II.

Background on the Science of Volatile Organic Compound Photochemical Reactivity

A. Introduction

To reduce excess ozone concentrations in non-attainment areas, control of ozone precursors such as volatile organic compounds (VOC) and oxides of nitrogen (NO_x), is needed. As part of California's ozone control strategy, we have been successfully implementing mass-based VOC emission controls for aerosol coating products. To further refine the current regulatory approach, in this rulemaking Air Resources Board (ARB) staff is proposing to use photochemical reactivity as the basis for regulating emissions from aerosol coatings. We believe this control approach has the potential to provide more flexibility to manufacturers, and could lead to a more effective and cost efficient ozone control strategy.

It has been known for several decades that individual VOCs vary in the amount of ozone potentially formed once emitted into the air. This concept is referred to as "reactivity." In the current Aerosol Coatings Regulation, total VOC content is limited on a percent-by-weight basis, without consideration of the differences in VOC reactivity. However, the science of reactivity now allows us to more effectively control VOC emissions by targeting reductions from VOCs that have a higher potential to form ozone.

Therefore, we are proposing to amend the Aerosol Coatings Regulation by replacing the January 1, 2002, mass-based limits with equivalent reactivity-based limits. The following sections provide background on the science of reactivity, and how the reactivity of VOCs is measured.

B. Background on the Science of Reactivity

The photochemical reactivity of a VOC is a measure of its potential to impact ozone levels. Years of research has led to our understanding that VOCs vary in their ability to contribute to ozone formation because they react at different rates and *via* different chemical mechanisms. In other words, the difference in the chemistry of each VOC, or its reactivity, determines its impact on ozone formation. These differences can be quantified and used in approaches to control emissions of VOCs.

The science of photochemical reactivity, or reactivity, has been evolving and expanding for several decades. Beginning in 1952, it was discovered that different organic compounds have different potentials to form ozone (Haagen-Smit *et al.*, 1952). The formation of ozone involves complex chemical interactions of VOCs with oxides of nitrogen, or NO_x , in the air. Within these interactions, it was discovered that VOCs differ in their abilities to form ozone. The variability in ozone-formation potentials was later verified by smog chamber experiments (Carter and Atkinson, 1989). In smog chamber studies a known amount of a VOC is injected into an experimental chamber under conditions that would generate the maximum amount of ozone. The reaction products of the chemical reactions and their amounts are measured and analyzed to help understand the chemical reaction rate and mechanism by which the VOC reacts. These smog chamber experiments yielded important information on the chemistry of VOCs. To account for the differences in the VOCs' abilities to form ozone, reactivity scales were developed (for example, Dodge, 1984; Bufalini et al., 1976). The United States Environmental Protection Agency (U.S. EPA), as early as 1977, recognized the variability of VOCs' ozone-forming potential and created a two-class reactivity scale for the regulatory control of VOCs: "negligibly reactive" and "reactive." California also applies this strategy in its consumer products regulations.

C. Development of Methods to Compare VOC Reactivities

To use the concept of reactivity a method is needed to quantify the impact of each VOC on ozone formation. One tool that allows for ozone measurement is a reactivity scale. Many scales have been proposed to quantify the ozone formation potential of VOCs. The complexity of these scales range from one considering only the hydroxyl (OH) radical reaction rate constant (see, for example, Darnall *et al.*, 1976) to those that incorporate detailed effects of ozone chemistry and ambient conditions using a box model or the more sophisticated three-dimensional Eulerian model (Carter, 1994; Harley *et al.*, 1993).

One of the earlier scales to measure VOC reactivity was based on the reaction of hydrocarbons with OH radicals (Darnall *et al.*, 1976). The scale proposed to account for the differences in reactivities by the VOC's chemical reaction rate constant. The chemical reaction rate constant (or how fast the initial reaction occurs) of the VOC with OH radical is important because it is the predominant reaction in the lower troposphere (the lowest 15 kilometer layer of atmosphere in which we live) and the OH radical is critical to the formation of photochemical smog. For many VOCs, reaction with the OH radical is the only atmospheric loss process. Thus, the reaction rate constant, k_{OH}, is the measurement of how rapidly the initial VOC reaction takes place. In addition, the k_{OH} rate constant is available for a large number of VOCs. However, because of the intricacies of the VOC-NO_x-air-irradiation system, there are significant inherent differences in the reaction mechanisms, which affect how much ozone is formed after the VOC has reacted with the OH radical. Because these differences have not been accounted for, the k_{OH} scale is considered insufficient for the ranking of rapidly reacting VOCs, and of ozone impacts of the VOCs with similar k_{OH} values.

