SAN JOAQUIN VALLEY UNIFIED AIR POLLUTION CONTROL DISTRICT

FINAL DRAFT STAFF REPORT

Proposed Amendments to Rule 1020 (Definitions)

February 21, 2013

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I. SUMMARY

Rule 1020 (Definitions) defines terms used throughout other San Joaquin Valley Air Pollution Control District (District) rules, including a list of compounds exempt from ozone regulations due to their low ozone forming potential. The District occasionally amends District Rule 1020 to update these definitions as they are revised by the Environmental Protection Agency (EPA). The District proposes to make several updates related to the list of exempt compounds, including adding several additional compounds and clarifying requirements for several existing compounds.

The first proposed rule amendment is to add dimethyl carbonate (DMC) and propylene carbonate (PC) to the District's list of exempt compounds within the definition of volatile organic compounds (VOC) (Section 3.53) as a response to EPA findings that DMC and PC have a low potential to form ozone in the atmosphere. EPA found that these compounds are less photo-chemically reactive than ethane and, thus, have a negligible contribution to ozone formation. EPA announced the exemption of DMC and PC in the Federal Register, effective February 2009 (included as Appendix B). By exempting these compounds, manufacturers of coatings or solvent cleaning materials have additional options with which to formulate low-VOC coatings and cleaning materials.

The District also proposes to remove unnecessary permitting requirements for two previously exempted compounds: methyl formate (MF) and tertiary-butyl acetate

(TBAc). Based on the District's analysis, the District determined that the current permit requirements included in Rule 1020 for MF and TBAc are not needed and will subsequently be removed.

The District evaluated the potential health impacts associated with these proposed amendments and concluded that they would not cause adverse health impacts. The District's analysis was based on worst-case assumptions, including assuming that the use of the proposed exempt compounds would be entirely new, when, in fact, their use would be in lieu of other chemical compounds that could often pose a greater risk. While these compounds are exempt from VOC regulations under Rule 1020, the District's permitting process evaluates the potential health risk from all new and modified operations to ensure that they do not cause significant health impacts to San Joaquin Valley (Valley) residents.

II. RULE DEVELOPMENT PROCESS

As part of the rule development process, the District posted draft amendments to Rule 1020 and solicited comments from the public, stakeholders, the California Air Resources Board (ARB), and EPA over a 30-day period just prior to hosting a public workshop on December 29, 2010. The District postponed further action on the proposed amendments to Rule 1020 based on a request by ARB to allow them an opportunity to further review the issue on a statewide basis. ARB ultimately did not publish such a review, and the District proceeded with evaluating and preparing the proposed amendments to Rule 1020, consistent with EPA' 2009 ruling.

The District will publish and make available the proposed amendments to Rule 1020 to stakeholders for review prior to a public hearing of the Governing Board to consider adoption of the proposed rule amendments. The District will evaluate comments received and incorporate them as appropriate. The proposed amendments are scheduled to be presented to the Governing Board during a public hearing on February 21, 2013.

III. BACKGROUND

Not all organic compounds have equal potential to form ozone in the atmosphere. EPA has revised the federal definition of VOCs several times to exclude organic compounds from the definition of VOCs based on their negligible contribution to ozone formation. By adding a compound to the list of exempt compounds, EPA is encouraging its use as a replacement for other chemicals that are significantly more likely to contribute to ozone formation. Effective February 2009, EPA added DMC and PC to the federal exempt compounds list on the basis that these compounds are less photo-chemically reactive than ethane and, thus, have negligible contribution to ozone formation. The

EPA announced the delisting of these chemicals in the Federal Register, which is attached as Appendix B.

If a chemical can be replaced by one with a lower potential to form ozone, the amount of ozone formed in the atmosphere will be reduced. Because both DMC and PC appear to be likely candidates to replace VOCs in a number of high-use products, the District proposes amendments to Rule 1020 (Definitions) to add DMC and PC to the District's list of exempt VOCs.

Previous District actions similarly amended Rule 1020 to exempt tertiary-butyl acetate (TBAc) and methyl formate (MF) as a result of EPA actions exempting such compounds. The previous District actions set a limit for use of TBAc and MF at one gallon per year per facility; use above that threshold currently requires the operator to get a Permit to Operate (PTO). During the evaluation and risk assessment for the current action (exemption of DMC and PC), District staff determined that the one-gallon threshold for TBAc and MF is redundant and unnecessary given the Risk Management Review required by District Rules 2201 (New and Modified Stationary Source Review) and 2020 (Exemptions) for all compounds with potential risk, especially cumulative risk of compounds that, by themselves, are below the District's significance threshold. Therefore, the proposed amendments to Rule 1020 (Definitions) include deletion of the TBAc and MF use limitations to reduce redundancy and improve clarity.

IV. DISCUSSION

The District received a request from Kowa American Corporation (Kowa) to amend Rule 1020 (Definitions) to include DMC and PC as exempt VOCs, as defined in Section 3.53 in the rule. In July 2004, Kowa petitioned the federal government to exempt DMC as a VOC. EPA approved the exemption of DMC and PC as VOCs in 2009 (see Appendix B) after several years of evaluation of the ozone-reducing values and environmental, toxicity, and safety profiles of these compounds.

Section 3.53 of Rule 1020 defines VOCs and lists compounds that are both organic and volatile, yet are considered by the District to have a low potential to form ozone, thus making them exempt from regulatory requirements. One of the proposed amendments to Rule 1020 changes the definition of VOC in Section 3.53 to add DMC and PC to the list of exempt compounds. By exempting DMC and PC, manufacturers of coatings or solvent cleaning materials have additional compounds with which to formulate low-VOC coatings and cleaning materials.

Dimethyl Carbonate (DMC)

DMC is a colorless, fast-evaporating solvent with a substantial polar nature, i.e. it is water soluble. Manufacturers and suppliers of DMC expect it to be an effective replacement for esters, glycol ethers, and ketones in formulations. For some cleaning applications, DMC may be used to replace isopropyl alcohol, although DMC is less polar than isopropyl alcohol and therefore may not work as efficiently as isopropyl alcohol. In addition, DMC has solubility and other properties that might make it a replacement for trichloroethylene in solvent cleaning operations.

The flash point (the lowest temperature at which a liquid can vaporize to form an ignitable mixture in air) of DMC is higher than some solvents already in wide-spread use like acetone, ethyl acetate, and methyl ethyl ketone (MEK), thus making DMC an attractive replacement in applications that use these solvents. It also has the potential to replace isopropyl alcohol and trichloroethylene in cleaning and solvent applications. By contrast, the flammability of DMC may limit its use in consumer coatings, indoor application coatings, and as a hand-wipe cleaning solvent.

DMC may also replace some compounds such as xylene, toluene, MEK and hexane, which have been identified as toxic air contaminants by the ARB. Based on the following information and the risk assessment detailed below, the exemption of DMC as a VOC is not expected to pose a significant health risk to Valley residents if substituted for a non-exempt VOC at District-regulated stationary sources.

Given that the most likely application of DMC is as a replacement in coatings or as a cleaning solvent, inhalation is expected to be the primary pathway of human exposure due to evaporation of the solvent. This exposure would be similar to any other paint, sealant and adhesive solvent that DMC would be intended to replace. There may also be some minor skin exposure from coatings splattering or careless mixing operations. Oral exposure would be rare and is limited to accidental ingestion.

Data from Kowa American, the manufacturer of this chemical, indicates that once DMC enters the body, it can be converted into methanol and carbon dioxide. The California Office of Environmental Health Hazard Assessment (OEHHA) conducted an assessment of the health effects of exposure to DMC. No data is available in the peer-reviewed literature for chronic exposure of humans to DMC. However, one teratology study conducted by Exxon in 1992 indicates maternal and developmental toxicity on mice when exposed to high (3,000 ppmv) inhalation exposure levels. No observed effects were reported at 1,000 ppmv exposure level. These results are consistent with the studies of the inhalation of methanol.

There are no data available on the chronic effects or carcinogenicity of DMC. Since so little toxicity information on DMC itself is available, the toxicity of methanol was used to develop risk screening values for DMC. The OEHHA-proposed interim acute screening value of 18,000 mg/m^3 and chronic screening value of 5,500 mg/m^3 are expected to be protective of anticipated adverse health effects, including the developmental toxicity observed in the Exxon study noted above. The OEHHA evaluation is attached as Appendix C.

No exposure guidelines have been established for DMC by the Occupational Safety and Health Agency (OSHA), the American Conference of Industrial Hygienists (ACGIH), or the National Institute for Occupational Safety and Health (NIOSH). However, Kowa American recommends an occupational exposure level of 200 ppmv over an 8-hour period based on the exposure limit established by OSHA and ACGIH for methanol, one of the chemicals to which the body converts DMC. This exposure level limit is in line with other solvents that DMC would replace.

