

California Environmental Protection Agency



Staff Report: Initial Statement of Reasons for Proposed Rulemaking

**PUBLIC HEARING TO CONSIDER PROPOSED AMENDMENTS
TO THE TABLES OF MAXIMUM INCREMENTAL REACTIVITY
(MIR) VALUES**

**Date of Release: September 18, 2009
Scheduled for Consideration: November 3, 2009**

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Acknowledgements

Staff wishes to thank and acknowledge John DaMassa and Ajith Kaduwela of the Air Resources Board's Planning and Technical Support Division for sponsoring the SAPRC-07 peer review, the Reactivity Research Advisory Committee for participating in the amendment process, and Priya Singh for her assistance for preparing report appendices.

This report has been prepared by staff of the California Air Resources Board. Publication does not signify that the contents reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Executive Summary

Proposal Summary

The Air Resources Board (ARB or Board) staff proposes to revise the table of Maximum Incremental Reactivity (MIR) values¹ for existing reactive organic compounds, and add about 380 new compounds or mixtures with MIR values, into section 94700 of title 17, California Code of Regulations (CCR). We also propose to modify MIR values for 24 bins of hydrocarbon solvents, in section 94701, title 17, CCR.

Background

The existing Tables of MIR Values are based on work of Dr. William Carter at the University of California, Riverside that was mainly conducted in the 1990's. The Tables of MIR Values are contained in two sections of title 17, CCR. Section 94700 contains the MIR values for individual reactive organic compounds and mixtures. Section 94701 contains the MIR values for 24 different bins of hydrocarbon solvents.

At its June 22, 2000, public hearing, the ARB approved amendments to the "Regulation for Reducing the Ozone Formed from Aerosol Coating Products", and approved Tables of MIR Values. The main component of the rulemaking was to establish reactivity limits for 36 aerosol coating categories based on the MIR scale. In Resolution 00-22, which approved the rulemaking action, the Board directed the Executive Officer to review the MIR values periodically to determine if modifications to the MIR values were warranted. This is because the chemical mechanism used to calculate the MIR values has been evolving and improving, as new chemical information becomes available. Since any changes to the MIR values would be technical in nature, the Board also delegated to the Executive Officer the authority to adopt regulatory amendments to the Tables of MIR Values, and to conduct public hearings and take other appropriate actions to make such amendments. This delegation of authority allows the Executive Officer (or his delegate) to conduct these activities on behalf of the multi-member Board, as provided in Health and Safety Code sections 39515 and 39516.

At its December 3, 2003, public hearing, the ARB added about 100 new compounds with associated MIR values into section 94700 of title 17, CCR, and updated the MIR values for 14 existing reactive organic compounds whose MIR values changed by at least 5 percent. The impetus for these changes was additional data and analyses provided by Dr. Carter. No change was made to section 94701 of title 17, CCR.

Description of the Proposed Regulatory Action

Staff proposes amendments to the existing MIR values contained in section 94700, title 17, CCR. Among other things, the MIR values used to calculate

¹ An MIR value describes the maximum amount of ozone likely to be formed by a volatile organic compound (VOC) reacting in the atmosphere. It is expressed in gram O₃ / gram VOC.

aerosol coating product reactivity and the reactivity limits specified in the aerosol coatings regulation (see title 17, CCR, section 94520-94528). The proposed changes to section 94700 are based on updated MIR values provided by Dr. Carter, which were peer reviewed by independent researchers and approved by the ARB's Reactivity Scientific Advisory Committee (RSAC) at a publically noticed meeting on March 25, 2009.

Staff proposes to add about 380 new compounds and mixtures, with their associated MIR values, to section 94700. These new compounds were added by Dr. Carter into his tabulation of MIR values while making assignments for the newly updated SAPRC-07 mechanism. Several of the new compounds were added at the request of stakeholders. Staff also proposes to update the MIR values for all the compounds that are currently listed in section 94700. A new column labeled "New MIR Value [Effective Date]" will be added to section 94700 to display the updated MIR values for the currently listed compounds, as well as the MIR values for the newly added compounds.

Finally, staff proposes to revise the MIR values for 24 bins of hydrocarbon solvents contained in section 94701, title 17, CCR. This revision is based on an alternative calculation scheme developed by Dr. Carter, which was made possible by the greater availability of solvent compositional data since 2000, and by the updated MIR values for individual hydrocarbon compounds associated with the development of the SAPRC-07 chemical mechanism. A new column labeled "New MIR Value [Effective Date]" will be added to section 94701 to display the updated MIR values for the bins.