In 1991, Derwent and Jenkin of the United Kingdom developed the Photochemical Ozone Creating Potential (POCP) (Derwent and Jenkin, 1991), which was defined by subtracting the emissions of a particular VOC from a 69-component mixture and re-running the photochemical model calculation. The POCP model was defined relative to ethene as the reference compound. This model showed that aromatic and olefinic compounds yielded the highest POCP values, while aliphatic hydrocarbons showed POCP values that increased steadily in multi-day trajectories. However, the Harwell mechanism used in the POCP scale was not validated against results from smog chamber experiments and therefore, may not be appropriate for evaluating the reactivities of VOCs in the atmosphere. Later, Andersson-Skold *et al.* (1992) refined several parameters of the POCP model and found that the maximum ozone difference and the 96-hour average ozone concentration gave the most consistent POCP values. On a 96-hour average, ethene and acrolein were found to be very efficient ozone producers, followed by higher alkenes, aromatics, alkanes, and ethers. Alcohols and ketones were found to be weaker ozone producers.

In 1984, Dodge studied the organic reactivities of VOC present in an urban air mixture (Dodge, 1984). A chemical mechanism was developed and tested against smog chamber experiments. This mechanism was found to have a reasonable fit to the available experimental data. VOC reactivity was expressed as the percent increase in maximum ozone per amount of hydrocarbon added to the urban mixture, and the calculations were performed based on the ratio of the concentration of the VOC to the concentration of the NO_x (also known as the VOC/NO_x ratio), characteristic of the air basin, and on the atmospheric composition. The differences in reactivity among the VOC tested were greater at lower VOC/NO_x ratios (<3-4), but the differences in reactivity decreased as the VOC/NO_x ratio increased. Thus, the use of hydroxyl rate constant, k_{OH}, is a good measure of reactivity at low VOC/NO_x ratios, but not at high ratios.

Since 1989, Carter and co-workers at Statewide Air Pollution Research Center (SAPRC) (and now continuing at the College of Engineering Center for Environmental Research and Technology) (Carter and Atkinson, 1989; Carter, 1994; 1996; 1999b; 2000; Carter *et al*., 1995) have been conducting the most extensive studies of incremental reactivities using smog chamber experiments and computer modeling. Carter defines the incremental reactivity as the maximum amount of ozone formed by the addition of a test hydrocarbon to the base reactive organic gas mixture, divided by the infinitesimal amount of the test hydrocarbon added. Data from these experiments have shown that the ozone formation potential of the VOCs depends significantly on the nature of their reaction mechanisms and the characteristics of the environment in which they react, with NO_x availability being the most important environmental factor. In general, VOCs are found to have the highest effects on ozone formation under relatively high NO_x conditions (i.e., low ROG/NO_x as in urban conditions), and to have low impact on ozone formation under limited NO_x conditions, which lead to high ROG/NO_x ratios.

The MIR, maximum ozone incremental reactivity (MOIR), and equal benefits incremental reactivity (EBIR) are three incremental reactivity scales developed by Carter from box models of 39 U.S. urban areas (selection based on conditions described by the U.S. EPA) (Bauges, 1990; Carter, 1994). Incremental reactivity is expressed as the number of additional grams of ozone formed per gram of VOC compound added to the base organic mixture. Incremental reactivity conveniently computes the ozone formation potential of a VOC when it is readily available for reaction in the troposphere.

The MIR is the incremental reactivity computed for conditions in which the NO_x concentration would maximize the base ROG reactivity. This scenario is typical in air parcels of low VOC-to-NO_x ratios such as urban centers, or air parcels in which ozone is most sensitive to VOC changes. These are typical of urban centers in where there are high emissions of NO_x and the chemistry is VOC-limited.

Because of the complexity of the atmosphere and nonlinear interactions of ozone precursors (Carter, 1996), computer models are used to calculate the general trends in reactivity of organic compounds. Accordingly, the reliability of such calculations would depend on the accuracy of the model’s descriptions of the physical as well as chemical environment of the “real world.” The MIR scale that would be used in these proposed amendments was developed using a simple zero-dimensional (“box”) photochemical model with a detailed chemical mechanism developed at the SAPRC (hereafter referred to as the SAPRC mechanism) (Carter, 1990; 2000).

