Addition to "Evaluation of Atmospheric Impacts of Selected Coatings VOC Emissions"

Background

Because emissions from architectural coatings are an important component of the stationary source volatile organic compounds' (VOC) inventory, the California Air Resources Board (ARB) approved a mass-based control measure for VOCs in architectural coatings in June 2000. The ARB also decided to evaluate the feasibility of reactivity-based regulations for architectural coatings because they can potentially make regulations more cost-effective and flexible. There are several issues regarding the feasibility of reactivity-based regulations. The uncertainties associated with the reactivity of VOCs in architectural coatings are considered to be a high priority.

ARB staff requested that Dr. Carter's proposal include a comprehensive analysis of the uncertainties associated with reactivity of VOCs used in architectural coatings. His analysis provides both a framework for discussions with industry of additional research needs and a useful summary for ARB staff as they evaluate the feasibility of a reactivity regulation for architectural coatings. The cost of addressing all of the tasks in Dr. Carter's comprehensive program exceeds the $60,000 allocated to this project. To select the highest priority tasks ARB staff from SSD and RD and Dr. Carter met with industry representatives at a meeting for the Reactivity Research Advisory Committee (RRAC). Everyone agreed that the highest priority should be assigned to improving the reactivity estimates for Texanol and petroleum distillates.

In view of these considerations, the ARB staff requested that Dr. Carter provide more specifics concerning the proposed work that can be carried out for the available funding. Given below are his recommendations concerning the specific tasks, based on the input and data available thus far. Reference is made to the full proposal for a more detailed discussion of the background, methods, and utility of these tasks.

Task 1. Application of a Direct Reactivity Measurement Method to Coatings Constituents.

As discussed in the proposal, under a current ARB project Dr. Carter is developing a method to measure the direct ozone formation potential for individual VOCs and complex mixtures such as petroleum distillates. Such data will have utility for evaluating mechanisms for individual compounds and for evaluating composition and reactivity estimation methods for petroleum distillates. It is assumed that by the time this project is funded a satisfactory method will be developed that can be applied to the types of compounds and petroleum distillates of interest in this project. If this is the case, the method will be applied to Texanol, a sufficient number of petroleum distillate mixtures (at least 5) to be useful for evaluating the reactivity estimation methods developed for them under Task 3 (see below), and, if possible, additional selected coatings VOCs.

Dr. Carter estimates that if the method has been satisfactorily developed and evaluation data on compounds with known mechanisms have been obtained as a result of the current program, the work needed for this project can be carried out for approximately $25,000[1]. This is based on assuming it can be done in approximately 1 month of full-time laboratory work using existing equipment and personnel in Dr. Carter's laboratory.

If it is determined that the method developed under the current ARB program will not be useful for evaluating Texanol or petroleum distillates without additional effort that is not covered by the estimated $25,000 cost, then we will make recommendations as to alternative options. One option would be to use the $25,000 for further development of this method, but this will only be considered if it is judged that this method may eventually lead to a useful method for reducing reactivity uncertainty for coatings, and the necessary funding cannot be obtained elsewhere. A more likely option will be to carry out chamber experiments for one or two selected petroleum distillate samples, to evaluate reactivity estimation methods to be developed under Task 3, discussed below.

It may also be useful to carry out additional experiments with Texanol if it is found that the experiments budgeted for under Task 2 are not sufficient. The decision on the option to employ will be determined by Dr. Carter and the ARB staff after discussions of the available options with the RRAC.

It is also possible that a satisfactory direct reactivity measurement method may not be available when this project begins but may become available at a later date during the three year span of this project. Therefore, the decision on which option to employ if the method is not initially suitable may be deferred until a later stage this project.

Task 2. Environmental Chamber Studies of Texanol

The section of the proposal entitled "Environmental Chamber Studies of Selected Coatings VOCs" discusses the possibility of conducting chamber experiments for several different types of VOCs, but because of limited funding the chamber studies for this project will focus on Texanol. The new chamber being developed under EPA funding will be employed. The EPA project will also cover the costs of the control and characterization runs that will be associated with the Texanol runs, so in effect the EPA will be co-funding this project. This means that it should be possible to conduct experiments representing a range of conditions needed for mechanism evaluation. We estimate that the cost per experiment in the new chamber will be in the $3500-4000 range, which means that probably 5 mechanism evaluation experiments can be carried out for a total cost for this task of about $20,000. This includes some provision for development of methods to handle and analyze this compound.

The proposal indicated that there was uncertainty concerning the feasibility of conducting experiments with Texanol because of its relatively low volatility, though it was indicated that the use of the larger EPA chamber should minimize the problems.

[1] The budget figures given for the various tasks do not count the estimated $7,000 to cover the cost for Dr. Carter's time in preparing the reports for this project and time and travel to meet and consult with the ARB staff or the RRAC.