As a component of this rule amendment project, the District evaluated the potential health risks associated with the use of DMC and determined that, when used in the small amounts allowed under the District's permitting exemptions (Rule 2020), the acute, chronic, and cancer risks are all significantly below the District's health risk thresholds. In fact, DMC may replace some compounds such as xylene, toluene, MEK, and hexane, which have been identified as toxic air contaminants by ARB. In line with the District's Risk-based Strategy, the inclusion of DMC as a VOC exempt compound would likely decrease the overall health risk to Valley residents if used to replace toxics compounds such as those identified above.

The District's *Risk Management Policy for Permitting New and Modified Sources* requires assessment of risks from toxic air contaminants (TAC). While DMC is not classified as a TAC, there are minor acute and chronic risks, as noted above, which require acknowledgement and assessment per District policy, especially the cumulative effect that such compounds have when combined with other compounds with potential risk. Given the thorough and cumulative requirements of the District's risk management policy, any use of DMC, or any other exempt VOC with known toxicity levels (and established Reference Exposure Level [REL] or screening levels), will be assessed and mitigated during the permitting process to ensure that the cumulative risk is below a hazard index of 1.0, which is the District's significance threshold.

Given the anticipated uses of DMC (solvents in coatings, adhesives, or sealants), there are potential uses that would not require permitting because of the amount of product used, and therefore may not be subject to the District's risk management policy and assessment. Rule 2020 (Exemptions), Section 6.8 (Surface Coating Operations) exempts "architectural surface coatings used for commercial or residential applications." Such coatings are regulated by ARB as consumer products and are not normally considered by the District. Similarly, worker exposure issues are the purview of the California OSHA. Surface coating operations, which are regulated by the District as a stationary source, are allowed to use, without permit, less than one quart of coating (which may contain DMC as a solvent or thinner) per day or less than eight gallons of coating per year within their facility. Therefore, the District's health risk assessment for this rule amendment is focused on these potentially unpermitted uses.

The District used AERMOD (a modeling program of EPA's Agency Regulatory Model Improvement Committee [AERMIC]) to determine the worst-case dispersion factors for emissions from a stationary source using a coating containing an exempt VOC. For comparison purposes, the District also evaluated other recently exempted VOCs—TBAc and MF—in addition to DMC. Staff selected coatings (containing VOCs) to analyze based on information in ARB's *Draft Report on the 2005 Architectural Coatings Survey* and include a solvent-based coating with 47% VOC content (by weight) and a water-based coating with 5% VOC content. Initially, staff evaluated four different scenarios for emissions from these coatings: urban dispersion from a volume source, rural dispersion from a volume source, dispersion from a spray booth with an uncapped stack, and dispersion from a spray booth with a capped stack. For all VOCs evaluated, the rural dispersion from a volume source using the solvent-based coating resulted in the highest acute, chronic, and cancer risk estimates given the exemption limits in Rule 2020—one quart per day for acute risk (assuming that the entire quart was used in one hour) and eight gallons per year for chronic and cancer risk. Table 1 summarizes the results from this worst-case scenario.

Table 1 – Risk Estimates for Exemption Use of DMC, MF, and TBAc

Compound	47% VOC in Solvent-Based Coating		
	Acute Risk 1 Quart in 1 Hour	**Chronic Risk** 8 Gallons in 1 Year	**Cancer Risk** 8 Gallons in 1 Year
Dimethyl Carbonate (DMC)	0.52	0.002051	N/A
Methyl Formate (MF)	0.67	N/A	N/A
tertiary-Butyl Acetate (TBAc)	0.39	N/A	3.01E-06

N/A indicates no risk exposure limits or screening values exist for the associated risk and compound.
The details of this analysis are included as Appendix D to this staff report.

Based on this analysis, an unpermitted source using any of the three compounds in reasonably anticipated ways would not pose an unacceptable risk. Furthermore, if usage rates of coatings containing these compounds exceed the limits in Rule 2020, a permit would be required, which would require a thorough and cumulative risk management review for all operations that require a permit and would regulate individual project risk as part of the permitting process.

Methyl Formate (MF) and Tertiary-Butyl Acetate (TBAc)

Currently, Sections 3.53.2 (applicable to TBAc) and 3.53.3 (applicable to MF) require any operator who elects to use more than one gallon per year (per facility) of either TBAc or MF to submit a permit application for the proposed use. Based on the District's evaluation of potential health risks associated with the use of these compounds, these use limitations are not necessary, given their small potential risk. Additionally, the District's permitting process evaluates the potential health risk from all new and modified operations, including use of these compounds, to ensure that they would not cause significant health impacts. Therefore, the District proposes to remove the permitting requirements included in Rule 1020 for TBAc and MF, while retaining their status as exempt compounds.

Propylene Carbonate (PC)

PC is an odorless, non-viscous, clear liquid with a low vapor pressure, and very slow evaporation rate. It is combustible, with flash point of 132°C. The compound is used in adhesives, paint strippers, and as a solvent for aerial pesticide application. PC is also used in more than 1,300 cosmetic products such as mascara, lip gloss, foundation, sunscreen, lip liner, deodorant, anti-aging creams, and concealers. Other known applications of PC include special-purpose lubricant, general-purpose degreasers for industrial use, rubberized coatings, and non-flat aerosol paint products. PC may also be used as a tail solvent, because of its slow evaporation rate, and in certain solvent cleaning applications.

PC is not listed as a hazardous air pollutant under the Clean Air Act. It contains no chlorine or bromine and, therefore, it does not deplete the stratospheric ozone. Based on available data, PC has low acute toxicity, and there is no established airborne occupational exposure limit for PC. Because this compound has been approved for use in cosmetics, and its relatively low toxicity based on the best available data, it is anticipated that including PC as a VOC exempt compound will not pose a significant added risk to Valley residents.

Table 2 summarizes the physical and chemical properties of the compounds DMC and PC might replace.

Table 2 – Comparison of Currently-Used Solvents, Dimethyl Carbonate and Propylene Carbonate

Property	Acetone	Ethylene Glycol	Isopropyl Alcohol	Methyl Acetate	Methyl Ethyl Ketone	Dimethyl Carbonate	Propylene Carbonate
Appearance	Colorless clear liquid	Colorless clear liquid	Clear colorless liquid	Colorless clear liquid	Colorless clear liquid	Clear colorless liquid	Colorless clear liquid
Odor	Ethereal	Odorless	Rubbing alcohol	Fragrance like	Sharp mint-like odor	Pleasant odor	Odorless
Molecular Formula	C_3H_6O	$HOCH_2$ CH_2OH	$(CH_3)_2CHOH$	CH_3COOCH_3	$CH_3COCH_2\ CH_3$	$(CH_3)_2CO_3$	$C_4H_6O_3$
Molecular Weight	58.08 g/mole	62.07 g/mole	60.09 g/mole	74.08 g/mole	72.11 g/mole	90.08 g/mole	102.09 g/mol
Density	2 g/mL	2.14 g/mL	2.1 g/mL	2.8 g/mL	2.5 g/mL	1.07 g/mL	1.25 g/mL
Boiling Point	56.2 °C	197.6 °C	82 °C	57 °C	80 °C	90 °C	242 °C
Melting Point	-95.35 °C	-13 °C	-89 °C	-98.05 °C	-86 °C	2 °C	-49.2 °C
Vapor Pressure	180 mmHg @ 20 °C	0.06 mmHg @ 20 °C	44 mmHg @ 25 °C	173 mmHg @ 20 °C	78 mmHg @ 20 °C	55 mmHg @ 25 °C	0.02 mmHg @ 20 °C
Solubility in Water	Soluble	Soluble	Miscible	Soluble	Soluble	Soluble	1-10%
Solvent Solubility	Not available	Slightly soluble	Not available	Easily soluble in methanol, diethyl ether	Miscible with most organic solvents	Miscible with most organic solvents	Not available
NFPA[A] Flammability Rating	3	1	3	3	3	3	1
Lower Explosive Limit	2.5%	3.2%	2.0%	3.1%	1.4%	4.2%	1.21%
Upper Explosive Limit	12.8%	36%	12.7%	16%	11.4%	12.9%	5.35%
Flash Point	-20 °C	111 °C	12 °C	-10 °C	-9 °C	18 °C	132 °C

[A] National Fire Protection Agency
[B] Based on methanol as surrogate
[C] OEHHA/ARB Approved Risk Assessment Health Values
[D] Permissible Exposure Level

Table 2 (continued) – Comparison of Currently-Used Solvents to Dimethyl Carbonate and Propylene Carbonate

