

EXECUTIVE OVERVIEW

Paints and Architectural Coatings Environmental Study (PACES)

The Volatile Organic Compound (VOC) content of architectural coatings has been regulated for decades with the intent of improving air quality, since in the presence of nitrogen oxides and sunlight, VOC emissions may promote accumulation of ground level ozone, which is a key component of urban smog. VOC content has become the primary indicator of environmental acceptability for coatings; this approach, however, has limitations:

- 1) While current regulations limit the VOC content of coatings, these regulations give little regard to “reactivity,” which is the variable ability of VOCs to promote accumulation of ground level ozone. Different VOCs have different degrees of reactivity: some VOCs may be orders of magnitude more reactive than others;
- 2) Current regulations assume that coating VOC contents have sufficient “atmospheric availability” to volatilize fully and persist in ambient air long enough to be consumed completely in reactions that promote ozone accumulation, while in reality some VOCs are only partially available;
- 3) Regulations do not take into account “life cycle” aspects of coatings, including performance factors such as coverage, durability, and service life. A full assessment requires “life-cycle analysis” to identify potential impacts on a broad range of media, including not only air quality, but also water quality, energy and material resource consumption, solid waste disposal, and human health and safety.

Given these concerns, in 2006 the paint and coatings industry initiated and agreed to fund the Paints and Architectural Coatings Environmental Study (PACES) to gather data on the environmental and societal impacts of regulations limiting the VOC content of architectural coatings. While the industry sponsored this research, the PACES Technical Advisory Committee comprised representatives of both coating manufacturers and coating regulators, including the U.S. Environmental Protection Agency (EPA), the California Air Resources Board (ARB), and California’s South Coast Air Quality Management District (SCAQMD). ARB and SCAQMD each provided substantial in-kind contributions by separately sponsoring PACES-related research.

The Research

The PACES project, to date, has included two separate phases of research, both of which were conducted in laboratories at renowned research universities – the University of California at Riverside’s College of Engineering Center for Environmental Research and Technology (CE-CERT) and the University of Texas at Austin.

Phase I Goals

The goals of the Phase I research were to:

- 1) Assess the current state of the science regarding the environmental impacts from the use of paints and architectural coatings in the U.S.;
- 2) Design and perform the necessary research that will provide more accurate emission factors and inventories that will better serve the environmental impact assessment of paints and architectural coatings;
- 3) Design and perform the necessary research that will provide a better understanding of emission rates and of the chemical composition of paints and architectural coatings in ambient environment and compare these results with VOCs from other sources;
- 4) Investigate the atmospheric availability and reactivity of VOC emissions from paints and architectural coatings to improve prediction of ozone and aerosol formation from these sources for a number of varying air quality scenarios; and
- 5) Conduct a life cycle assessment of paints and architectural coatings with respect to the total eco-system.

Phase I Results

The following is a short summary of the major findings from the Phase I PACES research that was completed the University of California at Riverside's College of Engineering Center for Environmental Research and Technology (CECERT).

Measurements of TPM in Ambient Air

TPM (Trimethyl Pentanediol Monoisobutyrate, a mixture of two isomers of ester alcohol better known by its Eastman Chemical Company trade name, Texanol®) is typically the most abundant VOC used in waterborne architectural coatings. Accurate measurements of TPM in ambient air are needed to help validate the inventory and address the critical issue of atmospheric availability. Historical "micro level" studies suggest that as much as 40% of TPM never evaporates from paint films, and is therefore not available for participation in ozone photochemistry. While concentrations of TPM have been measured for indoor applications to determine indoor concentrations, and in flow-through chambers to measure the emission rate as a function of time, there have been few reported attempts to measure TPM at the "macro level" in ambient air.

The Phase I PACES research focused on the development of analytical instrumentation and measurement protocols to determine the "macro" spatial and temporal distribution of TPM in ambient air in the Los Angeles Air Basin. An analytical system was successfully developed based on adsorption on Tenax TA followed by thermal volatilization, and was capable of detecting 5-10 ppt of TPM in the atmosphere. TPM was detected in all samples taken from both laboratory air and outdoor ambient air. Ambient TPM concentrations ranged from 10-70 ppt. Collocated sampling followed by spiking one of the pairs of sorbent tubes gave convincing evidence of correct peak identification by retention time although some further methods development was needed to provide unequivocal proof that TPM was being quantitatively detected. Measuring elevated TPM concentrations downwind of painting operations using a limited number of sample locations was not successful due to the unpredictable movement of the "plume" downwind of the operation.

Nevertheless, the ability to detect TPM in ambient air was clearly demonstrated and the system developed provided critical information in addressing atmospheric availability of coating VOCs in the assessment of their impact on ozone formation.