Although staff proposes to update the MIR values for all the existing compounds currently listed in section 94700 and the 24 hydrocarbon mixtures in section 94701, it should be noted that the MIR values dated July 18, 2001 must continue to be used by aerosol coating manufacturers. When the aerosol coatings regulation was developed, to provide stability to manufacturers as MIR values are updated to reflect improved science, the regulation specifies that the MIR values dated July 18, 2001 are to be used and those values are not to change until June 1, 2007 [see § 94523 (h)(2)(A)]. The exception to this is that any new compounds added in subsequent amendments to the Tables of MIR Values can be used once legally effective [see § 94523 (h)(2)(B)]. The 2007 date was put into the regulation to provide manufacturers a minimum timeframe in which the MIR values would remain the same.

The MIR values dated July 18, 2001, were also used as the basis for the reactivity limits for aerosol coating products. To ensure that the air quality benefits continue to be preserved it is important that the same set of MIR values are used both for the VOC reactivity limits and calculation of PWMIR. Therefore, while we are proposing to amend the Tables of MIR Values, the MIR values dated July 18, 2001, must continue to be used by aerosol coatings manufacturers until such time as the Aerosol Coatings Regulation is amended.

Any new compound proposed for addition to the Table in this rulemaking, with its associated MIR value, can be used, however.

This Initial Statement of Reasons (ISOR) describes the ARB staff's proposals and justifications for amending the Tables of MIR Values contained in sections 94700 and 94701 of title 17, CCR. The impacts on existing aerosol coating products, air quality, the environment, and the economy are expected to be neutral or slightly positive.

Recommendation

Staff recommends that the Executive Officer adopt these regulatory proposals. These proposals would help ensure that the ARB's reactivity-based VOC regulations are based on the most up-to-date science. In addition, it would provide more choices to the aerosol coating manufacturers by allowing the use of about 380 new compounds in aerosol coating formulations.

1 Introduction

This Initial Statement of Reasons describes the Air Resources Board (ARB or Board) staff's proposal and justification for amending the Tables of Maximum Incremental Reactivity (MIR) Values contained in sections 94700 and 94701 of title 17 in the California Code of Regulations (CCR). This report describes the scientific background and the process for developing these amendments. Staff proposes to add about 380 new compounds with associated MIR values into section 94700 and to update the MIR values for the existing compounds listed in that section. Staff also proposes to revise the MIR values for 24 bins of hydrocarbon solvent mixtures in section 94701. In addition, this report describes the impacts of the proposed amendments on the existing aerosol coating products, and the bin system, and other relevant information.

Reactivity is the term used for the quantification of how much different VOCs contribute to the photochemical formation of tropospheric ozone.

1.1 Regulatory Background

At its June 22, 2000, public hearing, the Air Resources Board approved amendments to the Regulation for Reducing the Ozone Formed from Aerosol Coating Products (the "Aerosol Coating Product Regulation;" sections 94520–94528, title 17, CCR), and proposed MIR Values. In Resolution 00-22, which approved that rulemaking action, the Board directed the Executive Officer to review the MIR values periodically to determine if modifications to the MIR values are warranted. Since any changes to the MIR values would be technical in nature, the Board also delegated to the Executive Officer the authority to adopt regulatory amendments to the Tables of MIR Values, and to conduct public hearings and take other appropriate actions to make such amendments. This delegation of authority allows the Executive Officer (or his delegate) to conduct these activities on behalf of the Board, as provided in Health and Safety Code sections 39515 and 39516.

In 2003, the ARB staff proposed amendments to Tables of MIR Values. Based on work by Dr. Carter (2003) of the University of California, Riverside (UCR), and in consultations with stakeholders, staff concluded that modifications to the Tables of MIR Values were needed. Dr. Carter provided a list of about 100 new VOCs with their respective MIR values, as well as a revised list of MIR values that have changed non-negligibly. Staff proposed to amend the MIR values for VOCs whose MIR values changed by at least 5 percent. The amended regulation was adopted on December 3, 2003, and became legally effective on June 7, 2004. That rulemaking added about 100 new compounds with associated MIR values and updated MIR values for 14 compounds.

The MIR values for hydrocarbon solvents that are in section 94701 are based on the average of their mean boiling ranges, aromatic content, and alkane content. These chemical characteristics allowed ARB staff to develop a system to assign

MIR values for solvent mixtures used in aerosol coatings that otherwise did not have an individually-assigned MIR value. This system consists of 24 bins of hydrocarbon solvents, classified as aliphatic or aromatic. Aliphatic hydrocarbon solvents consist predominantly of saturated (alkyl) hydrocarbons, while aromatic hydrocarbon solvents consist of monocyclic (single ring) and/or polycyclic (multiple ring) aromatic compounds. Subsequently, additional information became available on the chemical composition of hydrocarbon solvents represented in these bins. With this additional information, along with revised MIR values for individual compounds based upon the revised chemical mechanism SAPRC-07, an alternative method to calculate bin values (Carter and Malkina, 2005) was developed.