However, papers by Chang and co-workers[2] indicate that reasonably good analysis methods exist for Texanol, and, although it has some affinity for surfaces, it appears to be less than is the case for propylene glycol, a compound that Dr. Carter has already studied with some success[3]. Therefore, Dr. Carter now considers the probability of success in conducting useable experiments with Texanol to be relatively high. However, if problems are encountered then an alternative type of coatings-related VOC will be studied, to be determined after discussion with the ARB staff and the RRAC. The most likely alternative would be one or more petroleum distillate samples.

Task 3. Development and Evaluation of Procedures to Quantify Reactivities and Uncertainties for Petroleum Distillates

As discussed in the proposal and emphasized again at the RRAC meeting, Dr. Carter believes that the highest research priority concerning petroleum distillates is to evaluate information available concerning petroleum distillates and develop a systematic procedure to use the available information to derive reactivity estimates using any reactivity scale and to quantify compositional uncertainties for such mixtures. An important part of this project will be adapting the hydrocarbon reactivity "binning" approach so it can be used for compositional uncertainty quantification and other reactivity scales. This is discussed in the section of the proposal entitled "Development and Evaluation of Procedures to Quantify Reactivities and Uncertainties for Petroleum Distillates".

For this task to be successful, cooperation is needed with the industry groups who can provide compositional information concerning petroleum distillate samples, and information concerning variability of materials available in the marketplace. This is because the non-proprietary information provided by the ARB or available in current

[2] See for example, J. C. S. Chang, B. A Tichenor, Z. Guo and K. A. Krebs, "Substrate Effects on VOC Emissions from Latex Paint," *Indoor Air* 7, 241-247, 1999.
[3] Carter, W. P. L., D. Luo, and I. L. Malkina (1997b): "Investigation of the Atmospheric Ozone Formation Potential of Propylene Glycol," Report to Philip Morris, USA, May 2. Available at http://cert.ucr.edu/~carter/absts.htm #pgrept

surveys are insufficient to be useful for reactivity analysis. If this cooperation is not forthcoming, then it will be necessary to carry out a project to analyze petroleum distillates and their variability in the marketplace, which is beyond the scope of Dr. Carter's proposal. In this event, this task will be deferred until the later periods of this project, to allow time for the necessary data to become available.

Dr. Carter believes that this data and uncertainty analysis work needs to be carried out before any further environmental chamber experiments are carried out with petroleum distillates. The reason is that, for all or mostly alkane samples at least, the compositional uncertainty is probably more important than the chemical mechanism uncertainty. Dr. Carter has already studied five different types of petroleum distillate samples, and the results indicate that the SAPRC-99 mechanism can simulate the chamber data reasonably well provided that sufficient compositional information is available[4]. However, the representativeness of these five samples of the hydrocarbon solvents available in the marketplace is uncertain, and without additional information concerning compositional variability this uncertainty will be applicable for any additional types of petroleum distillates that may be studied.

Once the data analysis has been completed and a reactivity and uncertainty estimation method is derived, then experimental verification would be important. Because of limited funding for this project, and because chamber data are already available for several types of petroleum distillates, it is proposed that the experimental verification will consist of direct reactivity experiments, as discussed in the proposal. This will be carried out as part of Task 1, as discussed above. These data, in conjunction with the existing chamber data, may be sufficient to test the methods developed under this task of this program.

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[4] Carter, W. P. L., D. Luo, and I. L. Malkina, "Investigation of the Atmospheric Ozone Formation Potentials of Selected Branched Alkanes and Mineral Spirits Samples," Draft Report to Safety-Kleen Corporation, August 18, 2000; Carter, W. P. L., D. Luo, and I. L. Malkina, "Investigation of the Ozone Formation Potentials of Exxsol® D95, Isopar-M®, and the Exxate® Fluids," Draft Report to ExxonMobil Chemical Company, August 25, 2000. These reports are not yet available on the cert.ucr.edu website. See also the SAPRC-99 documentation report.

Because of limited funding and the availability of the previous data, environmental chamber experiments with mineral spirits samples will not be carried out for this project unless it is decided to cut back on Tasks 1 or 2. The priority for chamber experiments with petroleum distillates will be increased if it is determined that direct reactivity cannot be carried out, but only after the data analysis and uncertainty project is completed. However, as discussed in the proposal the new chamber and procedures being developed for the EPA will have a number of significant advantages over the chambers and procedures used in the previous studies, so using this new chamber for petroleum distillate studies would be very desirable. Attempts will be made to obtain additional funding for this purpose.

Because the experimental work for evaluating petroleum distillates is expected to be limited to direct reactivity determinations to be carried out in Task 1, the costs for this task are limited to Dr. Carter's time to conduct the data analysis and develop, evaluate, and document the reactivity and uncertainty estimation methods. The estimated cost for Dr. Carter's time for this is approximately $10,000.