Property	Acetone	Ethylene Glycol	Isopropyl Alcohol	Methyl Acetate	Methyl Ethyl Ketone	Dimethyl Carbonate	Propylene Carbonate
OSHA PEL [D]	1,000 ppmv	None	400 ppmv	200 ppmv	200 ppmv	200 ppmv [B,C]	None
Acute Inhalation REL	None	None	3,200 ug/m^3	None	18,000 ug/m^3	18,000 ug/m^3 [B,C]	None
Chronic Inhalation REL	None	400 ug/m^3	7,000 ug/m^3	None	None	5,000 ug/m^3 [B,C]	None
Carcinogenic	No	No	No	No	No	No	No

[A] National Fire Protection Agency
[B] Based on methanol as surrogate
[C] OEHHA/ARB Approved Risk Assessment Health Values
[D] Permissible Exposure Level

V. GLOBAL CLIMATE CHANGE AND GREENHOUSE GASES

The California Global Warming Solutions Act of 2006 (AB 32) created a comprehensive, multi-year program to reduce greenhouse gas (GHG) emissions in California, with the overall goal of restoring emissions to 1990 levels by the year 2020. In the coming years, ARB and the Legislature will be developing policies and programs to implement AB 32. The District believes that the evidence and the rationale that climate change is occurring is compelling and convincing. In addition to the long-term consequences of climate change, the District is concerned with the potential ramifications of more moderate but imminent changes in weather patterns. The Valley depends heavily on agriculture for its economy and has developed agricultural practices based on the last several decades of weather patterns. Unanticipated and large fluctuations in these patterns could have a devastating effect on the Valley's economy.

While there are many win-win strategies that can reduce both GHG and criteria/toxic pollutant emissions, when faced with situations that involve tradeoffs between the two, District staff believes that the more immediate public health concerns that may arise from an increase in criteria or toxic pollutant emissions should take precedence. The District's Governing Board adopted the Climate Change Action Plan (CCAP) in August 2008. For California Environmental Quality Act (CEQA) requirements, one of the goals of the CCAP is to establish District processes for assessing the significance of greenhouse gas impacts. The District has developed a policy and guidance for addressing greenhouse gases under CEQA.

VI. ANALYSES

A. Emission Reduction Analysis

Some manufacturers have expressed interest in replacing current coating solvents with these compounds, and emissions reductions would be expected from any VOC-containing solvents ultimately replaced by these newly exempted compounds. However, this action does not require the use of exempt compounds, and emissions reductions from the proposed amendments are therefore not claimed.

B. Cost-Effectiveness Analysis

Since use of these compounds is strictly voluntary, there is no forced additional cost to operators or manufacturers for using coatings or solvent cleaning blends that contain DMC, PC, MF, or TBAc.

C. Socioeconomic Analysis

California Health and Safety Code Section 40728.5 requires air districts to assess any socioeconomic impacts when adopting, amending, or repealing a rule that significantly affects air quality or emissions limitations. A socioeconomic impact analysis is not required for this rule amendment because the proposed amendments do not establish emission limitations and do not require the use of the exempt VOCs.

D. Environmental Impact Analysis

Pursuant to the California Environmental Quality Act (CEQA), the District has reviewed the possible environmental impacts of adding DMC and PC to the exempt compounds list contained in District Rule 1020 (Definitions). As presented in the Final Draft Staff Report, EPA considers these chemicals to be exempt volatile organic compounds; these chemicals are already in use in California in cosmetics and other products; and, while manufacturers and other businesses may choose to reformulate existing products, the Rule 1020 amendments establish no requirement to do so.

There is no substantial evidence in the whole record before the District that the proposed amendments to Rule 1020 would cause any adverse effects on the environment. The District finds that the project is exempt per the general rule that CEQA applies only to projects which have the potential for causing a significant effect on the environment (CEQA Guidelines §15061(b)(3)). For these reasons, the District is proposing to file a Notice of Exemption upon Board adoption of the proposed amendments to Rule 1020.

E. Rule Consistency Analysis

Under California Health and Safety Code Sections 40727 and 40727.2, before adopting or amending a regulation, an air district must make a rule consistency finding. The air district is to compare the emission limits, operating parameters, and recordkeeping requirements in its proposed regulation to corresponding elements in existing state or federal regulations that apply to the same equipment or source to ensure that requirements are not contradictory.

The proposed revisions to Rule 1020 do not include emission limits, operating parameters, or recordkeeping requirements. Furthermore, the proposed revisions align Rule 1020 definitions to definitions in other District and federal regulations. As such, Rule 1020 is consistent with other regulations on the same sources.

VII. REFERENCES

Air Quality: Revision to Definition of Volatile Organic Compounds--Exclusion of Propylene Carbonate and Dimethyl Carbonate, 74 Fed. Reg. 12, pp. 3437–3441. (2009, January 21). (to be codified at 40 CFR Part 51).

California Office of Environmental Health Hazard Assessment [OEHHA]. (2012, February 16). Memorandum: *Screening Values for Dimethyl Carbonate.*

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APPENDIX A

COMMENTS AND RESPONSES TO THE NOVEMBER 18, 2010 DRAFT VERSION OF RULE 1020

February 21, 2013

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SUMMARY OF SIGNIFICANT COMMENTS AND RESPONSES TO DRAFT RULE 1020 DATED NOVEMBER 18, 2010

EPA Region IX Staff Comments:

EPA Region IX staff has reviewed the draft amendments and indicated, via e-mail, that because the amendments are consistent with the EPA VOC definition they have no comments.

California Air Resources Board (ARB) Comments

1. **COMMENT:** The Air Resources Board is conducting indoor health assessments to estimate likely indoor exposures to DMC during realistic but high-exposure conditions. Since DMC may be used in paints and solvents, we are estimating exposures from painting a small, residential bathroom as well at auto repair shops. ARB expects to complete the assessment and send an advisory memo on DMC to California Air Pollution Control Officers Association (CAPCOA) next month (January 2011). The rule project should be delayed until the advisory memo is publicly available and the District has the opportunity to evaluate the memo's conclusions.

   RESPONSE: The District delayed the rule project and reviewed ARB's analysis. ARB's analysis related to consumer use of architectural coatings, which is outside the District's regulatory jurisdiction. ARB did not propose any action with regard to state-wide exemption of DMC. For this reason, the District is proceeding with the proposed amendments to Rule 1020 to exempt DMC consistent with the EPA ruling in 2009. The District will evaluate the use and risk of DMC at stationary sources consistent with its *Risk Management Policy for Permitting New and Modified Sources.*

Stakeholders submitting comments:

American Coatings Association (ACA)
Kowa American Corporation (KAC)
LyondellBasell Industries (LBI)

2. **COMMENT:** The coatings industry is under constant pressure to reformulate products to lower and lower VOC content. As a result there is a critical and urgent need for safe, effective and affordable exempt solvents and coating formulators need all available tools to formulate both lower VOC and reactivity coatings. As such, dimethyl carbonate and propylene carbonate should be added to the list of exempt compounds without any restrictions since these compounds were exempted by the US EPA, nearly every state in US and

many California Air Districts based on their negligible contribution to tropospheric ozone formation. (ACA, LBI)

RESPONSE: Comment noted. Please refer to the Final Draft Staff Report for language supporting the District's decision to amend Rule 1020.

3. **COMMENT:** Kowa American fully agrees with the proposed VOC exemption rule as written and strongly urges that the rule be adopted as soon as possible. We feel DMC being VOC exempt will allow your local businesses a much greater degree of flexibility in meeting the more stringent VOC restrictions. We also think that with the increasingly strict VOC regulations that having additional VOC exempt solvents is a form of regulatory relief that your constituents will welcome. (KAC)

   RESPONSE: Additional technical information about this chemical originally provided with this comment has been evaluated and incorporated into the Final Draft Staff Report as appropriate.

4. **COMMENT:** DMC should be subject to the same Authority to Construct (ATC) and Permit-to-Operate (PTO) requirements as methyl formate since the two chemicals share the common metabolite methanol. (LBI)

   RESPONSE: The proposed amendments to Rule 1020 reflect the deletion of use limits requiring and ATCs and PTOs for methyl formate.

5. **COMMENT:** ATC and PTO requirements should be removed for tertiary butyl acetate (TBAc) since new scientific evidence on tertiary butyl alcohol and TBAc and expert opinions confirm that neither compound poses a cancer risk to humans. (LBI)

   RESPONSE: The proposed amendments to Rule 1020 reflect the deletion of use limits requiring and ATCs and PTOs for TBAc.