The SAPRC mechanism is a “lumped molecule” mechanism, which is a modeling approach utilizing generalized species and reactions with parameters derived from the compound(s) being represented (Carter, 1990). This mechanism is designed to assess the differences in atmospheric impacts of individual VOCs and has been extensively evaluated against environmental chamber data (Carter *et al*., 1995). Despite having less detail to represent different physical processes (for example, pollutant transport) in the atmosphere, a box model allows a comprehensive evaluation of the ozone forming chemistry of an organic chemical based upon finite computer resources.

Studies have also addressed the appropriateness of using a simplified, zero-dimensional box model, to quantify the reactivities of VOCs. These studies involved comparing the MIR to other reactivity scales (such as peak ozone level) derived by using more sophisticated photochemical models such as a three-dimensional Eulerian model (3D Model) (see, for example, McNair *et al*., 1992; Bergin *et al,* 1998). Unlike the box model, a 3D model has a more comprehensive representation of different atmospheric physical processes such as multi-day transport, spatial and temporal variations of emissions. The results of these studies indicated that the box-model calculated MIR scale, using the SAPRC mechanism, is in agreement with other reactivity scales derived using more sophisticated models (Bergin *et al.*, 1995; 1998) and chemical mechanisms (Derwent *et al.,* 1998; Bergin *et al.*, 1998). Therefore, we conclude that the MIR scale provides a reliable description of hydrocarbon reactivities and, therefore, can be utilized for ozone control strategy decisions.

D. Appropriateness of the MIR Scale

In the previous section we discussed the chemical mechanism from which the MIR scale is derived, and concluded that the SAPRC mechanism reliably predicts the reactivities of VOCs. However, we also need to address the appropriateness of using the MIR scale in California's ozone control strategies. For ozone control strategies, the reactivity scale selected should be designed for the best overall air quality benefit. At the request of ARB, Dr. Carter studied 18 different methods (including MIR, MOIR, and EBIR) of ranking the reactivity of individual VOCs in the atmosphere using a single-cell trajectory model with the SAPRC90 chemical mechanism (Carter, 1994). Dr. Carter concluded that if only one scale is to be used for regulatory purposes in California, the MIR scale is the most appropriate.

Based on this recommendation, the ARB is proposing to use the MIR scale for the proposed amendments to the Aerosol Coatings Regulation. The MIR scale appears to be most accurate for VOC-limited conditions, such as in the South Coast Air Basin, in which VOC controls would be most effective. The MIR scale was also found to correlate well to scales based on integrated ozone yields, even in lower NO_x scenarios (McNair *et al.*, 1992; Bergin *et al.*, 1995; 1998). Currently, the MIR scale is used to derive reactivity adjustment factors in the Low Emission Vehicle/Clean Fuels regulations. (ARB, 1990c). The wider range of VOC incremental reactivities in the MIR scale also allows more choices in a manufacturer's selection of a lower-reactive VOC substitution for a relatively higher-reactive VOC solvent.

As further evidence of the MIR scale being appropriate for California, the VOC/NO_x ratios used for deriving the scale are observed throughout the state of California including such cities as San Diego, Los Angeles, Sacramento, and San Francisco (Carter, 1994).

To further validate the use of the MIR scale, at the suggestion of our Reactivity Scientific Advisory Committee (RSAC) and industry, ARB contracted with Dr. William Stockwell at the Desert Research Institute to conduct a review of the base mechanism (SAPRC99) from which the MIR scale is derived. The result of the review was encouraging. Stockwell concluded that Carter's mechanism represents "state of the science for air quality models" (Stockwell, 1999). The RSAC concurred with Stockwell at its October 8, 1999, meeting and found that SAPRC99 represents the most thoroughly reviewed and best documented chemical mechanism available.

E. Uncertainty of MIR Values

As mentioned above, the science of reactivity is still evolving and improving. Therefore, before assessing whether a reactivity-based control strategy is viable, a clear understanding of the VOCs used, the amount of each VOC used, and the reliability and completeness of the reactivity data available for those VOCs, in a given source category, is essential. Even though the aerosol category is well-defined, in light of gradual refinement of hydrocarbon reactivities in the future, we believe consideration for uncertainty needs to be made when using MIR values in regulatory applications (Carter, 2000). In the following paragraph, we provide information on the type of uncertainties that exist. In Chapter IV, we provide our proposal to address the uncertainty.