Coatings Application Activity Analysis

Relying on ARB survey data and sponsored research, a methodology to obtain specific coating emission inventory data for the Los Angeles Air Basin was developed, including differentiation of products and their associated VOC emission factors. The coatings were stratified according to quantity of coatings used, spatial distribution, temporal distribution, and type of application. Using this methodology, a gridded VOC emission inventory of coating application was developed for a two-week ozone episode in July 2002.

Based on a methodology that excludes disposal of waste paint and solvent from the inventory, coating VOC emissions and associated VOC emissions from the use of thinning, additive, and cleanup solvents were estimated. The estimate of the 2002 average daily statewide emissions (108.4 tons/day) was lower than the one estimated with the conventional approach (126.6 tons/day¹). In the new estimates, thinning and cleanup solvents are responsible for about 15-17% of the total coating-related VOC emissions. This is consistent with new estimates published by ARB.

Using population as a spatial surrogate, it was determined that 48.8 tons of the total statewide coating-related VOC emissions were emitted within the boundary of the Los Angeles Air Basin each day on an average. This can be as high as 54.5 tons/day in summer because of increased coating activity during summertime. The emissions during weekdays are significantly higher than during the weekend. Current ozone measurements in the Los Angeles Air Basin consistently show higher ozone concentrations during weekends compared to weekdays, contrary to the trend observed in coating VOC emissions.

It should be emphasized that the emission inventories developed in this task, although adjusted for the amount of coatings disposed, did not account for effects of atmospheric availability, because of limited data available at the time. As the understanding of atmospheric availability evolves, the methodology developed will allow for better quantification of these effects. In addition, the development of season-specific emission factors and the determination of a composite spatial surrogate are tools that can help improve the coating VOC emission inventory.

Life Cycle Assessment

Preliminary analysis, based on publicly available data, indicates that regulation of architectural coating VOC content appears to have decreased VOC emissions from such coatings over the last several decades. The volume usage of architectural coatings,

¹Average of the 2000 estimate (CARB, 2003a) and the 2004 estimate (CARB, 2006)

however, has increased significantly, possibly due to population growth, more coating consumption per capita (which could result from lower coverage, shorter durability, or changing personal preferences), or increased housing development. Comprehensive assessment of total environmental impacts of architectural coatings will require more data and study. Coverage and durability of coatings, and the reactivity and availability of their VOC contents, are important issues that need to be better quantified. Questions as to whether there is a need for reformulation of paint in the context of durability, cost, and environmental benefits remain unanswered. The focus of future research should be the acquisition of data needed to complete a comprehensive Life Cycle Assessment.

Phase II Goals

The goals of the Phase II research concentrated on the atmospheric availability of TPM at the macro and micro levels, and were to:

- 1.) Measure ambient concentrations of TPM several times during the year at several locations in the Los Angeles Air Basin;
- 2.) Apply stable isotope analysis to quantify the residual presence of TPM in painted stucco and gain a mechanistic understanding of its sequestration;
- 3.) Analyze samples of painted gypsum wallboard substrates that are several years old (“legacy samples” harvested from building materials in the Los Angeles Air Basin) for residual TPM emission and/or content; and
- 4.) Conduct a series of experiments to determine the fate of ethylene glycol (EG) and propylene glycol (PG) in latex paint, in order to determine the amount of EG and PG that remains in paint films over time.

Phase II Results

The following is a summary of the major findings of the Phase II PACES research. The University of California at Riverside’s College of Engineering Center for Environmental Research and Technology (CECERT) completed the field measurements of TPM concentrations in ambient air of the Los Angeles Air Basin. The remaining laboratory research was conducted at the University of Texas at Austin.

Ambient Measurements of TPM in Southern California

An analytical system that was capable of detecting TPM in ambient air was developed, based on adsorption on Tenax TA followed by thermal volatilization. TPM was successfully detected and quantified in ambient air at three locations in the Los Angeles Air Basin. TPM was detected in all samples of ambient air. Ambient TPM concentrations ranged from 5-40 ppt. Unreacted TPM constitutes approximately 0.01% of the total non-methane hydrocarbon (NMHC) concentrations in this air basin, and given its low rate of reactivity in ozone photochemistry, this would be an approximate upper limit for the incremental fraction of ozone that can be attributed to TPM.

Given the generally similar concentrations measured throughout the basin, it appears that

the sources of TPM emissions are fairly uniformly distributed. This would be expected in a highly developed area like the Los Angeles metropolitan area. Over the distance from Pico Rivera to Riverside, the change in the ratio between the two TPM isomers, which have different reactivities, indicates that the more reactive isomer has had time to react more fully before the moving air mass reaches Riverside. Consequently, Riverside air appears to contain a significant amount of TPM that originated upwind. Since the average concentrations are similar for all of the sites, the upwind sites would be expected to be a larger source of TPM than Riverside. This is also consistent with the higher intensity of housing development in the upwind areas.