APPENDIX B

FEDERAL REGISTER ANNOUNCEMENT OF USEPA EXEMPTING DIMETHYL CARBONATE AND PROPYLENE CARBONATE

February 21, 2013

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Federal Register / Vol. 74, No. 12 / Wednesday, January 21, 2009 / Rules and Regulations **3437**

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 51

[EPA–HQ–OAR–2006–0948; FRL–8763–7]

RIN 2060–AN75

Air Quality: Revision to Definition of Volatile Organic Compounds—Exclusion of Propylene Carbonate and Dimethyl Carbonate

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This action revises EPA's definition of volatile organic compounds (VOCs) for purposes of preparing state implementation plans (SIPs) to attain the national ambient air quality standard for ozone under Title I of the Clean Air Act (Act). This revision adds the compounds propylene carbonate and dimethyl carbonate to the list of compounds which are excluded from the definition of VOC on the basis that these compounds make a negligible contribution to tropospheric ozone formation.

DATES: This final rule is effective on February 20, 2009.

ADDRESSES: The EPA has established a docket for this action under Docket ID No. EPA–HQ–OAR–2006–0948. All documents in the docket are listed on the *http://www.regulations.gov* Web site. Although listed in the index, some information is not publicly available, i.e., confidential business information (CBI) or other information whose disclosure is restricted by statute. Certain other material, such as copyrighted material, will be publicly available only in hard copy. Publicly available docket materials are available either electronically in *http://www.regulations.gov* or in hard copy at the Docket ID No. EPA–HQ–OAR–2006–0948, EPA/DC, EPA West, Room 3334, 1301 Constitution Avenue, Northwest, Washington, DC. The Public Reading Room is open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number for the Public Reading Room is (202) 566–1744, and the telephone number for the Docket ID No. EPA–HQ–OAR–2006–0948 is (202) 566–1742.

FOR FURTHER INFORMATION CONTACT: William L. Johnson, Office of Air Quality Planning and Standards, Air Quality Policy Division, Mail code C539–01, Research Triangle Park, NC 27711, telephone (919) 541–5245.; fax number: 919–541–0824; e-mail address: *Johnson.WilliamL@epa.gov.*

SUPPLEMENTARY INFORMATION:

I. General Information

A. Does this action apply to me?

You may be an entity affected by this policy change if you use or emit propylene carbonate or dimethyl carbonate. States which have programs to control VOC emissions will also be affected by this change.

Category	Examples of affected entities
Industry ..	Industries that make and use coatings, adhesives, inks or which perform paint stripping or pesticide application.
States	States that control VOC.

This table is not intended to be exhaustive, but rather provides a guide for readers regarding entities likely to be affected by this action. This table lists the types of entities that EPA is now aware of that could potentially be affected by this action. Other types of entities not listed in the table could also be affected. If you have questions regarding the applicability of this action to a particular entity, consult the person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section. This action has no substantial direct effects on industry because it does not impose any new mandates on these entities, but, to the contrary, removes two chemical compounds from the regulatory definition of VOC, and therefore from regulation for federal purposes.

B. How is this preamble organized?

The information presented in this preamble is organized as follows:

Outline

II. Background

Tropospheric ozone, commonly known as smog, occurs when VOCs and nitrogen oxides (NO_X) react in the atmosphere. Because of the harmful health effects of ozone, EPA and state governments limit the amount of VOCs and NO_X that can be released into the atmosphere. The VOCs are those organic compounds of carbon which form ozone through atmospheric photochemical reactions. Different VOCs have different levels of reactivity—that is, they do not react to form ozone at the same speed or do not form ozone to the same extent. Some VOCs react slowly, and changes in their emissions have limited effects on local or regional ozone pollution episodes. It has been EPA's policy that organic compounds with a negligible level of reactivity should be excluded from the regulatory definition of VOC, so as to focus VOC control efforts on compounds that do significantly increase ozone concentrations. The EPA also believes that exempting such compounds creates an incentive for industry to use negligibly reactive compounds in place of more highly reactive compounds that are regulated as VOCs. The EPA lists these negligibly reactive compounds in its regulations (at 40 CFR 51.100(s)) and excludes them from the definition of VOCs.

Since 1977, EPA has used the reactivity of ethane as the threshold for determining negligible reactivity. Compounds that are less reactive than, or equally reactive to, ethane under the assumed conditions may be deemed negligibly reactive. Compounds that are more reactive than ethane continue to be considered reactive VOCs and therefore subject to control requirements. The selection of ethane as the threshold compound was based on a series of smog chamber experiments that underlay the 1977 policy.

In the past, EPA has considered three different metrics to compare the reactivity of a specific compound to that of ethane: (i) The reaction rate constant with the hydroxyl radical (known as k_{OH}), (ii) maximum incremental reactivities (MIR) expressed on a reactivity per gram basis, and (iii) MIR expressed on a reactivity per mole basis. Table 1 presents these three reactivity metrics for ethane and for the two compounds discussed in this rule. Differences between these three metrics are discussed below.

TABLE 1—REACTIVITIES OF ETHANE AND COMPOUNDS CONSIDERED FOR EXEMPTION

Compound	k_{OH} (cm^3/molecule-sec)	MIR (g O_3/mole VOC)	MIR (g O_3/gramVOC)
Ethane	2.4×10^{-13}	8.12	0.27
Propylene carbonate	6.9×10^{-13}	27.56	0.27
Dimethyl carbonate	3.49×10^{-13}	5.04	0.056

Notes:

1. k_{OH} value for ethane is from: R. Atkinson., D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, Jr., R. G. Hynes, M. E. Jenkin, J. A. Kerr, M. J. Rossi and J. Troe (2004), Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry

2. k_{OH} value for propylene carbonate is reported in: W.P.L. Carter, D. Luo, I.L. Malkina, E.C. Tuazon, S.M. Aschmann, and R. Atkinson (July 8, 1996), ''Investigation of the Atmospheric Ozone Formation Potential of t-butyl Alcohol, N-Methyl Pyrrolidinone and Propylene Carbonate.'' University of California—Riverside. *ftp://ftp.cert.ucr.edu/pub/carter/pubs/arcorpt.pdf.*

3. k_{OH} value for dimethyl carbonate is reported in: Y. Katrib, G. Deiber, P. Mirabel, S. LeCalve, C. George, A. Mellouki, and G. Le Bras (2002), ''Atmospheric loss processes of dimethyl and diethyl carbonate,'' J. Atmos. Chem., 43: 151–174.

4. All maximum incremental reactivities or MIR (g O_3/g VOC) values are from: W. P. L. Carter, ''Development of the SAPRC–07 Chemical Mechanism and Updated Ozone Reactivity Scales,'' Appendix B, July 7, 2008. This may be found at *http://www.engr.ucr.edu/~carter/SAPRC/saprc07.pdf.* These values have been revised slightly from those given in the proposal notice (72 FR 55717).

5. MIR (g O_3/mole VOC) values were calculated from the MIR (g O_3/g VOC) values by determining the number of moles per gram of the relevant organic compound.

The k_{OH} is the reaction rate constant of the compound with the OH radical in the air. This reaction is typically the first step in a series of chemical reactions by which a compound breaks down in the air and participates in the ozone forming process. If this step is slow, the compound will likely not form ozone at a very fast rate. The k_{OH} values have long been used by EPA as a measure of photochemical reactivity and ozone forming activity, and they have been the basis for most of EPA's previous exclusions of negligibly reactive compounds. The k_{OH} metric is inherently molar, i.e., it measures the rate at which molecules react.

The MIR values, both by mole and by mass, are more recently developed measures of photochemical reactivity derived from a computer-based photochemical model. These measures consider the complete ozone forming activity of a compound, not merely the first reaction step. Further explanation of the MIR metric can be found in: W. P. L. Carter, ''Development of Ozone Reactivity Scales for Volatile Organic Compositions,'' Journal of the Air & Waste Management Association, Vol 44, 881–899, July 1994.

The MIR values are usually expressed either as grams of ozone formed per mole of VOC (molar basis) or as grams of ozone formed per gram of VOC (mass basis). For comparing the reactivities of two compounds, using the molar MIR values considers an equal number of molecules of the two compounds. Alternatively, using the mass MIR values compares an equal mass of the two compounds, which will involve different numbers of molecules, depending on the relative molecular weights. The molar MIR comparison is consistent with the original smog chamber experiments, which compared equal molar concentrations of individual VOCs, that underlie the original selection of ethane as the threshold compound. It is also consistent with previous reactivity determinations based on inherently molar k_{OH} values. The mass MIR comparison is consistent with how MIR values and other reactivity metrics are applied in reactivity-based emission limits, specifically the California Air Resources Board rule for aerosol coatings (see *http://www.arb.ca.gov/consprod/regs/apt.pdf*).

Given the relatively low molecular weight of ethane, use of the mass basis tends to result in more VOCs falling into the ''negligibly reactive'' class versus the molar basis. This means that, in some cases, a compound might be considered less reactive than ethane and eligible for VOC exemption under the mass basis but not under the molar basis. One of the compounds considered in this action falls into this situation, where the molar MIR value is greater than that of ethane, but the mass MIR value is less than or equal to that of ethane. This compound is propylene carbonate.