As mentioned above, the MIR scale is calculated using the SAPRC chemical mechanism. This chemical mechanism includes experimentally determined or estimated reaction rate constants, as well as product yield (mechanistic) parameters of several thousand reactions. A previous version of the SAPRC mechanism, SAPRC90, was peer-reviewed (Gery, 1991) and the factors contributing to MIR uncertainty were identified (Stockwell *et al.*, 1994; Yang *et al.*, 1995; 1996; Yang and Milford, 1996). Since the development of SAPRC90, significant progress in atmospheric chemistry has been made (Atkinson, 1994; 1997; 2000). To reflect the latest developments in the science of hydrocarbon reactivity, the MIR scale was calculated using the SAPRC99 mechanism (Carter, 2000). The SAPRC99 mechanism is an extension of SAPRC90, which incorporates the latest information on atmospheric chemistry of various reactive organic compounds (ROC) and computational techniques.

Although the MIR values are calculated using a "state-of-the-science" chemical mechanism, the reactivity estimates of some ROC classes are still uncertain. This is partly because of some inconclusive scientific data (see, for example, Atkinson, 2000). To understand the uncertainties, it is important to note that the model calculated MIR value of a chemical is determined using both the base mechanism (in this case SAPRC-99), as well as the mechanism by which an individual compound reacts in the atmosphere. The base mechanism describes the reactions of inorganics and common products formed during the photo-oxidation of ROC. Because this base mechanism is used for calculating the reactivity of all chemicals, any change to the base mechanism is likely to have a "global" effect on MIR values. In other words, the uncertainty associated with changes to the base mechanism would likely be similar for all compounds. On the other hand, improvements in understanding how an individual compound reacts in the atmosphere, and what its reaction products are, would tend to change the MIR value for that compound only.

To assist us with understanding the amount and type of uncertainty associated with some MIR values, uncertainty classification "bins" for ROC reactivity were developed by Dr. Carter (Table II-1 below) (see also Appendix F). This Table provides a qualitative description on the nature of the mechanistic uncertainties of different individual organic compounds, and is reproduced from the documentation titled "Documentation for the SAPRC-99 Chemical Mechanism: An Updated VOC Reactivity Scale" (Carter, 2000).

Table II-1 Uncertainty Ranking and Description

Uncertainty Ranking	Description
1	Considered to be relatively certain, or some uncertainties but reactivity is not expected to change significantly.
2	Uncertain mechanism may change somewhat if refined, but change is expected to be less than a factor of two. If the compound is predicted to inhibit O_3, changes are not expected to affect predicted inhibition, but may affect magnitude of inhibition. This code is also used for compounds whose reactivities are expected to be highly sensitive to ambient conditions or to changes in the base mechanism.
3	Uncertain and may change if compound is studied (or studied further) or estimation methods are updated. Change in MIR could be as much as a factor of two. This code is also used for (1) compounds whose reactivities are expected to be sensitive to the representation of the reactive products, whose accuracy is difficult to test experimentally and (2) compounds whose reactivities are expected to be highly sensitive to ambient conditions or to changes in the base mechanism.
4	Uncertain and is expected to change if compound is studied or estimation methods are updated. It is recommended that uncertainty adjustments be employed in regulatory applications.
5	Non-negligible chance of the estimate being incorrect in significant respects. It is recommended that uncertainty adjustments be employed in regulatory applications.
6	Current mechanism is probably incorrect, but biases in atmospheric reactivity predictions are uncertain. It is recommended that uncertainty adjustments be employed in regulatory applications.
A	The reactivity of this compound is expected to be sensitive to ambient conditions and/or changes in the base mechanism.
B	Some uncertainty due to differences in reactivities of compounds represented by this class. Look at differences among compounds in this class for the magnitude of this uncertainty.
C	Parameterized mechanism used, with uncertain portions adjusted to fit chamber data for representative compounds.
D	Highly simplified “Placeholder” mechanism used to represent the approximate range of reactivity of this compound. Mechanism does not represent an estimate of the actual mechanism of the compound.
E	The current version of this mechanism does not represent these compounds, but based on previous studies they are expected to be O_3 inhibitors under all conditions.