1.2 Scientific Background

As discussed in previous amendments (ARB, 2000; 2003), the Tables of MIR Values are based on atmospheric chemical research that began in the mid-1970s, and continues. Numerous peer-reviewed scientific journal articles have been published on the concept of photochemical reactivity. The ARB has funded an extensive research program for more than 20 years to improve our understanding of the science of reactivity with the overall conclusion that consideration of VOC reactivity has merit as an ozone control strategy in California. The reactivity scale “Maximum Incremental Reactivity” (MIR), originally developed in early 1990s (Carter, 1994) will continue to be used in this proposed amendment since the scale is most appropriate for conditions where VOC controls would be most needed to reduce ambient ozone concentrations.

Since the last amendments (ARB, 2003), significant improvements have occurred to the SAPRC chemical mechanism, on which MIR values are based. For example, SAPRC-07 contains updated mechanisms for aromatic hydrocarbons, new mechanisms for chlorine chemistry, and improved mechanisms for amines. Because of these significant improvements, the MIR values resulting from SAPRC-07 have changed substantially from those derived from the previous mechanism, i.e., SAPRC-99. Hence, amendments to the Tables of MIR Values are needed to ensure that the best possible science is used in ARB’s regulations.

2 Scientific Basis for the Proposed Amendments

A number of activities provided the basis for the proposed amendments to the Tables of MIR Values that meet the Board’s directive. The first step toward review of the Tables to determine if modifications to the Tables are warranted began in 2003, when staff requested Dr. Carter at UCR to provide an updated chemical mechanism for use in calculating the MIR values, as well as the most current MIR values. A draft version of his final draft report (Carter, 2009a), was discussed at the Reactivity Research Advisory Committee (RRAC) meeting on August 28, 2007. In 2008-2009, a version of this report (Carter, 2009a) was peer-reviewed by four internationally respected experts in the field. This report and the results of the peer-reviews were distributed to the members of the ARB’s

Reactivity Scientific Advisory Committee (RSAC), which reviewed and approved it on March 25, 2009 (Appendix D). Based on Dr. Carter's report, the peer review, RSAC approval, and consultations with stakeholders, staff concluded that modifications to the "Tables of MIR Values" should be proposed.

2.1 SAPRC-07 Chemical Mechanism

The SAPRC-99 mechanism represented the state-of-the-art when the regulations were adopted in 2000. Since then, with continued progress in basic atmospheric chemistry, new information has become available concerning the reactions and ozone impacts of many individual VOCs. In addition, ARB staff is obligated to periodically review the reactivity scales used in regulations so they reflect the current state-of-the-science. Since the last update was made in 2003, a review and update of the MIR scale is now appropriate.

One of the major applications of the SAPRC mechanism is calculation of ozone reactivity scales for VOCs, including the MIR scale. The SAPRC-99 mechanism has been used to calculate MIR and other reactivity scales for many types of VOCs. A major reason to update this mechanism is to obtain an updated MIR scale based on the improved science.

To that end, ARB funded Dr. Carter to develop and document an updated version of the SAPRC mechanism, and use it to derive updated MIR and other VOC ozone reactivity scales. The report "Development of Ozone Reactivity Scale for Volatile Organic Compounds" (Carter, 2009a) sets forth the development of a completely updated version of SAPRC-99 (designated 'SAPRC-07'), and provides an update to the associated MIR values. The bulk of this report consists of the documentation of this mechanism and its evaluation, and the MIR scales. Most notably, SAPRC-07 contains updated mechanisms for aromatic hydrocarbons, new mechanisms for chlorine chemistry, and improved mechanisms for amines.

The performance of the SAPRC-07 mechanism in simulating ozone formation (and other measures of reactivity) was evaluated by conducting model simulations of over a thousand environmental chamber experiments carried out in several different environmental chambers at four laboratories. For the vast majority of the VOCs and mixtures, the performance for SAPRC-07 was similar to that of SAPRC-99, though mechanism parameters had to be adjusted to obtain comparable fits.

2.2 Scientific Peer Review

The ARB contracted with independent scientists with expertise in atmospheric chemistry to provide peer reviews of Dr. Carter's report and the associated MIR values. These peer reviewers include:

- R.G. Derwent, M.E. Jenkin, and M.J. Pilling, United Kingdom (2008);

- M. Azzi, S. White, and D. Angove, Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia (2008);
- R. Harley, University of California at Berkeley (2009);
- W.R. Stockwell, Howard University (2009).

Dr. Carter (2009b) responded to these reviews, and concluded that changes to the mechanism were not currently indicated. However, the review of Stockwell (2009) revealed an error in the base mechanism, and Dr. Carter independently found errors concerning an organic species that needed to be corrected. The SAPRC-07 mechanism was therefore revised, its evaluation and documentation updated, and its reactivity scales were recalculated (Carter, 2009a). Although none of the current MIR values differ from the values of a previous version tabulated by Carter (2007) by more than 4%, the proposed Table of MIR Values incorporates these changes.