The EPA has considered the choice between a molar or mass basis for the comparison to ethane in past rulemakings and guidance. The design of the VOC exemption policy, including the choice between a mass and mole basis, has been critiqued in the published literature.[1] Most recently, in ''Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans'' published on September 13, 2005 (70 FR 54046), EPA stated:

''* * * a comparison to ethane on a mass basis strikes the right balance between a threshold that is low enough to capture compounds that significantly affect ozone concentrations and a threshold that is high enough to exempt some compounds that may usefully substitute for more highly reactive compounds. * * * When reviewing compounds that have been suggested for VOC exempt status, EPA will continue to compare them to ethane using k_{OH} expressed on a molar basis and MIR values expressed on a mass basis.''

Relying on a comparison of mass MIR values consistent with this guidance, EPA proposed to revise its definition of VOC at 40 CFR 51.100(s) to add propylene carbonate and dimethyl carbonate to the list of compounds that are exempt because they are negligibly reactive since they are equal to or less reactive than ethane on a mass basis. For propylene carbonate, EPA invited comment on the alternative use of a molar basis for the comparison of these compounds to ethane.

The technical rationale for recommending an exemption for each of the individual compounds is given below:

A. Propylene Carbonate

Huntsman Corporation submitted a petition to EPA on July 27, 1999, requesting that propylene carbonate be exempted from VOC control based on its low reactivity relative to ethane.

Propylene carbonate (CAS registry number 108–32–7) is an odorless non-viscous clear liquid with a low vapor pressure (0.023 mm Hg at 20(C) and low evaporation rate compared to many other commonly used organic solvents. It has been used in cosmetics, as an adhesive component in food packaging, as a solvent for plasticizers and synthetic fibers and polymers, and as a solvent for aerial pesticide application.

[1] Basil Dimitriades, ''Scientific Basis of an Improved EPA Policy on Control of Organic Emissions for Ambient Ozone Reduction.'' Journal of the Air & Waste Management Association, 49:831–838, July 1999.

Huntsman submitted several pieces of information to support its petition, all of which have been added to the docket for this action. One of these pieces of information was ''Investigation of the Atmospheric Ozone Formation Potential of t-butyl Alcohol, N-Methyl Pyrrolidinone and Propylene Carbonate'' by William P. L. Carter, Dongmin Luo, Irina L. Malkina, Ernesto C. Tuazon, Sara M. Aschmann, and Roger Atkinson, University of California at Riverside, July 8, 1996. Table 8 of that reference lists the MIR for propylene carbonate (on a gram basis) as 1.43 times higher than that of ethane. However, in Table 1 above, EPA has shown a 2007 MIR value that was taken from more recent 2007 data from Dr. Carter's Web site. This 2007 MIR value is lower than that of ethane on a mass basis.

From the data in Table 1, it can be seen that propylene carbonate has a higher k_{OH} value than ethane, meaning that it initially reacts more quickly in the atmosphere than ethane. A molecule of propylene carbonate is also more reactive than a molecule of ethane, as shown by the molar MIR (g O_3/mole VOC) values, since equal numbers of moles have equal numbers of molecules. However, a gram of propylene carbonate is less reactive, or creates less ozone on the day of its emission to the atmosphere, than a gram of ethane. This is because propylene carbonate has a molecular weight (102), which is over three times that of ethane (30), thus requiring less than a third the number of molecules of propylene carbonate to weigh a gram than the number of molecules of ethane needed to weigh a gram.

Based on the mass MIR (g O_3/g VOC) value for propylene carbonate being equal to or less than that of ethane, EPA finds that propylene carbonate is ''negligibly reactive'' and therefore exempt for the regulatory definition of VOC at 40 CFR 51.100(s). EPA took comments on whether the comparison of propylene carbonate to ethane should instead be made on the basis of the molar MIR (g O_3/mole VOC) value. None of the comments received during the public comment period opposed using the g O_3/g VOC basis. In fact, the comments which addressed that issue supported the use of the MIR on a g O_3/g VOC basis for granting exemptions.

B. Dimethyl Carbonate

The EPA received a petition from Kowa America Corporation on July 29, 2004 seeking an exemption from the regulatory definition of VOC for dimethyl carbonate. This petition asserted that dimethyl carbonate (DMC) is less photochemically reactive than ethane and asked for the exemption on that basis.

Dimethyl carbonate (CAS registry number 616–38–6) may be used as a solvent in paints and coatings. The petitioner anticipated that it might be used in waterborne paints and adhesives because it is partially water soluble. It is also used as a methylation and carbonylation agent in organic synthesis. It can be used as a fuel additive.

In support of its petition, the petitioner presented articles which give k_{OH} and MIR values for the compound. These articles have been placed in the docket.

As shown in Table 1, DMC has a greater k_{OH} value than ethane, which indicates that DMC will likely initially react more quickly in the atmosphere. However, the MIR values for DMC calculated on either a mass or mole basis are less than that of ethane, which indicates lower reactivity overall. Based on these data, EPA finds that DMC is ''negligibly reactive'' and therefore exempt from the regulatory definition of VOC at 40 CFR 51.100(s). Because both the mass and molar MIR values of DMC are less than those of ethane, this chemical meets EPA's exemption criteria under either MIR metric.

III. Response to Comments

EPA proposed these actions on October 1, 2007 (72 FR 55717) and took public comment on the proposal. Here is a summary of the comments received during the public comment period and EPA's response. There was no request for a public hearing on the proposal and none was held.

There were four comment letters submitted to the docket during the public comment period. One comment letter was from an individual. Two were from chemical companies. One comment letter was from a trade association. The comments are summarized below.

Comment: The Web site reference for the latest MIR values contained an error. The site which was listed as *http://pah.cert.ucr.edu/carter/SAPRC/scales07.xls* should have been *http://pah.cert.ucr.edu/~carter/SAPRC/scales07.xls.*

Response: We left out the ~ sign in the Web address which made it incorrect. The latest MIR data which is used in this final rule may be found in Appendix B of the July 7, 2008 report by William P. L. Carter ''Development of the SAPRC–07 Chemical Mechanism and Updated Ozone Reactivity Scales.'' This report may be found at *http://www.engr.ucr.edu/~carter/SAPRC/saprc07.pdf.*

Comment: One commenter corrected certain technical information about the evaporation rate of dimethyl carbonate which was listed in the docket.

Response: This correction is noted, but this minor change did not impact whether or not EPA should finalize the exemption petition.

Comment: One commenter supported the use of the latest MIR values for making VOC exemption determinations. There were no comments opposing the use of the latest MIR values.

Response: EPA acknowledged recent MIR values which were made public shortly before the proposal to grant VOC exemption to propylene carbonate and dimethyl carbonate, but based the proposal on older MIR values which had been previously published. EPA is using the latest MIR values for this final rule.[2] The use of the newer MIR values does not change the conclusion about the VOC exemption of propylene carbonate and dimethyl carbonate.

Comment: The two industry commenters, and the trade association comment letter each expressed support for the VOC exemption of propylene carbonate and dimethyl carbonate.

Response: EPA acknowledges this support and notes that there were no comments opposing these exemptions.

Comment: Three commenters opposed separate tracking and reporting for propylene carbonate and dimethyl carbonate. Two of these commenters also expressed opposition for separate tracking for any VOC exempt compounds.

Response: Although the rule preamble encourages record keeping for propylene carbonate and dimethyl carbonate, there is no requirement for this in the rule itself. Record keeping for other exempt compounds is not the subject of this rulemaking, so comments about that are not relevant to this action.

Comment: Three of the commenters support the use of the mass-based MIR approach versus the mole-based approach. One of the commenters submitted as part of his comments a November 15, 1999 letter written by William P.L. Carter supporting the use of impact per mass as an appropriate basis for comparing ozone reactivities when making VOC exemption decisions. This Carter letter had previously been submitted to EPA as part of the tertiary butyl acetate VOC exemption rule making (69 FR 69298).

[2] The MIR values used for this rule may be found in Appendix B of the July 7, 2008 report by William P.L. Carter ''Development of the SAPRC–07 Chemical Mechanism and Updated Ozone Reactivity Scales.'' This report may be found at *http://www.engr.ucr.edu/carter/SAPRC/saprc07.pdf* or in the docket for this rule.

There were no comments opposing the use of the mass-based MIR approach.