The ARB also contracted with Dr. William Stockwell at the Desert Research Institute in Reno, Nevada, to conduct a peer-review of the documentation for SAPRC-99. This review was conducted to ensure that both the mechanism and MIR scale derived from it are of high scientific quality (Stockwell, 1999). As part of the peer-review of the SAPRC-99 mechanism Stockwell was asked to review MIR value uncertainty and the “bins” developed by Dr. Carter. The final report was approved on November 29, 1999, by the RSAC.

Both Carter and Stockwell came to the conclusion that some adjustment is necessary to account for uncertainty of MIR values, however they differed on how uncertainty should be addressed (Carter, 2000; Stockwell, 1999). Carter's more qualitative assessment based on compound specific uncertainty, suggests that MIR value adjustments are needed for compounds in uncertainty bin numbers four or above. However, the quantitative approach of Stockwell indicated that all MIR values needed to be adjusted, with a slightly higher adjustment to the "less certain" chemicals. To reconcile their conclusions ARB staff reviewed the data to determine how best to apply uncertainty factors in the proposed amendments.

Stockwell performed an analysis of the previously published and the latest MIR values (Carter, 1994; 2000) and found that there was an increase in calculated hydrocarbon reactivities among uncertainty groups. However, no significant relationship was found between the MIR variability (as measured by the coefficients of variation) and assigned uncertainty groups. This observation suggests that common mechanistic factor(s) may be involved in contributing to the MIR uncertainty of all groups and is consistent with the "global effect" of the based mechanism update (see above). In addition, the MIR coefficients of variation reported in Stockwell's analyses are in agreement with those in a Wang and Milford study, in which MIR uncertainties were analyzed based on uncertainties in product yields and chemical rate parameters using Monte Carlo procedures (Yang *et al.*, 1995; Stockwell, 1999).

An additional analysis conducted by Stockwell (1999) showed that the percentage change in MIRs increased with Carter's uncertainty bin assignments. Because MIR values for well-studied chemicals are expected to be relatively "stable" (i.e., small percentage change in MIR value), is an indication that significant improvements have been made, especially, in studying the chemistry of individual "uncertain" VOCs. This interpretation is consistent with Carter's evaluation of compound specific mechanistic uncertainties (as shown in Table II-1) due to available experimental data.

These uncertainties do not need to preclude regulatory development, as long as the source category considered for regulation consists of compounds that have been well-characterized, such that the MIR values are "certain." To deal with uncertainty, within the regulation, adjustment factors can be applied to MIR values for compounds that have not been extensively studied. In this way even if MIR values change, as more data become available, the air quality benefit would be preserved. Our proposal to account for the uncertainties is described in Chapter IV of this Technical Support Document.

F. ARB's Commitment to Reactivity-based Control Strategies

The ARB is committed to evaluating the feasibility of reactivity-based regulations for certain source categories. As evidence of the Board's commitment, the ARB has funded research projects to improve and refine the science of VOC photochemical reactivity. A partial listing of reactivity research funded by ARB is shown below:

- Development of Reactivity Scales Via 3-D Grid Modeling of California Ozone Episodes. 98-309: University of California, Berkeley.

- Improvement of Speciation Profiles for Aerosol Coatings. 98-306: California Polytechnic State University Foundation, San Luis Obispo.

- Linkages Between Measurements of Multifunctional and Polar Organics in Chamber Studies and the Ambient Environment. 98-311: University of California, Davis.

- Atmospheric Chemistry of Selected Linear, Branched, and Cyclic C_{10} Alkane Components of Mineral Spirits. 97-312: University of California, Riverside.

- Development and Application of Improved Methods for Measurement of Ozone Formation Potentials of Volatile Organic Compounds. 97-314: University of California, Riverside.

- Uncertainty Analyses of Chemical Mechanisms Derived from Environmental Chamber Data. 95-331: University of California, Riverside.

- Investigation of Atmospheric Reactivities of Selected Stationary Source VOCs. 95-308: University of California, Riverside.

- Development And Application of an Updated Photochemical Mechanism for VOC Reactivity Assessment. 92-329: University of California, Riverside.

- Product Studies of the Atmospherically Important Reactions of Alkenes and Aromatic Hydrocarbons. 94-311: Statewide Air Pollution Research Center, University of California, Riverside.