2.3 Reactivity Scientific Advisory Committee (RSAC)

In 1996, as a commitment to ensuring that the use of reactivity as an ozone control strategy was based on the best possible science, the ARB formed the Reactivity Scientific Advisory Committee (RSAC), to provide scientific advice on using reactivity in California's regulations. The RSAC makes recommendations to the ARB on the science related to VOC reactivity, and plays a critical role in reactivity-related activities at the ARB. The RSAC is made up of six independent scientists with expertise in atmospheric reactivity of VOCs:

- Prof. John Seinfeld, California Institute of Technology (Chairman)
- Prof. Roger Atkinson, University of California, Riverside
- Dr. Jack Calvert, National Center for Atmospheric Research (retired)
- Prof. Harvey Jeffries, University of North Carolina, Chapel Hill
- Prof. Jana Milford, University of Colorado, Boulder
- Prof. Ted Russell, Georgia Institute of Technology

Because the amendments proposed in this document are premised from a "scientific basis", an external scientific peer review is required by Health and Safety Code section 57004 for the scientific portion of the proposed amendments, i.e., the updated MIR values. To comply with this requirement, staff requested the RSAC to review the updated MIR values.

Previously, the RSAC has supported and approved of the use of the reactivity concept (i.e., MIR scale) in regulatory control strategies. At its meeting on March 25, 2009, the RSAC accepted the four peer reviews on the SAPRC-07 chemical mechanism used in the MIR scale and endorsed the use of SAPRC-07 as representing the state-of-the-art in urban atmospheric chemical reaction mechanisms. In addition, the RSAC found that the updated MIR values were arrived at in an appropriate scientific manner (Appendix D).

3 Revision to MIR Values for Individual Compounds

ARB staff has compared data for VOCs and mixtures with SAPRC-07 derived MIR values, with those in regulation based on the 2003 update to SAPRC-99 chemical mechanism. The comparison found that about 380 additional VOCs and mixtures and associated MIR values have been added. We also found that use of the SAPRC-07 mechanism has led to a general decrease in MIR values of about 5 percent for the VOC base mixture, and changes in compound-specific mechanisms has led to an average decrease (excluding outliers) in relative MIR values of about 7 percent. This translates into an overall decrease in MIR values for VOCs of about 12 percent. Some additional points are summarized below:

- The change in MIR value was less than 30 percent for about 92 percent of the VOCs, compared to the 2003 Table.
- MIR values changed by more than 10 percent for 70 percent of the VOCs tabulated in 2003.
- About 70 VOCs have MIR values that changed more than 30 percent (see Table 1).
- Amines and halogenated compounds had the largest changes (excluding 3-methoxy-1-butanol, where the SAPRC-99 mechanism had an error).

Based on our review, staff proposes that the regulatory MIR values dated July 7, 2004 derived using the SAPRC-99 mechanism be replaced in its entirety by the values derived from SAPRC-07 (Carter, 2009a), with the exception that negative values be replaced by zero. Although the change in MIR values was less than 30 percent for most of the VOCs, most of the VOCs changed over 10 percent. We are also proposing that the approximately 380 additional compounds and mixtures, with their associated MIR values, be added to the list. The newly added compounds fall into several chemical classes and are listed in Appendix B.

Appendix A contains a revised table for individual compounds that generally includes the same compounds listed in the previous version, as well as several new compounds. The revised table has been re-ordered to list compounds by chemical class. However, a few compounds listed in the previous table were found to be listed erroneously; “1-methyl-*trans*-2-pentene” is not listed in the revised table, and “methyl ethyl ketone oxime” was double-listed in the previous table through inclusion of its synonym “methyl ethyl ketoxime.”

Regarding compounds with negative numbers (ozone inhibitors) in Dr. Carter’s listing of MIR values, the most significant deviation from zero was found with some amines. Dr. Carter (2009a) discussed a reaction mechanism for the amines based on available chamber data, but concluded that their ozone impact is uncertain due to variations in the amount of emitted amines available for reaction in the gas-phase. In consideration of such uncertainties, staff proposes (for regulatory purposes) to use a “zero” MIR value for some amines and any other possible ozone inhibitors, which is consistent with the MIR values previously adopted by ARB (2000, 2003). In addition, six compounds, marked

with ** in Appendix A, are still assigned “upper limit” MIR (ULMIR) values. In these cases, insufficient data were available to derive an MIR value. However, to allow continued use of these compounds, staff proposes the revised upper limit MIR values described in Dr. Carter’s report (2009a) to be used in this update.

