Appendix C

Workshop Notice and Materials

Winston H. Hickox
Agency Secretary

Air Resources Board

Alan C. Lloyd, Ph.D.
Chairman
1001 I Street • P.O. Box 2815 • Sacramento, California 95812 • www.arb.ca.gov

Gray Davis
Governor

March 20, 2003

Dear Sir or Madam:

I am writing to invite you to participate in a public workshop to discuss the proposed amendments to the "Tables of Maximum Incremental Reactivity (MIR) Values" (Title 17, California Code of Regulations, sections 94700 and 94701) for reactive organic compounds. As you may know, the California Air Resources Board (ARB) has adopted a regulation for reducing the ozone formed from aerosol coating emissions, by establishing reactivity-based VOC limits for 36 categories of aerosol coatings. These limits are based on the "Tables of MIR Values."

At the public hearing where the above regulation was adopted, the Board directed staff to review the "Tables of MIR Values" 18 months after the effective date of the amendments (July 18, 2001), and every 18 months thereafter, to determine if modifications to the MIR values are warranted. After considering new information that has become available and consultation with stakeholders, we are recommending that modifications to the "Tables of MIR Values" should be pursued.

The date and location of the meeting is:

Date:	April 23, 2003
Time:	10:00 a.m. – 11:30 a.m.
Location:	Air Resources Board Conference Room 550 1001 I Street, 5th Floor Sacramento, California 95812

At the meeting, we will review the current MIR values, discuss the proposed changes to the "Tables of MIR Values," as well as the process for updating the "Tables of MIR Values." A meeting agenda and other relevant materials will be posted at http://www.arb.ca.gov/research/reactivity/reactivitywhatsnew.htm by April 4, 2003. A toll phone number will be also included in the agenda for those who are interested in participating by phone.

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Website: http://www.arb.ca.gov.

We look forward to meeting and working with you as we develop the proposal. If you have any questions regarding the meeting, please contact Dr. Eileen McCauley, Manager, Atmospheric Processes Research Section, at (916) 323-1534 or emccaule@arb.ca.gov, or Dr. Dongmin Luo, Air Resources Engineer, Atmospheric Processes Research Section at (916) 324-8496 or dluo@arb.ca.gov.

If you have special accommodation or language needs, please contact Ms. Marlena Elliott, Secretary, at (916) 445-0753 or melliott@arb.ca.gov as soon as possible. TTY/TDD/STS users may dial 7-1-1 for the California Relay Service.

Sincerely,

/S/

Richard Corey, Chief
Research and Economic Studies Branch

Enclosure

cc: Eileen McCauley, Ph.D., Manager
Atmospheric Processes Research Section
Research and Economic Studies Branch

Dongmin Luo, Ph.D., P.E.
Atmospheric Processes Research Section
Research and Economic Studies Branch

Ms. Marlena Elliott, Secretary
Research and Economic Studies Branch

Public Workshop to Discuss Proposed Amendments to Tables of Maximum Incremental Reactivity Values

Time:	10 am to 11:30 am (PDT) April 23, 2003
Location:	Cal/EPA Headquarters Room 550 1001 "I" Street Sacramento, CA 95812
Toll Number:	1-630-395-0027
Passcode:	12008
Leader:	Dongmin Luo

Agenda

1. Welcome and Introduction
2. Regulatory Background
3. Scientific Background
4. Proposed Regulatory Process
5. Public Comments
6. Closing

Public Workshop to Discuss Proposed Amendments to Tables of Maximum Incremental Reactivity Values

April 23, 2003

Research Division
Stationary Source Division
California Air Resources Board

Background

- Board approved amendments to the Aerosol Coating Products Regulation on June 22, 2000
  - Also approved new subchapter containing maximum incremental reactivity (MIR) values
- Legally effective on July 18, 2001
- Established reactivity limits for 36 coating categories, based on MIR scale

Board Resolution and Directive to Executive Officer

- Review MIR values 18 months after effective date of amendments
  - And every 18 months thereafter
  - Make revisions, if necessary
- Directed amendments to update the Tables of MIR Values to be conducted through an Executive Officer Public Hearing