Response: EPA specifically requested comment on this subject for propylene carbonate since the mole based MIR value for that compound is higher than that of ethane and using the mole based MIR value would not allow the exemption for propylene carbonate. Because there were no comments opposed to the use of the mass based approach, EPA is proceeding to grant these exemptions on a mass based MIR basis in keeping with the September 13, 2005 interim guidance on control of volatile organic compounds in ozone state implementation plans which says ''EPA will continue to compare them [i.e., compounds] to ethane using k_{OH} expressed on a molar basis and MIR values expressed on a mass basis.''

Comment: One commenter, who was the petitioner for dimethyl carbonate, said that the company recommended exposure limit of 200 ppm time weighted average 8 hour for dimethyl carbonate is identical to that of methyl acetate, an existing VOC exempt solvent. This commenter also said that methyl acetate like DMC has the potential for hydrolyzing to form methanol in the body and therefore they would be similar in their toxicity profiles and safety handling requirements. The commenter also denied a statement in Hawley's Condensed Chemical Dictionary that DMC is both toxic by inhalation and a strong irritant.

Response: In the proposal, EPA said ''While EPA does not have information to suggest that the proposed exemptions could increase health risks due to possible toxicity of the exempted compounds, we invite the public to submit comments and additional information relevant to this issue.'' The comments here are the only comments EPA received regarding health effects of these compounds. These comments have not led EPA to identify unusual health risks from the compounds.

IV. Final Action

This action is based on EPA's review of the material in Docket ID No. EPA–HQ–OAR–2006–0948. The EPA hereby amends its definition of VOC at 40 CFR 51.100(s) to exclude propylene carbonate and dimethyl carbonate from the regulatory definition of VOC for use in ozone SIPs and ozone controls for purposes of attaining the ozone national ambient air quality standard.

The revised definition will also apply for purposes of any federal implementation plan for ozone nonattainment areas (*see* e.g., 40 CFR 52.741(a)(3)). States are not obligated to exclude from control as a VOC those compounds that EPA has found to be negligibly reactive. However, if this action is made final, states should not include these compounds in their VOC emissions inventories for determining reasonable further progress under the Act (*e.g.*, section 182(b)(1)) and may not take credit for controlling these compounds in their ozone control strategy.

Excluding a compound from the regulatory definition of VOC may lead to changes in the amount of the exempt compound used and the types of applications in which the exempt compound is used. Although the final rule has no mandatory reporting requirements, EPA urges states to continue to inventory the emissions of these compounds for use in photochemical modeling.

V. Statutory and Executive Order Reviews

A. Executive Order 12866: Regulatory Planning and Review

This action is not a ''significant regulatory action'' under the terms of Executive Order 12866 (58 FR 51735, October 4, 1993) and is therefore not subject to review under the Executive Order.

B. Paperwork Reduction Act

This action does not impose any new information collection burden under the provisions of the *Paperwork Reduction Act,* 44 U.S.C. 3501 *et seq.* Burden is defined at 5 CFR 1320.3(b). This action is deregulatory in nature and removes requirements rather than adds requirements. The regulation is a rule change that revises a definition of volatile organic compound and imposes no record keeping or reporting requirements.

C. Regulatory Flexibility Act

The Regulatory Flexibility Act (RFA) requires an agency to prepare a regulatory analysis of any rule subject to notice and comment rulemaking requirements under the Administrative Procedure Act or any other statue unless the agency certifies that the rule will not have a significant economic impact on a substantial number of small entities. Small entities include small businesses, small organizations, and small governmental jurisdictions.

For purposes of assessing the impacts of this action on small entities, small entity is defined as: (1) A small business as defined by the Small Business Administration's (SBA) regulations at 13 CFR 121.201); (2) a small governmental jurisdiction that is a government of a city, county, town, school district, or special district with a population of less than 50,000; and (3) a small organization that is any not-for-profit enterprise which is independently owned and operated and is not dominant in its field.

After considering the economic impacts of this final action on small entities, I certify that this rule will not have a significant economic impact on a substantial number of small entities. This rule will not impose any requirements on small entities. This rule concerns only the definition of VOC and does not directly regulate any entities. The RFA analysis does not consider impacts on entities which the action in question does not regulate. See *Motor & Equipment Manufacturers Ass'n* v. *Nichols,* 142 F. 3d 449, 467 (D.C. Cir. 1998); *United Distribution Cos.* v. *FERC,* 88 F. 3d 1105, 1170 (D.C. Cir. 1996), cert. denied, 520 U.S. 1224 (1997). Pursuant to the provision of 5 U.S.C. 605(b), I hereby certify that the rule will not have an impact on small entities.

D. Unfunded Mandates Reform Act

This action contains no federal mandates under the provisions of Title II of the Unfunded Mandates Reform Act of 1995 (UMRA), 2 U.S.C. 1531–1538 for state, local, and tribal governments and the private sector. Since this rule is deregulatory in nature and does not impose a mandate upon any source, this rule is not estimated to result in the expenditure by state, local and tribal governments or the private sector of $100 million in any 1 year. Therefore, the Agency has not prepared a budgetary impact statement or specifically addressed the selection of the least costly, most cost-effective, or least burdensome alternative. Because small governments will not be significantly or uniquely affected by this rule, the Agency is not required to develop a plan with regard to small governments. This action is also not subject to the requirements of section 203 of the UMRA because it contains no regulatory requirements that might significantly or uniquely affect small governments. As discussed above, this final rule does not impose any new requirements on small governments.

E. Executive Order 13132: Federalism

Executive Order 13132, entitled ''Federalism'' (64 FR 43255, August 10, 1999), requires EPA to develop an accountable process to ensure ''meaningful and timely input by state and local officials in the development of regulatory policies that have federalism implications.'' ''Policies that have federalism implications'' is defined in the Executive Order to include regulations that have ''substantial direct effects on the states, on the relationship between the national government and the states, or on the distribution of power and responsibilities among the various levels of government.''

This final rule does not have federalism implications. It will not have substantial direct effects on the state, on the relationship between the national government and the states, or on the distribution of power and responsibilities among the various levels of government, as specified in Executive Order 13132. This rule concerns only the definition of VOC. Thus, Executive Order 13132 does not apply to this rule.

F. Executive Order 13175: Consultation and Coordination With Indian Tribal Governments

This rule does not have tribal implications, as specified in Executive Order 13175 (65 FR 67249, November 9, 2000). It will not have substantial direct effects on tribal governments, on the relationship between the federal government and Indian Tribes, or on the distribution of power and responsibilities between the federal government and Indian Tribes, as specified in Executive Order 13175. This action does not have any direct effects on Indian Tribes. Thus, Executive Order 13175 does not apply to this rule.

G. Executive Order 13045: Protection of Children From Environmental Health and Safety Risks

EPA interprets Executive Order 13045 (62 FR 19885, April 23, 1997) as applying only to those regulatory actions that concern health or safety risks, such that the analysis required under section 5–501 of the Executive Order has the potential to influence the regulation. This final rule is not subject to Executive Order 13045 because it does not establish an environmental standard intended to mitigate health or safety risks.

H. Executive Order 13211: Actions That Significantly Affect Energy Supply, Distribution, or Use

This final rule is not a ''significant energy action'' as defined in Executive Order 13211 (66 FR 28355, May 22, 2001), because it is not likely to have a significant adverse effect on the supply, distribution, or use of energy. Further, we have concluded that this rule is not likely to have any adverse energy effects.

I. National Technology Transfer Advancement Act

Section 12(d) of the National Technology Transfer and Advancement Act of 1995 (''NTTAA''), Public Law 104–113, section 12(d) (15 U.S.C. 272 note) directs EPA to use voluntary consensus standards in its regulatory activities unless to do so would be inconsistent with applicable law or otherwise impractical. Voluntary consensus standards are technical standards (*e.g.*, materials specifications, test methods, sampling procedures, and business practices) that are developed or adopted by voluntary consensus standards bodies. NTTAA directs EPA to provide Congress, through OMB, explanations when the Agency decides not to use available and applicable voluntary consensus standards.

This action does not involved technical standards. Therefore, EPA did not consider the use of any voluntary consensus standards.

J. Executive Order 12898: Federal Actions To Address Environmental Justice in Minority Populations and Low-Income Populations

Executive Order 12898 (59 FR 7629 (Feb. 16, 1994)) establishes federal executive policy on environmental justice. Its main provision directs federal agencies, to the greatest extent practicable and permitted by law, to make environmental justice part of their mission by identifying and addressing, as appropriate, disproportionately high and adverse human health or environmental effects of their programs, policies, and activities on minority populations and low-income populations in the United States.

EPA has determined that this final rule will not have disproportionately high and adverse human health or environmental effects on minority or low-income populations because it does not affect the level of protection provided to human health or the environment. The final rule amendment is deregulatory and does allow relaxation of the control measures on sources. However, this is not expected to lead to increased ozone formation since the compounds being exempted have been determined to have negligible photochemical reactivity.

