CALIFORNIA'S REACTIVITY PROGRAM

Eileen McCauley
California Air Resources Board

This presentation will touch on four aspects of California's reactivity program. First, it will cover ARB's existing Low Emission Vehicle/Clean Fuels regulation and a consumer products regulation which is under development. Second, it will provide a very brief summary of some of the research the California Air Resources Board (ARB) is currently funding in the field of reactivity. Lastly, it will cover the internal reactivity team and external advisory groups.

Before discussing reactivity, however, it is necessary to provide some background on California's VOC regulations in general. California has an effective system of VOC control based on mass reductions. This concept is continued in California's State Implementation Plan for Ozone which contains adopted and proposed mass-based reductions in VOC emissions for several different source categories. Thus, it is important that any regulation that uses reactivity provides equivalent ozone reductions to the reductions predicted from mass-based controls. However, mass-based controls alone may not be sufficient for California to attain the federal ozone standard. For this reason, the ARB is investigating possible uses of hydrocarbon reactivity in our regulations. In addition, reactivity may provide a means for designing control measures that are more cost effective and provide greater flexibility to the affected industries.

The ARB was the first regulatory agency to enact a regulation that uses reactivity in a more complex manner than the simple two bin exemption type of regulation. In the late 1980s, a method was needed to compare the emissions of alternatively fueled vehicles (i.e., ones that use a fuel other than gasoline, such as compressed natural gas or methanol) to the emissions from gasoline fueled vehicles. An advisory board was formed, and recommended the use of reactivity to adjust the weight of emissions so that the limits reflect the ozone-forming potential of the emissions rather than the simple mass. The Low Emission Vehicle/Clean Fuels regulation, which was adopted in 1990, uses Reactivity Adjustment Factors (RAF) to set the limits on vehicle emissions. A RAF

is the ratio of the exhaust reactivity of the alternative fueled vehicle to the exhaust reactivity of the conventionally fueled vehicle. The exhaust reactivity is calculated by taking the sum of the mass fraction of each compound times the reactivity of the compound summed over all the compounds in the exhaust.

In designing this regulation, several important scientific issues needed to be addressed. The first was the selection of a reactivity scale to be used in the regulation. Dr. William P. L. Carter's Maximum Incremental Reactivity (MIR) scale was chosen by ARB because it was determined to be the most appropriate reactivity scale to complement California's NOx control program. The MIR scale is defined in terms of environmental conditions in which ozone production is most sensitive to changes in hydrocarbon emissions and, therefore, represents conditions where hydrocarbon controls are most effective. As such, it complements ARB's NOx control program, which is designed to reduce ozone under conditions that are sensitive to NOx reductions. Another issue was the degree of uncertainty in the RAFs. Because RAFs are ratios of reactivities, they are similar to relative reactivities. A number of studies have found that relative reactivities have much smaller uncertainties than absolute reactivities. Work done by Yang and Milford found that uncertainties in RAFs are on the order of 15%, while uncertainties in the associated MIRs values were closer to 30 to 70%.

ARB is currently developing the California Low Emissions and Reactivity (CLEAR) regulation for aerosol coatings which would establish reactivity based limits as a voluntary alternative to the mass-based VOC limits for aerosol coatings. In this proposed regulation, a product's reactivity would be calculated as the sum of the weight percent of each VOC multiplied by its MIR value. The regulation is currently in the development stage and two public workshops will be held in the coming months. The dates for the workshops will be posted at http://www.arb.ca.gov/consprod/regact/aerocoat/aerocoat.htm. It is scheduled to be presented to the Board for consideration in the spring of 2000.

In designing a regulatory option that will include reactivity, there are a number of challenges that need to be met. First of all, it is necessary that the regulation provide equivalent ozone reductions as the mass-based regulation. It must be enforceable and

should be flexible, simple, and cost effective. As previously stated, there are also a number of specific technical challenges which need to be addressed. The issue of uncertainty in the LEV regulation has been discussed. A different approach is being considered for the proposed consumer product regulation. For that regulation Dr. Carter was asked to assign each compound to a category or bin based on the degree to which he thinks the MIR value could change based on future research. The majority of compounds in the aerosol coating inventory belong to bins which are expected to change relatively little. The MIRs of compounds in bins with higher uncertainty may be adjusted to reflect the higher uncertainty.