Current Tables of MIR Values

- Based on the work of Dr. William Carter at UCR
  - Section 94700: MIR values for individual compounds
  - Section 94701: MIR values for hydrocarbon solvents

Using the MIR Values

- MIR values dated July 18, 2001 used to calculate PWMIR values for aerosol coatings
- MIR values for aerosol coatings unchanged until June 1, 2007
- Only new compounds added to existing Table can be used in aerosol coatings

Section 94701: MIR Values for Hydrocarbon Solvents

- ARB developed method for assigning MIR values for hydrocarbon solvents
  - Separate table of 24 bins based on Dr. Carter's work at UC Riverside
  - MIR values for bins are based on average boiling range and aromatic content of hydrocarbon solvents
  - Bin MIR values reviewed by Dr. Carter

Why Update MIR Values?

- Board resolution requires us to review the list every 18 months.
- Preliminary calculation indicates some of MIR values have changed non-negligibly.
- Over 100 compounds have been added to the SAPRC mechanism.
- Ensure continuous use of "best science" in regulations.
- Staff determined that the update is appropriate.

Summary of MIR Review

- The MIR values reviewed by Dr. Carter
- No major revisions on the chemical mechanism (SAPRC) and the reactivity calculation scenarios or procedures
- Some corrections or modifications to some mechanisms, emissions assignments, and files and software programs
- 106 new compounds or mixtures added

Summary of MIR Review-2

- Among 670 VOC compounds or mixtures, MIR values changed:
  - > 10% for 14 compounds
  - > 5% for 26 compounds
  - > 1% for 305 compounds
  - < 1% for the remaining compounds
- Continuous use of upper limit estimates recommended
- Only n-pentadecane with >5% MIR change used as surrogate for bin system development

Regulatory Development Process

- Public outreach
  - Public workshop (April 23, 2003)
  - Reactivity Research Advisory Committee
  - Other stakeholder meetings
- Public comments (May 23, 2003)
  - Deadline for additional new compounds with associated MIR value
- Staff report (July 2003)
- Executive Office Public Hearing (Sept. 2003)

Staff Report Outline

- Proposed amendments to the regulation
- Effects of the proposed amendments
- Compliance with the proposed amendments
  - Impacts on existing bin system
  - Impacts on existing products
- Economic impact
- Environmental impact

Executive Officer Public Hearing

- Technical nature of proposed amendments
- Same regulatory process required as for Board hearing
- Executive Officer conducts the hearing

Future Activities

- Currently surveying various consumer product categories
  - Will evaluate feasibility of reactivity-based regulation for some categories
  - Updated MIR values would be used as basis
- Evaluating feasibility of reactivity-based Suggested Control Measure for architectural coatings

Useful Information

- The EPA's Advanced Notice of Proposed Rulemaking on revised VOC policy
- Other reactivity-based regulations
  - Clean Fuel and Low Emission Vehicle regulations (amended in Nov. 2001)

Useful Web Sites

- Reactivity Program
  http://www.arb.ca.gov/research/reactivity/reactivity.htm
- Consumer Products Program
  http://www.arb.ca.gov/consprod/consprod.htm
- Low Emission Vehicle Program
  http://www.arb.ca.gov/regact/levii01/levii01.htm
- Architectural Coatings Program
  http://www.arb.ca.gov/coatings/arch/arch.htm

Comments?

Calculating Product-Weighted MIR

Contents	Weight Fraction	MIR	Weighted Reactivity
acetone	0.300	0.43	0.129
toluene	0.150	3.97	0.596
propane	0.200	0.56	0.112
xylene	0.050	7.37	0.369
butane	0.200	1.33	0.266
solids	0.100	0	0.000
Total	1.000		1.472

Product MIR= 1.47 g O_3/g product

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RIVERSIDE, CALIFORNIA 92521-0434

February 6, 2003

Mr. Richard Corey
Chief, Research and Economics Branch
Research Division
California Air Resources Board
1001 I Street
P.O. Box 2518
Sacramento, California 95812

Re: Expanded List of Updated Maximum Incremental Reactivity (MIR) Values

Dear Mr. Corey:

You may remember that on October 26, 2002 I provided an updated list of Maximum Incremental Reactivity (MIR) values that your staff requested for the CARB's regulatory needs. These were calculated using the current version of my SAPRC-99 chemical mechanism, as described in my previous letter and also summarized below. Since that time, at the request of industry groups I added 9 new categories of VOCs for which I have calculated MIR values. I also was informed that the previous list had an incorrect molecular weight for diethyl benzene isomers, which resulted in the MIR's for those compounds being ~10% too high. I understand from Dongmin Luo of your staff that it is not too late to add new VOCs to your regulatory list, and that there is a desire from some industry groups that at least some of these new chemicals be included. Therefore, I am providing the CARB with an updated tabulation that includes these 9 new VOC categories and corrects the data for the diethylbenzenes. The previous list also had missing uncertainty assignments and upper limit MIR estimates for some of the added VOCs, and this has also been corrected.

An Excel file containing the updated reactivity tabulation is available at my reactivity web site at http://www.cert.ucr.edu/~carter/reactdat.htm, and is also being sent to you and Dr. Dongmin Lou of your staff as an email attachment. The summary page of the file, giving the updated MIR values, is attached.

The updates and additions made to the MIR tabulation relative to the relative to the values used in your current aerosol coatings rule is given below. Much of this is essentially the same as the discussion given in the letter of October 26, but is duplicated here for the convenience of those who may not have access to the October 26 letter.

Since neither the chemical mechanism nor the reactivity calculation scenarios or procedures have undergone any major revisions since the MIR values incorporated in the current aerosol coatings rule were calculated, one would not expect changes in MIRs for most of the species. However, some corrections have been made to some mechanism and emissions assignments for certain VOCs, and modifications or corrections have been made to some of the files and software programs. This has resulted in resulting in non-negligible MIR changes for a small number of VOCs and very small changes for many others. In particular, of the ~670 VOC categories on your list for which I have recalculated MIR values, the MIR's for 14 have changed by more than 10%, 26 have changed by more than 5%, and 305 have changed by more than 1%. In addition, in the process of making assignments for my mechanism for various emissions inventories, for other projects, and at the request of certain industry groups I have added 106 of new VOC categories for which MIRs have been calculated. Table 1, attached, lists the VOCs whose MIRs have changed by more than 5%, and Table 2 lists the new VOC categories that have been added to the current list. Footnotes to Table 1 indicate the reasons or probable reasons for the changes. (These tables are available in Word format at ftp://ftp.cert.ucr.edu/pub/carter/SAPRC99/s99corr3.doc.)

Note that Table 1 is exactly the same as the corresponding table in the October 26 letter, but that Table 2 includes the 9 new VOC categories as well as those given in the previous letter. In addition, the MIR's for some of the new species added on October 26 and listed on Table 2 have changed slightly in this update. This is because for this update their MIR's were calculated using the "adjusted product" method as described in Section III.M of the SAPRC-99 documentation report (Carter, 2000), while for the October 26 version they were calculated using the fixed product method. As described in the SAPRC-99 documentation, the adjusted product method provides a slightly more detailed estimated mechanism for deriving estimated mechanisms for MIR calculations that does not require significantly more calculation effort, so it was incorporated as part of this update. The model species list included with the reactivity tabulation provided electronically (or at by above-referenced reactivity web site) now includes a column indicating whether the adjusted product method was used when deriving the mechanism used in the MIR calculation.

The tabulation used in your current regulation includes MIRs for a number of species that were derived by CARB staff based on the upper limit estimation method. I did not review these estimates, but I presume that they were made using the appropriate procedures and parameters. No updates have been made to the recommended procedures that would affect these upper limit MIR estimates, so I do not recommend any changes being made to these upper limit estimates. In addition, as indicated on Table 1, a few VOC categories for which you have made upper limit estimates are included on the current tabulation with lower estimated MIR values. My estimates of the uncertainties for the reactivities of these compounds have not been reduced, so I recommend that you continue to use the upper limit estimates for those compounds for your regulatory scale.