Table 1. Compounds and Mixtures with
MIR Value Changes of More than 30 percent

Compound	MIR (gm O ₃ / gm VOC)		
	2003	2009	Change
2-amino-2-methyl-1-propanol	15.08	-2.57	
2-(chloromethyl)-3-chloropropene	1.13	6.85	506%
3-methoxy-1-butanol	0.97	3.75	287%
1,2-dichloroethane	0.10	0.21	107%
<i>trans</i> -1,2-dichloroethene	0.81	1.65	103%
nitroethane	12.79	0.06	-100%
2-nitropropane	16.16	0.10	-99%
nitromethane	7.86	0.06	-99%
1-nitropropane	16.16	0.20	-99%
peroxyacetic acid	12.62	0.52	-96%
1,2-dibromoethane	0.05	0.10	96%
methyl ethyl ketoxime	22.04	1.52	-93%
morpholine	15.43	1.85	-88%
triethyl amine	16.60	3.66	-78%
dimethyl amine	9.37	2.95	-69%
mesityl oxide (2-methyl-2-penten-4-one)	17.37	6.31	-64%
1-amino-2-propanol	13.42	5.17	-61%
3,5,5-trimethyl-2-cyclohexenone	10.58	4.48	-58%
indene	3.21	1.48	-54%
unspeciated C9 alkane(s)	2.13	0.99	-54%
propionic acid	0.79	1.17	49%
triethanolamine	2.76	4.08	48%
phenol	1.82	2.69	48%
furan	16.54	8.86	-46%
dichloromethane	0.07	0.04	-45%
ARB hydrocarbon bin 5	2.56	1.47	-43%
diethanolamine	4.05	2.36	-42%
ARB hydrocarbon bin 20	1.49	0.89	-41%
ARB hydrocarbon bin 3	2.52	1.53	-39%
1,3-diethyl-5-pentyl cyclohexane	0.99	0.61	-39%
1,2-propylene glycol diacetate	0.94	0.58	-39%
ARB hydrocarbon bin 4	2.24	1.37	-39%
isobornyl methacrylate	8.64	5.37	-38%
methane	0.01	0.01	38%
unspeciated C11 aromatics	4.96	6.82	38%
1,1,2-trichloroethane	0.06	0.08	37%

Compound	MIR (gm O ₃ / gm VOC)		
	2003	2009	Change
2-methyl-3,5-diisopropyl heptane	0.78	0.49	-37%
ARB hydrocarbon bin 1	2.08	1.33	-36%
6-methyl tridecane	0.62	0.40	-36%
C13 monosubstituted naphthalene	3.86	2.47	-36%
C12 monosubstituted naphthalene	4.20	2.69	-36%
6-methyl tetradecane	0.57	0.37	-36%
methyl naphthalenes	4.61	2.96	-36%
1-methyl naphthalene	4.61	2.96	-36%
2-methyl naphthalene	4.61	2.96	-36%
5-methyl dodecane	0.64	0.41	-36%
1,1-dichloroethane	0.10	0.07	-35%
4,5-dimethyl-heptyl acetate	0.96	0.63	-35%
2-methyl-2,4-pentanediol	1.04	1.39	34%
<i>p</i> -xylene	4.25	5.69	34%
chloroform	0.03	0.02	-33%
unspeciated C12 aromatics	4.53	6.02	33%
1-octanol	2.01	1.35	-33%
2,7-dimethyl-3,5-diisopropyl heptane	0.69	0.47	-33%
5-methyl undecane	0.72	0.49	-32%
acetic acid	0.50	0.66	32%
4,7,9-trimethyl-decyl acetate	0.55	0.37	-32%
ARB hydrocarbon bin 12	0.81	0.55	-32%
5-methyl-hexyl acetate	0.79	0.54	-32%
4-octanol	3.07	2.10	-32%
3-isopropyl-heptyl acetate	0.71	0.49	-31%
2,3,6-trimethyl-4-isopropyl heptane	1.24	0.85	-31%
ARB hydrocarbon bin 19	0.88	0.61	-31%
3,4-diethyl hexane	1.20	0.83	-31%
ARB hydrocarbon bin 11	0.91	0.63	-31%
3,4-dimethyl-hexyl acetate	1.16	0.81	-30%
2,2,3,3-tetramethyl butane	0.44	0.31	-30%

4 Revision to MIR Values for Hydrocarbon Solvent Bins

The calculation of the ozone impacts of hydrocarbon solvents (HCS) requires approximations because they are complex mixtures with exact compositions usually unknown. Reactivity estimates for complex hydrocarbon mixtures can be made, provided sufficient compositional information is available. However, the type of compositional analysis required for a comprehensive reactivity evaluation requires extensive analytical information that is expensive to obtain and is not generally probably available for most hydrocarbon solvent products. Because of this, ARB staff (2000) developed and proposed a “bin” system with MIR values

estimated for 24 different types of hydrocarbon solvents. These bins were subsequently adopted.

