be responsible for preparation of periodic progress reports, as well as the Final Report. Throughout

the project, weekly meetings of the principal investigator, co-investigator, and student research assistants will be held, to review information and timetables, and to discuss potential roadblocks and their resolution. The Principal Investigator and the Co-Investigator will share primary responsibility for data management and analysis of experimental results, quality assurance and quality control, and drawing interim conclusions needed to guide timely progress of the project. Statistical significance of conclusions will be verified through out the Tasks by the use of standard test methods such as those specified by ASTM International. Where appropriate, critical experiments will be designed and conducted to arrive at conclusions in the most efficient manner. Student research assistants will conduct the bulk of the hands-on experimental work and assist in analyzing results. All project workers will contribute to the preparation of reports.

Ray Fernando is the principal investigator (PI) and project director. He has worked in the field of polymers and coatings for more than twenty-five years. His experience includes fifteen years of service in coating industry. Dr. Fernando will oversee all aspects of the project, direct research, search literature, conduct interviews, design experimental approaches, analyze data, write reports, make presentations and handle all budgetary items.

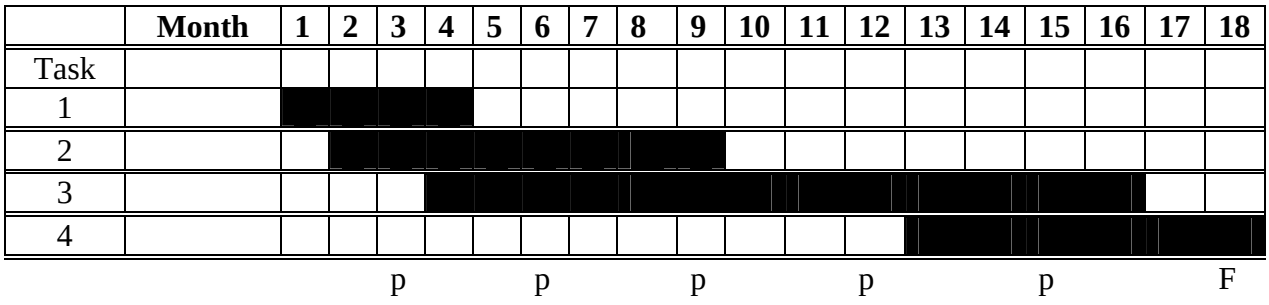
Dane Jones is the co-investigator (CI), and he has thirty years of experience in the polymers and coatings field, especially on VOC related issues. He is also experienced in the application of infrared and Raman spectroscopy in the study of coatings. His Ph.D. work applied Raman and infrared spectroscopy to the study of motion in simple molecules. He has participated in and directed several CARB funded projects related to coatings. Recently, he has completed a project to develop a comprehensive VOC analysis method for architectural coatings. He will search literature, conduct interviews, design experimental approaches, analyze data, and assist in writing reports and preparing presentations.

The graduate student will be identified as soon as the project is funded. This will be a full time student in the Polymers and Coatings Science MS program at Cal Poly. The student will have a broad background in polymers and coatings and will be experienced in waterborne and solvent based coatings, and VOC analysis including use of GC and GC/MS. The graduate student will assist in some aspects of literature search and preparation of project reports. The graduate student's primary responsibility will be to conduct hands-on experimental work throughout the project.

The undergraduate student will be identified as soon as the project is funded. This will be a full time student in the Polymers and Coatings Concentration in the Chemistry and Biochemistry Department at Cal Poly. The student will have a background in polymers and coatings and will be experienced in polymer and coating testing including VOC analysis. The student will assist in some aspects of literature search. This student's primary responsibility will be to assist preparation of coatings, running tests, and organizing results for review by PI or CI. The two students will be working under both PI and CI who will train, advise and supervise the students.