- Experimental Studies of Atmospheric Reactivities of Volatile Organic Compounds. A032-096: University of California, Riverside.

- Experimental Investigation of the Atmospheric Chemistry of Aromatic Hydrocarbons and Long-Chain Alkanes. A032-067: University of California, Riverside.

- Development and Application of an Up-To-Date Photochemical Mechanism for Airshed Modeling and Reactivity Assessments. A932-094: University of California, Riverside.

- Review of the Updated Maximum Incremental Reactivity Scale of Dr. William Carter. 98-401: Desert Research Institute; Reno, Nevada.

In addition to funding research, the ARB established the RSAC to advise the ARB on the science of reactivity. The RSAC is an independent panel of scientists with various areas of expertise in the field of atmospheric chemistry. The RSAC has met four times.

Another advisory group, the Reactivity Research Advisory Committee (RRAC), has also been formed. The RRAC is comprised of consumer product manufacturers, raw material suppliers, and other interested stakeholders. The purpose of the RRAC has been to identify important VOCs used in consumer products that warrant further reactivity characterization. The goal has been to ensure that reactivity regulations being developed for consumer products are based on sound VOC reactivity data. This group has met seven times and has provided valuable input on commercially important VOCs to study further to reliably assess their reactivity. Based on their suggestions, additional research was funded by ARB and completed (ARB, 1998).

G. ARB's Current Use of Reactivity

The research funded by the ARB has led to incorporation of VOC reactivity into regulatory strategies. In fact, the ARB was the first regulatory agency to enact a regulation which uses reactivity in a more complex manner than U.S. EPA's "bright-line" approach in their VOC exemption process (ARB, 1990c).

The Low Emission Vehicle/Clean Fuels (LEV/CF) Regulations (ARB, 1990c) established increasingly stringent standards for emissions of nonmethane organic gases (NMOG), NO_x, carbon monoxide, and formaldehyde. As part of the regulation, to encourage use of alternatively fueled vehicles (AFV), the ARB established a process to account for the differences in reactivity of the NMOG emissions. The regulation allows AFVs to have a higher mass of NMOG emissions as long as the ozone formation potential of the AFV emissions are no more than those of a conventionally fueled vehicle (CFV). Emissions are compared through the use of reactivity adjustment factors (RAFs). A RAF is defined as the ratio of the exhaust reactivity (per gram) of an AFV to the exhaust reactivity of a comparable CFV. For an AFV, the mass emission rates of NMOG exhaust are adjusted by the RAF prior to comparison with the emission standards specified in the regulation (ARB, 1990c).

It is important to note that the LEV/CF Regulations established the MIR scale as the most appropriate for use in California regulations. To determine the reactivity of exhaust, the emission rate of each NMOG species is converted to mass of ozone using the MIR scale. These are then summed to estimate the reactivity of the entire exhaust sample (ARB, 1990c).

H. A Reactivity-based Regulation for Aerosol Coatings

The ARB began regulating the VOC emissions from consumer products in 1989 when they adopted the Antiperspirants and Deodorants Regulation. This regulation has been followed with the adoption of mass-based VOC limits for 47 categories of consumer products and 35 categories of aerosol coatings. The current State Implementation Plan (SIP) commitment for consumer products, including aerosol coatings, calls for an additional 30 percent reduction in VOC emissions. In 1995, however, when the SIP was approved, we recognized that reaching this target emission reduction, solely on a mass basis, would be difficult to achieve. In light of that, ARB committed to investigate reactivity-based control strategies for consumer products.

To that end, ARB staff has been working with consumer product stakeholders through the Reactivity Subgroup (see Chapter V for further information) since 1995. This work has culminated in the reactivity-based proposal for aerosol coatings that is the subject of this rulemaking. This effort is viewed as a pilot project to determine the feasibility of additional reactivity-based measures for other source categories.

The ARB adopted revised limits (effective January 1, 2002) for aerosol coatings in 1998 (ARB, 1998a). At that time, the Board recognized that the mass-based limits presented particularly difficult reformulation challenges for water-based aerosol coatings, and directed staff to come back to them with an alternative voluntary reactivity-based proposal. A voluntary reactivity-based regulation would provide a viable compliance path for water-based coatings, given their comparatively low reactivity. However, during development of the voluntary reactivity regulation proposal, staff and several representatives of the aerosol coating industry came to the conclusion that it was preferable to pursue a proposal to replace the January 1, 2002, mass-based VOC content limits with equivalent mandatory reactivity-based limits.