The SAPRC-07 chemical mechanism provides revised MIR values for most HCS constituents. Since ARB staff proposes a major revision to the Tables of MIR Values, revisions for hydrocarbon solvent bins is also appropriate. The current method assigns bin MIR values based on correlations between boiling points and MIR values. To calculate the MIR for each bin, an alternative method was developed by Carter and Malkina (2005) to derive a chemical composition for each hydrocarbon bin, and uses MIR values for each of the constituents.

4.1 Current Method

Because of the need to derive reactivity estimates for hydrocarbon solvents in its aerosol coatings regulations, the ARB (2000) developed a general “bin” procedure to estimate MIR values for hydrocarbon solvents based on their boiling point ranges, aromatic fractions, and types of alkanes primarily present. This method assumes that the overall reactivity of a hydrocarbon solvent can be separated into the contribution from its chemical constituent classes: *n*-alkanes, branched-alkanes, cycloalkanes, and substituted aromatics. A boiling point-MIR relationship was developed for each class, and composition-weighted surrogate mixtures were used to calculate the hydrocarbon solvent reactivity for different boiling ranges. This method is described in Appendix C of the staff report (ARB, 2000). This estimation technique was tested against hydrocarbon solvents compositions provided by the Chemical Manufacturers Association (now American Chemistry Council). The bin specifications and their corresponding existing MIR assignments are shown on Table 2 (ARB, 2003). The speciation data were scarce for aromatic hydrocarbon solvents, and the surrogate mixture approach was not used for determining their reactivity. Instead, the aromatic hydrocarbon solvent classification scheme (bin 21-24) was constructed based on the boiling range.

4.2 Proposed Revision

Carter and Malkina (2005) developed an alternative method to determine MIR values for the HCS bins, using more detailed composition data that had become available. Their main sources of data were the ARB 2000 solvent database, and data from an ARB-funded research report (Censullo et al., 2002). Additional data were provided by the American Chemistry Council (Jaques, 2004) and Exxon-Mobil (Medeiros, 2004). Carter and Malkina (2005) analyzed the available compositional data and other relevant information for representatives of various types of hydrocarbon solvents, and developed a method to estimate MIR values for hydrocarbon solvents with limited compositional information.

Instead of the ARB (2000) method of assigning bin MIR values based on correlations between boiling points and MIR values for various types of compounds, the alternative method derives a chemical composition for each hydrocarbon solvent bin, and then uses the MIR values for the constituents to calculate the MIR for each bin. Using this method, Carter (2009a) included in his tabulation bin MIR values based on the SAPRC-07 mechanism. Table 2 shows the resulting MIR values and compare them to the existing bin MIR values.

Table 2. Comparison of Hydrocarbon Solvent Bin MIR Values

Bin	Average Boiling Point (Degree F)	Criteria	MIR 2001*	MIR 2009**
1	80-205	Alkanes (< 2% Aromatics)	2.08	1.33
2	80-205	N- & Iso-Alkanes (\geq 90% and < 2% Aromatics)	1.59	1.23
3	80-205	Cyclo-Alkanes (\geq 90% and < 2% Aromatics)	2.52	1.53
4	80-205	Alkanes (2 to < 8% Aromatics)	2.24	1.37
5	80-205	Alkanes (8 to 22% Aromatics)	2.56	1.47
6	>205-340	Alkanes (< 2% Aromatics)	1.41	1.08
7	>205-340	N- & Iso-Alkanes (\geq 90% and < 2% Aromatics)	1.17	0.95
8	>205-340	Cyclo-Alkanes (\geq 90% and < 2% Aromatics)	1.65	1.34
9	>205-340	Alkanes (2 to < 8% Aromatics)	1.62	1.35
10	>205-340	Alkanes (8 to 22% Aromatics)	2.03	1.88
11	>340-460	Alkanes (< 2% Aromatics)	0.91	0.63
12	>340-460	N- & Iso-alkanes (\geq 90% and < 2% Aromatics)	0.81	0.55
13	>340-460	Cyclo-Alkanes (\geq 90% and < 2% Aromatics)	1.01	0.79
14	>340-460	Alkanes (2 to < 8% Aromatics)	1.21	0.91
15	>340-460	Alkanes (8 to 22% Aromatics)	1.82	1.48
16	>460-580	Alkanes (< 2% Aromatics)	0.57	0.47
17	>460-580	N- & Iso-Alkanes (\geq 90% and < 2% Aromatics)	0.51	0.43
18	>460-580	Cyclo-Alkanes (\geq 90% and < 2% Aromatics)	0.63	0.54
19	>460-580	Alkanes (2 to < 8% Aromatics)	0.88	0.61
20	>460-580	Alkanes (8 to 22% Aromatics)	1.49	0.89
21	280-290	Aromatic Content (\geq 98%)	7.37	7.44
22	320-350	Aromatic Content (\geq 98%)	7.51	7.39
23	355-420	Aromatic Content (\geq 98%)	8.07	6.66
24	450-535	Aromatic Content (\geq 98%)	5.00	3.76

* ARB method; ** Carter method.