Note that a few VOC categories on the tabulation, such as benzaldehyde, have negative estimated MIRs, while the table in your regulation uses zero for the MIR. Although this is a policy issue that is up to the CARB, I recommend you continue using zero values for the MIRs for these species in your regulations.

I hope this is useful to the CARB. If you or your staff have any questions or issues about this new tabulation or any of the changes or new species that were added, please let me know.

Sincerely,

William P. L. Carter
Research Chemist

Cc: Dr Dongmin Luo
Atmospheric Processes Research Section

Table 1. Listing of VOC species or categories whose MIR values have changed by more than 5%.

Model Name	Description	MIR (gm O_3 /gm VOC)			Note
		Updated	Previous	Change	
CL2IBUTE	2-(chloromethyl)-3-chloropropene	3.13	1.13	177%	[a]
AMP	2-Amino-2-Methyl-1-Propanol	4.75	15.08	-68%	[b]
TM-AMINE	Trimethyl Amine	7.06	16.60	-57%	[b]
244M2C5E	2,4,4-trimethyl-2-Pentene	8.52	5.85	46%	[c]
METHANE	Methane	0.014	0.01	39%	[d]
CYC-C15	C15 Cycloalkanes	0.65	0.99	-34%	[e]
PROPACID	Propionic Acid	0.79	1.16	-32%	[f]
ACETACID	Acetic Acid	0.50	0.71	-30%	[f]
2ETHXACD	2-Ethyl Hexanoic Acid	3.49	4.41	-21%	[f]
ME-BR	Methyl Bromide	0.017	0.02	-16%	[d]
CH3-CL	Methyl Chloride	0.034	0.03	15%	[d]
CHCL3	Chloroform	0.034	0.03	14%	[d]
ETOX	Ethylene Oxide	0.044	0.05	-11%	[d]
DPGOME2	Dipropylene Glycol Methyl Ether isomer (2-[2-methoxypropoxy]-1-propanol)	2.70	3.02	-11%	[g]
C7-OLE1	C7 Terminal Alkenes	4.20	4.56	-8%	[h]
1-HEPTEN	1-Heptene	4.20	4.56	-8%	[h]
11BR2-C2	1,2-Dibromoethane	0.046	0.05	-7%	[d]
C15-OLE1	C15 Terminal Alkenes	1.27	1.37	-7%	[h]
1-C15E	1-Pentadecene	1.27	1.37	-7%	[h]
ME-FORM	Methyl Formate	0.064	0.06	6%	[h]
DGBE	2-(2-Butoxyethoxy)-Ethanol	2.87	2.70	6%	[h]
CL2-ME	Dichloromethane	0.066	0.07	-6%	[d]
N-C18	n-C18	0.44	0.47	-6%	[i]
48DM-C14	4,8-Dimethyl Tetradecane	0.55	0.58	-5%	[i]
N-C15	n-Pentadecane	0.53	0.56	-5%	[i]

[a] The representation of the mechanism of this compound was changed. However, the mechanism is highly uncertain and the upper limit MIR probably should be used.

[b] The "previous" value is the CARB staff's estimated upper limit MIR. The upper limit value should continue to be used in the regulation for consistency with the current policy for treatment of uncertainty.

[c] The structure for this compound was incorrectly specified as that for 2,4,4-trimethyl-2-hexene when calculated previously.

[d] Change due to round-off error, since the CARB tabulation had only two significant figures. The MIR's are the same to two significant figures.

[e] The reason for this change could not be determined. This compound is represented using the lumped molecule method, and the calculated MIRs for the species used to represent it have not changed significantly.

[f] The estimated mechanisms for organic acids have changed due to a modification in the estimation of branching ratios for the initial OH reaction at various positions around carboxylic acid groups.

[g] Assignments for this compound could not be found on the previous databases.

[h] The change for C_7 or the C_{15} terminal alkenes is due to the change for 1-heptene or 1-pentadecene, respectively. The change for these higher molecular weight 1-alkenes must be due to some small change in the base mechanism or scenario assignments because the mechanism and the rate constants used are the same.