Developing a reactivity-based regulation for chemically formulated products presents new challenges, and may not prove viable for all source categories. Staff also recognizes that the science of reactivity is still evolving and further improvements will need to be made. It is also true that, at present time, not all VOCs have been thoroughly studied to reliably assess their reactivity (Carter, 1999b). For a given consumer products category, such as aerosol coatings, over 100 different VOC ingredients are used in formulations. Therefore, to develop a successful reactivity program for chemically formulated products, the following elements are required:

- an inventory of completely speciated VOC data for individual products within the source category;

- a scale that allows a comparison of VOC reactivities based on appropriate atmospheric conditions;

- an inventory that consists largely of VOCs that have well-characterized reactivities;

- product sales data that allow weighting of VOC reactivities; and,

- a method to establish limits that achieves an equivalent ozone reduction benefit.

The aerosol coatings category was selected for development of the first consumer product reactivity-based regulation because the above elements are available. A recent survey provided detailed speciated VOC data and sales information. A review of the aerosol coatings data also showed that, on a mass basis, over 80 percent by weight of VOCs reported have been sufficiently studied to allow reliable MIR estimates.

A further challenge is to ensure that the already-committed to mass-based VOC reduction is preserved. Therefore, the first step is to convert the VOC tonnage commitment, on a category-by-category basis, into an equivalent ozone reduction. The methodology to calculate reactivity limits, including conversion to an equivalent ozone reduction is discussed in Chapter IV of this Technical Support Document.

ARB staff intends to use this proposed regulation as a pilot project which provides a model for additional reactivity-based regulations.

REFERENCES

Air Resources Board. (1990c), Proposed Regulations for Low Emission Vehicles and Clean Fuels, Staff Report and Technical Support Document. August 1990.

ARB. (1998), 1998 Air Pollution Research, 1989-Present, Research Division, California Air Resources Board.

Air Resources Board. (1998a), Initial Statement of Reasons for the Proposed Amendments to the Regulations for Reducing Volatile Organic Compound Emission from Aerosol Coatings, Antiperspirants and Deodorants, and Consumer Products, October 2, 1998.

Air Resources Board. (1999), The California Consumer Products Regulations, Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 8.5, Article 3, Aerosol Coatings Products, sections 94520-94528.

Andersson-Skold, Y., Grennfelt, P. and Pleijel, K. (1992) Photochemical Ozone Creation Potentials: A Study of Different Concepts. *Journal of the Air and Waste Management Association*, **42**(9), 1152-1158.

Atkinson. (1994), Gas-phase tropospheric chemistry of organic compounds. *Journal of Physical and Chemical Reference Data*, Monograph **No.2**.

Atkinson. (1997), Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and Alkenes. *Journal of Physical and Chemical Reference Data*, **26**, 251-290.

Atkinson. (2000), Atmospheric chemistry of VOCs and NO_x. *Atmospheric Environment*, **34**, 2063-2101.

Bauges, K., (January 1990), “Preliminary Planning Information for Updating the Ozone Regulatory Impact Analysis Version of EKMA, Draft Document.” Source Receptor Analysis Branch, TSD, U.S. EPA, Research Triangle Park, N. Carolina. [*as cited in Carter, W. P. L. (1998) Development and Application of an Up-To-Date Photochemical Mechanism for Airshed Modeling and Reactivity Assessment. Final Report to the California Air Resources Board, Contract No. A932-094.*].

Bergin, M. S., Russell, A. G., and Milford, J. B. (1995), Quantification of Individual VOC Reactivity Using a Chemically Detailed, Three-Dimensional Photochemical Model. *Environmental Science and Technology*, **29**, 3029-3037, 1995.

Bergin M.S., Russell, A.G., and Milford, J.B. (1998), Effects of chemical mechanism uncertainties on the reactivity quantification of volatile organic compounds using a three-dimensional air quality model. *Environmental Science and Technology,* **32**, 694-703.

Bufalini J.J., Walter, T.A., and Bufalini, M.M. (1976) Ozone formation potential of organic compounds. *Environmental Science and Technology*, **10**, 908-912.