Availability Experiments for TPM Using Stable Isotope Marking

Data on residual TPM retained in the paint film were determined by two methods: stable isotope analysis and chemical extraction. The methods showed good agreement, both indicating a steady decline in the presence of TPM in the paint film. Approximately 50% of the applied TPM was “lost” from the paint film within the first three months following painting. After six months, slightly less than 90% of the original TPM was lost from the paint film.

At eleven months after painting, the paint/stucco matrix retained approximately 12% of the mass of isotope-marked TPM applied. While no attempt was made to monitor air emissions during the entire eleven months, it may be assumed that the majority of the “missing” TPM was emitted to air. Slightly less than half of the residual ^{13}C isotope marker remained in the sample matrix as unreacted TPM. Solid phase Nuclear Magnetic Resonance (NMR) analysis indicated that the remainder (approximately 6.7%) of the ^{13}C molecules reacted with the stucco substrate or the paint film. The NMR data do not provide enough information to determine the type of reaction or reactions that occurred. The absence of a ^{13}C -oxygen bond, however, suggests either a dehydration reaction or a reverse transesterification reaction. Additional experimentation would be required to definitively establish the actual reaction and reaction byproducts.

Analysis of Harvested Building Materials for TPM Emissions and Residual TPM

An analysis of harvested building materials was conducted to determine the presence of TPM. Three samples of gypsum wallboard were obtained, two from California and one from Texas. The elapsed time from the last application of paint to the time of analysis ranged from approximately 9 years to 17 years. The harvested samples were put into small chambers and the air in the chambers analyzed for TPM.

All of the samples emitted low levels of TPM, with annual emission rates ranging from $4.7 \text{ mg/m}^2\text{yr}$ to $51 \text{ mg/m}^2\text{yr}$. Following the emissions test, the legacy samples were analyzed for retained TPM. All of the legacy samples contained residual TPM. Residual concentrations ranged from 300 mg/m^2 to over $2,000 \text{ mg/m}^2$. Comparing the annual emission rates to the retained mass of TPM indicates that decades would be required to completely deplete the residual TPM, less any portion retained permanently.

Availability Analysis of Ethylene Glycol and Propylene Glycol in Latex Paint Applied to Gypsum Wallboard and Stucco

The environmental fate of ethylene glycol (EG) and propylene glycol (PG) applied as a component of latex paint was investigated. A total of twelve samples were used. The samples were divided equally between semi-gloss paint and flat paint. The samples were further sub-divided between gypsum wallboard and stucco substrates. The emissions of EG and PG were monitored for the first five days and then periodically monitored for a total of twelve weeks. At the end of twelve weeks the samples were analyzed for residual EG and PG.

EG and PG Emissions from latex paint exhibited a dependence on the type of paint and type of substrate. For example, when semi-gloss paint was applied to gypsum wallboard only 3% of the applied mass of EG and 7% of the total mass of PG was emitted in the first 24 hours. When flat paint was applied to gypsum wallboard, the emission of EG and PG in the first 24 hours increased to 16% and 23% for EG and PG, respectively. Compared to the gypsum wallboard samples, emissions of EG and PG increased when latex paint was applied to a stucco substrate. After semi-gloss paint was applied to stucco, the emissions in the first 24 hours were 35% and 38% for EG and PG, respectively. For flat paint applied to stucco, the emissions in the first 24 hours increased to 49% for EG and 72% for PG.

After twelve weeks the samples were crushed and the residual EG and PG was extracted. When applied as a component of semi-gloss paint, a fraction of both EG and PG was retained. The residual PG accounted for 28% and 56% of the applied mass of PG to stucco and gypsum wallboard, respectively. The residual mass of EG was 38% for gypsum wallboard and 20% for stucco. There was no residual EG or PG recovered 12 weeks after the application of flat paint to either gypsum wallboard or stucco.

Conclusions and Possible Future Research

The PACES project has succeeded, first of all, in demonstrating the viability of a collaborative model for research involving industry, government, and academia. Additionally, the research work products to date have generated new data that is anticipated to find useful application in the context of regulatory policy, product formulation, and assessment of coating impacts. PACES Phase II research, in particular, may provide a defensible technical basis for future regulatory policies that account for the variable atmospheric availability of latex paint cosolvents. Finally, the PACES project has established a foundation for future research, including continuing investigations into life cycle analysis of coatings, improvement of the coating emissions inventory, and development of more accurate air quality modeling of coating impacts under changing airshed conditions (e.g., lower NO_x scenarios).