Another technical challenge that must be met is the development of accurate chemical speciation profiles. To calculate the reactivity of a mixture, whether vehicle exhaust or a consumer product, it is necessary to know the identities and quantities of all of the different compounds in the mixture. The ARB is committed to improving their speciation profiles and is currently funding research to develop improved profiles for aerosol coatings.

An enormous amount of research has been done to develop the science of reactivity to the point where it can be used in a regulation with confidence. The ARB is just one of many funding agencies that have supported research in the fields of atmospheric chemistry, mechanism development, uncertainty analysis, and the calculation and/or measurement of actual reactivity values. ARB is currently funding a number of research projects that are related to reactivity. One such project is investigating the primary products formed from the reaction of OH radical with three model C10 alkanes: n-decane, 3,4-diethylhexane, and n-butylcyclohexane. Another project will develop improved methods for evaluating reactivity, as well as methods to assess the reactivity of “sticky” VOCs that cannot be studied using standard methods. ARB is also funding a project to determine which environmental chamber parameters contribute most to the uncertainty in the estimate of reactivity for selected aromatic and oxygenated hydrocarbons.

A related project, which will be discussed at the October 8, 1999 meeting of the Reactivity Scientific Advisory Committee (RSAC), is a peer review of SAPRC99 by Dr. William Stockwell. SAPRC99, Dr. Carter’s latest chemical mechanism, will be used to

calculate the MIR values used in the CLEAR regulation. On the recommendation of the Reactivity Scientific Advisory Committee and Dr. Carter a peer review of SAPRC99 was funded. The purpose of the review was to ensure that the reactivity values in the CLEAR regulation are the best that are available with the current base of knowledge.

Other research currently underway is investigating the reactivities of several VOCs, such as cyclohexane, cyclhexanone, octanol, and several other compounds; developing improved speciation profiles for aerosol coatings; and compiling a public database of potentially useful solvents with lower reactivities. Lastly, ARB is funding a study to determine reactivity values using an urban airshed model and compare the calculated reactivity values to the MIR values.

The third aspect of ARB's reactivity program is an internal reactivity team. The team consists of staff from several different divisions and has the goal of investigating how reactivity may fit into existing and future board programs. The team reviews the effectiveness of ARB's current uses of reactivity, examines the technical basis for quantifying reactivity, and provides recommendations to the Executive Officer regarding the use of reactivity in regulatory programs. Members of the team recently presented two papers at the Air Pollution 99 conference: *Assessment of the organic compound reactivity concept for regulatory applications in California* and *Photochemical reactivity of organic compounds in central California: A grid-based modeling study*. Copies of either of these papers can be obtained from Dr. Ajith Kaduwela, team leader, at akaduwel@arb.ca.gov.

The last aspect of ARB's reactivity program is a mechanism to benefit from the expertise of scientists and stakeholders outside the Board. ARB has formed two advisory committees, the Reactivity Scientific Advisory Committee (RSAC) and the Reactivity Research Advisory Committee (RRAC). The RSAC consists of six noted experts in the fields of atmospheric chemistry: John Seinfeld, Roger Atkinson, Jack Calvert, Harvey Jeffries, Jana Milford and Ted Russell. This committee reviews issues concerning reactivity and makes recommendations to the Board, based on their knowledge of the science. The RRAC is comprised of over 20 representatives from industry. These committee members provide technical assistance on reactivity related issues for consumer products and aerosol coatings. For example, the RRAC provided

valuable suggestions which helped guide ARB's research on MIR values for compounds found in consumer products.

In conclusion, the ARB believes that reactivity-based regulations, when properly designed to provide ozone reduction that is equivalent to that provided by mass-based regulations, can be an effective ozone control strategy while offering compliance flexibility to affected industries. A large body of scientific information is available to support the development of these reactivity-based regulations. However, to further refine the effectiveness of this ozone control strategy, the ARB will continue to support additional research to increase the understanding of hydrocarbon reactivity. The California Air Resources Board believes that hydrocarbon reactivity has the potential to add significantly to its ability to protect public health and welfare through the effective and efficient reduction of air pollution in a cost-effective manner.