Carter, W.P.L. and Atkinson, R. (1989) Computer Modeling Study of Incremental Hydrocarbon Reactivity. *Environmental Science and Technology*, **23**(7), 864-880.

Carter, W.P.L. (1990), A detailed mechanism for the gas-phase atmospheric reactions of organic compounds. *Atmospheric Environment*, **24**, 481-581.

Carter, W.P.L. (1994), Development of Ozone Reactivity Scales for Volatile Organic Compounds. *Journal of the Air and Waste Management Association* **44,** 881-899.

Carter, W.P.L., Pierce, J.A., Malkina, I.L., and Luo, D. (1995), Environmental chamber studies of maximum incremental reactivities of volatile organic compounds. *Atmospheric Environment*, 29, 2499-2511.

Carter, W.P.L. (1996), Computer modeling of environmental chamber measurements of maximum incremental reactivities of volatile organic compounds. *Atmospheric Environment*, 29, 2513-2517.

Carter, W.P.L. (1999b), Development and Application of Improved Methods for Measurement of Ozone Formation Potentials of Volatile Organic Compounds. Quarterly Report to the California Air Resources Board, Contract No. 97-314, for the Period July 1 through September 30, 1999.

Carter, W.P.L. (2000), Documentation of the SAPRC-99 chemical mechanism for VOC reactivity assessment. Final report to California Air Resources Board, Contract No. 92-329 and No. 95-308.

Darnall, K.R., A.C. Lloyd, A.M. Winer, and J.N. Pitts, Jr. (1976), Reactivity Scale for Atmospheric Hydrocarbons Based on Reaction with Hydroxyl Radical. *Environmental Science and Technology,* 10(7):692-696.

Derwent, R. G. and Jenkin, M.E. (1991) Hydrocarbons and the Long-Range Transport of Ozone and PAN across Europe. *Atmospheric Environment*, **25A**(8), 1661-1678.

Derwent, R.G., Jenkin M.E., Saunders, S.M., Piling, M.J. (1998), Photochemical ozone creation potential for organic compounds in northwest Europe calculated with a master chemical mechanism. *Atmospheric Environment*, **32**, 2429-2441.

Dodge, M. C. (1984) Combined Effects of Organic Reactivity and NMHC/NO_x Ratio on Photochemical Oxidant Formation - A Modeling Study. *Atmospheric Environment*, **18**(8), 1657-1665.

Gery, M.W. (1991), Review of the SAPRC-90 mechanism. Final Report to California Air Resources Board, Contract No. A132-055.

Haagen-Smit, A. J., Bradley, C. E. and Fox, M. M. (1952) Formation of Ozone in Los Angeles Smog. Proceedings of the Second National Air Pollution Symposium, Discussions on Fundamental Chemistry and Physics of the Atmosphere, 1952.

Harley, R. A., Russell, A. G., McRae, G. J., Cass., G. R. and Seinfeld, J. H. (1993) Photochemical Modeling of the Southern California Air Quality Study, *Environmental Science and Technology*, **27**(2), 378-388.

McNair, L., A. Russell, and M.T. Odman. (1992), Airshed Calculation of the Sensitivity of Pollutant Formation to Organic Compound Classes and Oxygenates Associated with Alternative Fuels. *Journal of the Air and Waste Management Association* 42:174-178, 1992.

Stockwell, W.R., Yang, Y.J. and Milford, J.B. (1994) A compilation of estimated uncertainty factors for rate constants in W.P.L. Carter’s detailed mechanism. Final Report to Auto/Oil Air Quality Improvement Program, Coordinating Research Council.

Stockwell, W.R. (1999), Review of the updated maximum incremental reactivity scale of Dr. William Carter. Final Report to California Air Resources Board. Contract No. 98-401.

Yang, Y.J., Stockwell, W.R., and Milford, J.B. (1995), Uncertainties in incremental reactivities of volatile organic compounds. *Environmental Science and Technology*, **29**, 1336-1345.

Yang, Y.J., Stockwell, W.R., and Milford, J.B. (1996), Effect of chemical product yield uncertainties on reactivities of VOCs and emissions from reformulated gasolines and methanol fuels. *Environmental Science and Technology*, **30**, 1392-1397.

Yang, Y.J. and Milford (1996), Quantification of uncertainty in reactivity adjustment factors from reformulated gasoline and methanol fuels. *Environmental Science and Technology*, **30**, 196-203.