[i] The reactivities of these compounds are expected to be highly sensitive to small changes in the base mechanism or scenario conditions. The mechanisms for these compounds were not changed.

Table 2. Listing of VOC compounds and categories that have been added to the list.

Model Name	Description	MIR (gm O_3 / gm VOC)	Notes
BCYC-C8	C8 Bicycloalkanes	1.75	
13E5PCC6	1,3-Diethyl-5-Propyl Cyclohexane	0.96	
C3M2-C5E	Cis-3-Methyl-2-Pentene	12.84	
M-ET-TOL	m-Ethyl Toluene	9.37	
P-ET-TOL	p-Ethyl Toluene	3.75	
O-ET-TOL	o-Ethyl Toluene	6.61	
O-DE-BEN	o-Diethyl Benzene	5.92	[a]
M-DE-BEN	m-Diethyl Benzene	8.39	[a]
P-DE-BEN	p-Diethyl Benzene	3.36	[a]
1235MBEN	1,2,3,5 Tetramethyl Benzene	8.25	
INDENE	Indene	3.21	
ME-INDAN	Methyl Indans	2.83	
C12-TET	C12 Tetralin or Indane	2.33	
IAMOH	isoamyl alcohol (3-methyl-1-butanol)	2.73	
2ME1C4OH	2-methyl-1-butanol	2.60	[b]
MIBUCBN	4-methyl-2-pentanol (methyl isobutyl carbinol)	2.89	
23M1C5OL	dimethylpentanol (2,3-dimethyl-1-pentanol)	2.51	
1M1C7OL	5-methyl-1-heptanol	1.95	
TMCYC6OH	trimethylcyclohexanol	2.17	
26M2C7OH	dimethylheptanol (2,6-dimethyl-2-heptanol)	1.07	
26M4C9L	2,6-dimethyl-4-heptanol	2.37	
MENTHOL	menthol	1.70	
1-C10-OH	1-decanol	1.22	
37M1C8L	3,7-dimethyl-1-octanol	1.42	
268M4C9L	Trimethylnonanolthreoerythro; 2,6,8-Trimethyl-4-nonanol	1.55	
14-C4-OH	1,4-butanediol	3.22	
PNTAERYT	pentaerythritol	2.42	
2E13HXOL	2-Ethyl-1,3-hexanediol	2.62	
13DXOLAN	1,3-dioxolane	5.47	
14DXANE	1,4-dioxane	2.71	
IPROIPR	diisopropyl ether	3.56	
EGDEE	ethylene glycol diethyl ether; 1,2-diethoxyethane	2.84	
ACETAL	acetal (1,1-diethoxyethane)	3.68	
44MHX3O	4,4-Dimethyl-3-oxahexane	2.03	
2M12M1MP	2-methoxy-1-(2-methoxy-1-methylethoxy)-propane	2.09	
3MEOC3OH	3-methoxy-1-propanol	4.01	
TH2FURM	tetrahydro-2-furanmethanol	3.54	
PROC3OH	n-propoxypropanol	3.84	
TEGLYCL	triethylene glycol	3.41	
DPGEE	dipropylene glycol ethyl ether	2.75	
TETGLCL	tetraethylene glycol	2.84	
1BOEO2PR	1-(butoxyethoxy)-2-propanol	2.08	
DBNP	glycol ether dpnb {1-(2-butoxy-1-methylethoxy)-2-propanol}	1.96	
GBUTYACT	gamma- butyrolactone	1.15	
IPRFORM	Isopropyl Formate	0.42	
IAMACET	isoamyl acetate (3-methylbutyl acetate)	1.18	
2M1BACET	2-methyl-1-butyl acetate	1.17	
MAMACET	methyl amyl acetate (4-methyl-2-pentanol acetate)	1.46	
C5PROPAT	n-pentyl propionate	0.79	[b]