For aliphatic solvents, the alkane fractions were given in terms of distributions of carbon numbers and distributions of alkane types (normal, branched, or cyclic). Alkane fractions were assigned to distributions of detailed model species for normal, branched, and cyclic alkanes of specified carbon numbers. Normal alkanes had specific MIR values assigned, and the generic branched and cyclic alkane model species were represented in the model using individual compounds chosen to be representative of the categories.

For aromatic solvents, a “typical” aromatic composition for the purpose of MIR estimates was derived. The total aromatic content and the carbon number distributions of the aromatic fractions were used; the latter were estimated from the boiling point ranges of hydrocarbon solvents.

Estimates of carbon number distributions were derived from the boiling point ranges of a large list of compounds. After estimating the weight fractions of each chemical class, the average boiling point was used to derive their carbon number distributions. This procedure, combined with the given total weight fractions for the various constituent types, gave derived compositions of the mixtures in terms of chemical class for each carbon number.

Dr. Carter compared the two methods with each other and with explicitly calculated MIR values for representative solvents for which analytical data were available. Both methods were comparable for the primarily alkane solvent bins 2 and 6-17 and for the aromatic bins 21-23, predicting most to within $\pm 25\%$. However, the ARB bin assignments for the lighter hydrocarbon bins 1 and 3-5, tend to be higher than calculated by the new method, by $\sim 25\text{-}50\%$. This is believed due to a recalculated lower MIR value for cyclohexane, which is present in those bins. The heavy aromatic bins changed because new compositional data suggest that these may contain more naphthalene constituents than previously estimated.

Because this method performed well for predicting MIR values of analyzed solvents, staff find it to be appropriate for use for regulatory reactivity scale updates. This method also enables the convenient recalculation of bin MIR values whenever the underlying chemical mechanism is updated. Therefore, ARB staff proposes to revise the methodology to calculate MIR values for hydrocarbon bins accordingly. The proposed 2009 bin values are also listed in Table 2.

5 Process for Developing this Proposal

In 1996, the ARB established the Reactivity Research Advisory Committee (RRAC), which is comprised of representatives from consumer product manufacturers, raw material suppliers, and other interested stakeholders. The goal of the RRAC has been to ensure that reactivity regulations developed for consumer products are based on sound VOC reactivity data. The RRAC has provided valuable input on commercially important VOCs to study further to reliably assess their reactivity. Based on their suggestions, the ARB initiated several research projects.

A number of public meetings have been held to discuss the process for updating the MIR values. The first discussion occurred at the RRAC meeting on August 28, 2007. At that meeting, Dr. Carter presented results from the ARB-sponsored research project (CARB, 2007) that led to the SAPRC-07 mechanism. ARB staff

discussed peer review and implementation of SAPRC-07, and discussed possible amendments to the Table of MIR Values. In general, RRAC members supported the need for amending the Tables of MIR Values.

Another meeting of the RRAC was held on March 25, 2009. Dr. Carter discussed the RSAC review of his SAPRC-07 mechanism and his revised method to derive hydrocarbon bin MIR values. ARB staff gave a presentation on updating the MIR values, and informed the RRAC that ARB would hold a public hearing later in 2009 to adopt in regulation the SAPRC-07 mechanism derived MIR values.

In addition, a public workshop was held on August 4, 2009, to discuss the proposed amendments to the Tables of MIR Values. A workshop notice was distributed to the ARB's reactivity as well as consumer product list server subscribers. Workshop materials including a staff presentation and a version of Dr. Carter's MIR report (Appendix C) were also posted at the reactivity web site (<http://www.arb.ca.gov/research/reactivity/reactivity.htm>) prior to the workshop. At the workshop, staff presented the rationale for updating the MIR values. The process of developing the amendments and staff report were discussed. Participants at the workshop appeared to support the need to update the MIR values. The relevant materials presented at the RRAC meetings and public workshop can be found in Appendix E.

6 Proposed Amendments to the Tables of MIR Values

Staff proposes amendments to the existing Tables of MIR Values contained in sections 94700 and 94701, title 17, CCR. The proposed changes are based on updated MIR values provided by Dr. Carter, which were peer reviewed and approved by the ARB's Reactivity Scientific Advisory Committee. The proposed amendments are intended to provide MIR values based on the most up-to-date reactivity science.