K. Congressional Review Act

The Congressional Review Act, 5 U.S.C. 801 *et seq.*, as added by the Small Business Regulatory Enforcement Fairness Act of 1996, generally provides that before a rule may take effect, the agency promulgating the rule must submit a rule report, which includes a copy of the rule, to each House of Congress and to the Comptroller General of the United States, Section 804 exempts form section 801 the following types of rules: (1) Rules of particular application; (2) rules relating to agency management or personnel; and (3) rules of agency organization, procedure, or practice that do not substantially affect the rights or obligations of non-agency parties, 5 U.S.C. 804(3). The EPA is not required to submit a rule report regarding this action under section 801 because this is a rule of particular applicability to manufacturers and users of these specific exempt chemical compounds. This action is not a ''major rule'' as defined by 5 U.S.C. 804(2). Therefore, this rule will be effective on February 20, 2009.

List of Subjects in 40 CFR Part 51

Environmental protection, Administrative practice and procedure, Air pollution control, Ozone, Reporting and recordkeeping requirements, Volatile organic compounds.

Dated: January 13, 2009.

Stephen L. Johnson,

Administrator.

■ For reasons set forth in the preamble, part 51 of chapter I of title 40 of the Code of Federal Regulations is amended as follows:

PART 51—REQUIREMENTS FOR PREPARATION, ADOPTION, AND SUBMITTAL OF IMPLEMENTATION PLANS

■ 1. The authority citation for Part 51, Subpart F, continues to read as follows:

Authority: 42 U.S.C. 7401, 7411, 7412, 7413, 7414, 7470–7479, 7501–7508, 7601, and 7602.

§ 51.100 [Amended]

■ 2. Section 51.100 is amended at the end of paragraph (s)(1) introductory text by removing the words ''and perfluorocarbon compounds which fall into these classes:'' and adding in their place a semi-colon and the words ''propylene carbonate; dimethyl carbonate; and perfluorocarbon compounds which fall into these classes:''.

[FR Doc. E9–1150 Filed 1–16–09; 8:45 am]

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APPENDIX C

OEHHA SCREENING VALUES FOR DIMETHYL CARBONATE

February 21, 2013

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Office of Environmental Health Hazard Assessment

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Matthew Rodriquez
Secretary for
Environmental Protection

Edmund G. Brown Jr.
Governor

MEMORANDUM

TO: Linda Murchison
Chief, Planning & Technical Support Division
Air Resources Board

FROM: Melanie A. Marty, Ph.D MM
Chief, Air Toxicology and Epidemiology Branch

DATE: February 16, 2012

SUBJECT: SCREENING VALUES FOR DIMETHYL CARBONATE

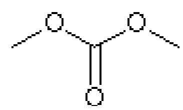
I am responding to ARB's request to evaluate the potential health effects associated with use of DMC, to support your review of a petition to exempt DMC from the VOC definition in ARB's consumer products regulation. My staff has summarized the available data on the toxicity of DMC and its metabolites, and developed screening values for use in your review. The available data are limited, with no lifetime inhalation study of DMC. For that reason OEHHA staff has in part relied on the reference levels established for methanol, a DMC metabolite, to develop acute and chronic screening levels (see attachment). Use of these screening values as part of the evaluation of exposure scenarios should help identify whether the use of DMC in consumer products may pose potential health risks. The limited data preclude development of a formal REL proposal at this time. However, these DMC screening values can be used to assist in ARB's review of the DMC exemption petition based on the REL for methanol.

If you have any questions, please call Dr. Jim Collins of my staff at 510 622-3146.

Dimethyl Carbonate

(CAS# 616-38-6)

(Synonyms: Carbonic acid, methyl ester; methyl carbonate)



1 Introduction

Dimethyl carbonate has been used as a reagent in methylation reactions (HSDB, 2009), and has possible uses in paints, coatings, and adhesives. On January 13, 2009 the United States Environmental Protection Agency (U.S. EPA) granted a Volatile Organic Compound (VOC) exemption to dimethyl carbonate (USEPA, 2009) since it makes a negligible contribution to tropospheric ozone formation. In a letter dated March 2, 2009, Kowa American submitted to the California Air Resources Board (ARB) an Application for VOC Exempt Status for dimethyl carbonate in California. The application contains limited toxicological information. As part of its consideration of exempt status for a VOC, ARB asked the Office of Environmental Health Hazard Assessment (OEHHA) to review the toxicology of dimethyl carbonate.

Dimethyl carbonate does not have a Threshold Limit Value (TLV) for worker exposure. U.S. EPA also does not have any health values for exposure of the general public to dimethyl carbonate. OEHHA notes that increased public exposure is likely if dimethyl carbonate is exempted from VOC regulation, and its use becomes more widespread in California. There are insufficient data available for dimethyl carbonate to allow the development of Reference Exposure Levels (RELs) for dimethyl carbonate. Instead we used what data are available to us in developing acute and chronic screening values for dimethyl carbonate to compare to estimated exposures from use in California. Additionally, we discuss formation and toxicity of possible dimethyl carbonate metabolites.

2 Physical and Chemical Properties of Dimethyl Carbonate (HSDB, 2009)

Description	Colorless liquid; pleasant odor
Molecular formula	C3-H6-O3
Molecular weight	90.08
Density	1.0636 @ 25°C/15°C
Boiling point	90-91ºC
Melting point	0.5ºC
Vapor pressure	55.364 mm Hg @ 25ºC
Odor threshold	Not found
Log Kow	0.23 (estimated) (Meylan and Howard, 1995; SRC, 2009)
Bioconcentration factor	3.16 (estimated) (Kowa American, 2009)
Solubility	Miscible with alcohol and ether; Insoluble in water (HSDB, 2009); Solubility = 13.9 g/100 g water (Kowa American, 2009)
Flammability	Highly flammable
Conversion factor	3.68 µg/m^3 per ppb @ 25ºC

3 Toxicity of Dimethyl Carbonate

3.1 Metabolism of Dimethyl Carbonate

Dimethyl carbonate is readily hydrolyzed to carbon dioxide and methanol in the environment and presumably in the body via esterases (Kowa America, 2009). Methanol is metabolized to formaldehyde, which is then further oxidized to formic acid.

3.2 Animal Toxicity of Dimethyl Carbonate

The International Uniform Chemical Information Database (IUCLID) dataset (European Commission, 2000) indicates the following data gaps for dimethyl carbonate: chronic toxicity, genotoxicity, carcinogenicity, reproductive and developmental toxicity, neurotoxicity, immunotoxicity, aquatic toxicity, and toxicity to terrestrial organisms.

The IUCLID dataset lists a rat 4 hour LC_{50} of > 140 mg/L (> 38,000 parts per million (ppm)).

The IUCLID dataset reports that dimethyl carbonate is slightly irritating to the rabbit eye and not irritating to rabbit skin. No dose information is stated.

In a 10-day developmental toxicity study (Exxon, 1992; Bevan and Beyer, 1995), mated female CD-1 mice (96 per dose level) were exposed by inhalation to 0, 300, 1000, or 3000 ppm dimethyl carbonate during gestational days (gd) 6 through 15 for 6 h/day. The females were euthanized on gd 18, and the fetuses from the first 30-32 pregnant dams were weighed, sexed, and examined for external, visceral, and skeletal alterations. Maternal body weights and body weight gains were significantly reduced at 3000 ppm (Table 1).

Table 1. Maternal body weights on gestation days 0, 15, and 18

Dimethyl carbonate	0 ppm	300 ppm	1000 ppm	3000 ppm
Day 0	28.38±1.36 (32)	29.24±1.82 (31)	28.63±1.56 (30)	28.78±1.72 (32)
Day 15	43.47±2.60 (32)	43.03±3.66 (31)	42.80±2.54 (30)	39.23±3.55* (30)
Day 18	51.92±3.40 (30)	51.23±4.69 (30)	51.67±3.11 (30)	45.92±4.90* (30)

* $p<0.01$ vs. control. Values are mean ± 1 SD (number of dams)

Food consumption was significantly reduced at 1000 and 3000 ppm, indicating an adverse effect on the mothers. Gestational parameters affected at 3000 ppm included post-implantation loss due to increased resorptions, and altered sex ratio (fewer males surviving). Fetal body weights/litter were reduced at 3000 ppm indicating a gross adverse effect on the fetus (Table 2) and the number of growth-stunted fetuses (<1 g body weight) was increased.