Table 2, continued

Model Name	Description	MIR (gm O_3 / gm VOC)	Notes
5MC7-ACT	5-Methylheptyl Aceate	0.73	
MELAURAT	methyl dodecanoate {methyl laurate}	0.53	
ME-MYRST	methyl myristate {methyl tetradecanoate}	0.47	
MEOPRACT	methoxypropanol acetate	1.97	
12PGDACT	1,2-Propylene glycol diacetate	0.94	[b]
DPGNPE1	Dipropylene glycol n-propyl ether isomer #1	2.13	[b]
DPGMEA1	Dipropylene glycol methyl ether acetate isomer #1	1.41	[b]
DPGMEA2	Dipropylene glycol methyl ether acetate isomer #2	1.58	[b]
DPGMEA	Dipropylene glycol methyl ether acetate	1.49	[b]
GLY-ACET	glyceryl triacetate	0.57	
DIPRADP	diisopropyl adipate	1.42	
IBUTACD	isobutyric acid	1.22	
BUTACD	butanoic acid	1.78	
MALACD	malic acid	7.51	
3MBUTAC	3-Methylbutanoic acid	4.26	
ADIPACD	adipic acid	3.37	
HOPRACR	hydroxypropyl acrylate	5.56	
NBUACRAT	n-butyl acrylate	5.52	
IBU-ACRT	isobutyl acrylate	5.05	
ATRPNEOL	a-terpineol	5.16	
2MEXAL	2-methyl-hexanal	3.97	
MIPRK	Methyl Isopropyl Ketone	1.64	
24C5-K	2,4-pentanedione	1.02	
2PRCC6K	2-propyl cyclohexanone	1.71	
4PRCC6K	4-propyl cyclohexanone	2.08	
IBHK	2,6,8-trimethyl-4-nonanone; Isobutyl heptyl ketone	1.86	[b]
2M2C5E4O	mesityl oxide (2-methyl-2-penten-4-one)	17.37	
ISOPRON	isophorone {3,5,5-trimethyl-2-cyclohexenone}	10.58	
1C9E4ONE	1-nonene-4-one	3.39	
DOHACT	dihydroxyacetone	4.02	
C8-PHEN	C8 Alkyl Phenols	2.07	
C9-PHEN	C9 Alkyl Phenols	1.86	
C10-PHEN	C10 Alkyl Phenols	1.68	
C11-PHEN	C11 Alkyl Phenols	1.54	
C12-PHEN	C12 Alkyl Phenols	1.42	
EGPHE	2-Phenoxyethanol; Ethylene glycol phenyl ether	3.61	[b,c]
CCL4	Carbon Tetrachloride	0	
ME-BR2	Methylene Bromide	0	
C6-ALK	Unspeciated C6 Alkanes	1.48	
C7-ALK	Unspeciated C7 Alkanes	1.79	
C8-ALK	Unspeciated C8 Alkanes	1.64	
C9-ALK	Unspeciated C9 Alkanes	2.13	
C10-ALK	Unspeciated C10 Alkanes	1.16	
C11-ALK	Unspeciated C11 Alkanes	0.90	
C12-ALK	Unspeciated C12 Alkanes	0.81	
C13-ALK	Unspeciated C13 Alkanes	0.73	
C14-ALK	Unspeciated C14 Alkanes	0.67	
C15-ALK	Unspeciated C15 Alkanes	0.61	
C16-ALK	Unspeciated C16 Alkanes	0.55	

Table 2, continued

Model Name	Description	MIR (gm O_3 / gm VOC)	Notes
C17-ALK	Unspeciated C17 Alkanes	0.52	
C18-ALK	Unspeciated C18 Alkanes	0.49	
C10-ARO	Unspeciated C10 Aromatics	5.48	
C11-ARO	Unspeciated C11 Aromatics	4.96	
C12-ARO	Unspeciated C12 Aromatics	4.53	
MS-802	Composite mineral spirit (naphthas or lactol spirits) (CARB Profile ID 802)	2.02	
MS-CP96	Thinning Solvent/Mineral Spirits (Cal Poly Slo. 1996)	1.99	
ISOPARM	Exxon Isopar(r) M Fluid	0.65	

[a] October 26 list had incorrect molecular weight.

[b] New model species added January 24, 2003

[c] Mechanism estimated as discussed in Footnote 101 in the revised Table C-1 available wit the full reactivity tabulation at http://www.cert.ucr.edu/~carter/reactdat.htm.