V. Schedule

Task 1: Literature / product review
Task 2: Substrate characterization
Task 3: Benchmark testing of existing formulated commercial products
Task 4: Prepare final report



p = Quarterly Progress report
F = Deliver final report

VI. Qualifications of the Cal Poly Team

Raymond H Fernando (Principal Investigator): The PI has conducted research in the coatings field for the past twenty-five years, beginning with his PhD thesis research on rheology and application behavior of waterborne coatings and other aqueous systems. During the twelve years he served at Armstrong World Industries, Inc., the PI has been involved in researching coatings for a wide range of architectural interior furnishings – floor coverings and acoustical ceiling tile products. The PI's research in these areas included waterborne and solvent based coatings -- their formulation as well as application. In addition to the key performance attributes of concern, effects of emissions from these coatings within interior spaces have always been an integral part of the products he researched. The PI was a Program Manager for Armstrong World Industries, running the coatings research program that supports global manufacturing and marketing needs of the company's Building Products Division, before he joined Air Products and Chemicals, Inc. in 1999. At Air Products, he continued his research related to emulsion polymers and nano-scale materials for coatings. Since joining Cal Poly, SLO in 2002, he has maintained research activities on waterborne and solvent based coatings, and nanotechnology applications in coatings. He has several patents and many publications in these areas. Also, he has presented his research results at many national and international conferences.

Dane R. Jones (Co-Investigator): The CI has been on the faculty of Cal Poly, SLO, since 1976. He oversaw development of both the undergraduate and graduate polymers and coatings programs at Cal Poly. He has extensive contacts with industrial and regulatory coatings scientists in California and throughout the U.S. As a visiting scientist, he studied coatings formulations at the Dunn-Edwards Corporation. He consults for several California coatings and raw materials manufacturers. He has participated in and directed several CARB funded projects including development of a solvent database, VOC analysis of aerosol coatings, relationship of

hiding and VOC in coatings, and most recently, development of a comprehensive VOC analysis method for architectural coatings. He has several publications related to VOC development. He also participated in development of the national standard for recycled paint products.

VII. References

1. *"Low-VOC Waterborne Coatings for Wood Based on Nitrocellulose-Acrylic Latex"*, Haag, H.F., J. Coat. Technol., 64(814), 19, 1992
2. *"Development of Ultra-Low VOC Wood Furniture Coatings"*, Huang, E.W., Watkins, L., and McCrillis, R.C., Proceedings of EPA Pollution Prevention Conference on Low- and No-VOC Coating Technologies", San Diego, CA, 1993.
3. *"Primerless Latex Paint with Tannin Blocking"*, Rota, D.D., Madigan, L., Bell, E.C., and Martuch, R.A., US Patent No. 6,531,223 B1, 2003
4. *"The Nine Muses of Sarcophagus – Hearst Castle California: Spectroscopic Investigation of the Painted Decoration"*, Jones, D., Frey, T., Scezesniak, M., Barov, S. and Farber, C., Presented at IRUG VIII International Conference, Florence, Italy, 2004
5. *"Atomic Force Microscopy"*, Chernoff, D.A., and Magonov, S., in "Comprehensive Desk Reference of Polymer Characterization and Analysis", Brady, F.R. (Ed.), Oxford University Press, 2003
6. *"Getting Physical with Your Chemistry: Mechanically Investigating Local Structure and Properties of Surfaces with the Atomic Force Microscope"*, Heinz, W.F., and Hoh, J.H., J. Chem. Ed., 82(5), 695, 2005
7. *"A Study of Latex Film Formation by Atomic Force Microscopy. 2. Film Formation vs Rheological Properties: Theory and Experiment"*, Lin, F., and Meier, D.J., Langmuir,12, 2774-2780, 1996
8. *"Film Formation from Monodisperse Acrylic Latices: 5. Drying and Ageing in Coalescing Agent Containing Latex Films"*, Zohrehvand, S., and Nijenhuis, K., J. Coll. Interface Sci., 288, 75-82, 2005