Specifically, staff proposes to add about 380 new compounds with their associated MIR values to section 94700. Staff also proposes to update the MIR values for all the compounds that are currently listed in section 94700. As proposed, a column labeled "New MIR Value [Effective Date]" will replace the column "New MIR Value (July 7, 2004)". This column will specify the updated MIR values for the currently listed compounds, as well as the MIR values for the newly added compounds (Appendix A).

Staff also proposes to change the MIR values for 24 hydrocarbon solvent bins contained in section 94701, title 17, CCR. The proposed bin MIR values are based on methodology developed by Carter and Malkina (2005). A new column labeled "New Bin MIR Values [Effective Date]" is proposed for addition to section 94701 to display the updated MIR values for the 24 bins of hydrocarbon solvents (Appendix A).

Although staff proposes to update the MIR values for all the existing compounds currently listed in section 94700 and the 24 hydrocarbon mixtures in section 94701, it should be noted that the MIR values dated July 18, 2001 must continue to be used by aerosol coating manufacturers. When the aerosol coatings regulation was developed, to provide stability to manufacturers as MIR values are updated to reflect improved science, the regulation specifies that the MIR values dated July 18, 2001 are to be used and those values are not to change until June 1, 2007 [see § 94523 (h)(2)(A)]. The exception to this is that any new compounds added in subsequent amendments to the Tables of MIR Values can be used once legally effective [see § 94523 (h)(2)(B)]. The 2007 date was put into the regulation to provide manufacturers a minimum timeframe in which the MIR values would remain the same.

The MIR values dated July 18, 2001, were also used as the basis for the reactivity limits for aerosol coating products. To ensure that the air quality benefits continue to be preserved it is important that the same set of MIR values are used both for the VOC reactivity limits and calculation of PWMIR. Therefore, while we are proposing to amend the Tables of MIR Values, the MIR values dated July 18, 2001, must continue to be used by aerosol coatings manufacturers until such time as the Aerosol Coatings Regulation is amended. Any new compound proposed for addition to the Table in this rulemaking, with its associated MIR value, can be used, however.

7 Environmental Impacts

In this rulemaking, staff proposes to amend the Tables of MIR Values. Only aerosol coating products now rely on the Tables of MIR Values for regulatory compliance. Several other California's programs such as the California Low Emission Vehicles/Clean Fuel Regulation and the reformulated Gasoline program use the MIR values. Since each program maintains a separate table of MIR values, the proposed amendments are expected to have no significant impact on these programs. Therefore, the environmental impact analysis presented here will be specific to this source category.

Our analysis shows that amending the Tables of MIR Values would have neither positive nor adverse environmental impacts. This is because the proposed amendments do not impose any requirements leading to a physical change in the environment. Moreover, aerosol coating manufacturers must continue to use the July 18, 2001, MIR values. Should manufacturers opt to reformulate with newly added compounds, we would anticipate no impact because manufacturers must still comply with the existing reactivity limits in section 94522(a)(3)(A).

Staff considered the potential impacts on tropospheric ozone concentrations, particulate matter (PM), global warming, stratospheric ozone depletion, water quality, and landfill loading. Staff also examined the possibility of increased use of toxics, potential impacts on the State Implementation Plan for ozone, as well as environmental justice issues. However, because the proposed amendments

do not impose any requirements leading to a physical change in the environment, no significant negative impacts were identified.

The updated MIR values would also be used for future rulemakings for other source categories. Source categories under consideration include other consumer products, architectural coatings, and pesticides.

8 Economic Impact

There is no adverse impact on affected business. The proposed changes to the Tables of MIR Values do not require any manufacturer to take any action at this time. The aerosol coating manufacturers affected by the proposed amendments are not required to use any of the newly added compounds. A manufacturer may choose to use the newly added compounds to meet the already existing limits if doing so is economically advantageous. The updated Table of MIR Values provides additional choices to manufacturers that may use any of the new compounds in their reformulation process to meet the reactivity limits.

No costs are anticipated for either State Government or Local Agencies.

9 Recommendation

Staff recommends that the Executive Officer adopt this regulatory proposal. The proposal described herein is necessary so that ARB's reactivity-based VOC regulations are based on the best possible science. The impacts on existing aerosol coating products, air quality, the environment, and the economy are expected to be neutral.

10 References

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Appendices

- Appendix A: Proposed Amendments to the Tables of Maximum Incremental Reactivity (MIR) Values, sections 94700 and 94701, title 17, California Code of Regulations
- Appendix B: List of Newly Added Volatile Organic Compounds
- Appendix C: "Updated Maximum Incremental Reactivity Scale and Hydrocarbon Bin Reactivities for Regulatory Applications," Final report to California Air Resources Board, September 10, 2009.
- Appendix D: Letter from Chair, Reactivity Scientific Advisory Committee
- Appendix E: Public Meeting & Workshop Notices and Materials