Table 2. Fetal body weight as a function of dimethyl carbonate concentration

Dimethyl carbonate	0 ppm	300 ppm	1000 ppm	3000 ppm
Males	1.24±0.10 (193)	1.27±0.12 (154)	1.24±0.10 (179)	1.12±0.14* (137)
Females	1.10±0.10 (157)	1.19±0.12 (181)	1.20±0.10 (155)	1.07±0.15* (140)

* $p<0.01$ vs. control. Values are mean ± 1 SD (number of fetuses)

Total incidences of fetal malformations were significantly increased at 3000 ppm and included cleft palate (Table 3), multiple malformations of the bones of the skull, and fused vertebral arches. Skeletal variations, including misshapen sternebrae (breastbones), rudimentary cervical ribs, and well-formed cervical or lumbar ribs, were also increased at 3000 ppm. The No Observed Adverse Effect Level (NOAEL) for maternal and developmental toxicity was 1000 parts per million (ppm) (Exxon, 1992; Bevan and Beyer, 1995). In a developmental toxicity in mice, the NOAEL for inhaled methanol was also 1000 ppm (Rogers et al., 1993).

Table 3. Some significantly increased external malformations

Dimethyl carbonate	0 ppm	300 ppm	1000 ppm	3000 ppm
Total fetuses (total litters)	350 (30)	337 (30)	334 (30)	277 (29)
External malformations				
Cleft palate	3 (2)	0	1 (1)	140 (26)**
Microtia (small ear)	0	0	0	24 (5)*
Low set ear(s)	0	0	0	13 (5)*
Imperforate anus	0	0	0	5 (3)*
Ectrodactyly#	0	0	0	4 (2)*

* $p < 0.05$ vs. control; ** $p < 0.01$ vs. control. Values are number of fetuses with malformations (number of litters affected).
# complete or partial absence of one or more digits

Song et al. (2002) tested three gasoline oxygenates, dimethyl carbonate, ethanol anhydrous, and methyl tertiary butyl ether (MTBE) in the single cell gel electrophoresis (Comet) assay in L-929 mouse fibroblasts. They reported that dimethyl carbonate did not cause DNA damage in the assay (MTBE was positive in the assay). No other studies of genotoxicity were identified. Thus there is a gap in direct data on genotoxicity for dimethyl carbonate.

3.3 Human Toxicity of Dimethyl Carbonate

Dimethyl carbonate is mildly toxic by ingestion and moderately toxic by the intraperitoneal route (Lewis, 1996, in Sax's Dangerous Properties of Industrial Materials: HSDB, 2009). No data were available in the peer-reviewed literature for chronic exposure of humans to dimethyl carbonate. Since so little toxicity information on dimethyl carbonate itself is available, the toxicity of its metabolites is summarized in the following sections.

4 Toxicity of the Metabolites of Dimethyl Carbonate (Methanol, Formaldehyde, and Formic Acid)

Since dimethyl carbonate breaks down to methanol and carbon dioxide, and methanol is metabolized to formaldehyde and formic acid, we briefly review the toxicity of the metabolites. In response to Health and Safety Code Section 44300 *et seq*., OEHHA reviewed the toxicology of formaldehyde and methanol and developed acute and chronic RELs for formaldehyde and methanol (OEHHA 1999; OEHHA, 2000; OEHHA, 2008) and an inhalation cancer unit risk factor for formaldehyde (OEHHA, 2009). The current health values are tabulated below (Table 4).

Table 4. Reference Exposure Levels and cancer inhalation unit risk values

Chemical	*Acute REL*	*Chronic REL*	*Unit Risk (cancer)*
Methanol	28,000 μg/m^3	4000 μg/m^3	None
Formaldehyde	55 μg/m^3	9 μg/m^3	6 x 10^{-6} (μg/m^3)$^{-1}$

4.1 Toxicity of Methanol

The National Toxicology Program reviewed methanol, concentrating on its reproductive and developmental toxicity (NTP-CERHR, 2003). An expert panel judged that the human data were insufficient to evaluate the developmental toxicity of methanol but concluded, based on data from rodents, that developmental toxicity was the most sensitive reproductive endpoint of concern for humans from methanol exposure. Other general reviews of methanol toxicity include Roe (1955) and Kavet and Nauss (1990).

Inhalation of methanol by humans is associated with headache and narcosis due to methanol itself. Ingestion of methanol induces blindness in humans (Roe 1955). Medinsky and Dorman (1995) reviewed the disposition of methanol and of formate, its first metabolite, in humans, non-human primates, and rodents after neurotoxic doses

Formate is also formed endogenously from serine and is detoxified to CO_2 and H_2O by a tetrahydrofolate (THF)-dependent pathway. Rodents detoxify formate more rapidly than primates. Species (e.g., rodents) with high liver THF levels are less sensitive to neurotoxicity due to large doses of methanol than species with low THF levels (e.g., humans and non-human primates). The capacity of primates to detoxify formate from low level methanol inhalation can be extrapolated to assess human risk from methanol.

Cynomolgus monkeys exposed to 10-200 ppm [^{14}C]methanol for 2 hours have blood levels of methanol-derived formate that are 100- to 1000-fold *lower* than endogenous levels of formate (Dorman et al., 1994). Healthy human volunteers exposed at rest or during exercise to 200 ppm methanol for 6 hours (Lee et al., 1992) or exposed to 20 mg/kg orally have elevated blood levels of methanol, but blood formate levels are not significantly increased above endogenous levels. Deficiencies in THF may prolong elevated blood levels of formate and increase the likelihood of toxicity. Monkeys with low THF levels exposed to 900 ppm [^{14}C]methanol for 2 hours had methanol-derived blood formate levels below endogenous levels (Dorman et al., 1994). Medinsky and Dorman (1995) suggested that humans may not be at added risk of neurotoxicity from low level methanol exposure by inhalation.

Since dimethyl carbonate is metabolized in the body to methanol, we reviewed a study of methanol by the oral route. Sprague-Dawley rats (30 animals/sex/dose) were gavaged daily with 0, 100, 500, or 2500 mg/kg/day methanol (U.S. EPA, 1986). At six weeks, 10 rats/sex/dose group were subjected to interim necropsy and the other 20 were dosed until necropsy at 90 days. No differences between dosed and controls were found for body weight gain, food consumption, and gross or microscopic evaluations. There were elevated levels of serum glutamate pyruvate transaminase (SGPT, alanine aminotransferase), serum alkaline phosphatase (SAP), and increased, but not statistically significant, liver weights in both male and female rats at the highest dose. These effects could be treatment-related although there were no liver lesions detected by histopathology. In addition, brain weights in both high-dose males and females were significantly less than control group. The U.S. EPA considered 500 mg/kg/day of methanol a NOAEL for rats (U.S. EPA, 2008).

4.2 Toxicity of Formaldehyde

Formaldehyde gas is listed under Proposition 65 as a chemical known to the State to cause cancer. In 2006, the International Agency for Research on Cancer (IARC) classified formaldehyde as carcinogenic to humans (Group 1) (IARC, 2006). Although the listing under Proposition 65 relates to inhalation exposure, the IARC classified formaldehyde as carcinogenic to humans with sufficient evidence in humans and in experimental animals, without reference to route of exposure. IARC noted tumors in rat studies by the oral route: statistically significant increases in forestomach papillomas in one study; statistically significant increases in gastrointestinal leiomyosarcomas in a drinking water study (which included transplacental exposure); and a statistically significant increase in haemolymphoreticular tumors [lymphomas and leukemias] in high dose males in another drinking water study. IARC also concluded that "there is strong but not sufficient evidence for a causal association between leukaemia and occupational exposure to formaldehyde." The Agency for Toxic Substances and Disease Registry has produced a comprehensive review of the toxicity of formaldehyde (ATSDR, 1999).

The non-cancer adverse health effects of airborne formaldehyde are due to its irritation of mucous membranes. As a result of its solubility in water and high reactivity, formaldehyde is efficiently absorbed into the mucus layers protecting the eyes and respiratory tract where it rapidly reacts, leading to localized irritation. Acute high inhalation exposure may lead to eye, nose and throat irritation, and in the respiratory tract, nasal obstruction, pulmonary edema and dyspnea. Prolonged or repeated exposures have been associated with allergic sensitization, asthma-like symptoms, histopathological changes in respiratory epithelium, and decrements in lung function. Children, especially those diagnosed with asthma, may be more likely to show impaired pulmonary function and symptoms of asthma than are adults following chronic exposure to formaldehyde. However, in the case of dimethyl carbonate exposure, formaldehyde would only be formed internally where it is rapidly metabolized to formate. Thus, respiratory tract irritation from the formaldehyde metabolite is not an issue in this case.

4.3 Toxicity of Formic Acid

Formic acid has been used in workplaces for decades and has an acceptable workplace exposure level (TLV) of 5 ppm (ACGIH, 2007).

Since formic acid is one of the metabolites of methanol, staff looked for relevant toxicity studies on it in the open literature. Although much of the toxicity data is from inhalation exposure, in the present application the concern is the internal level of formic acid (or formate ion) in solution due to metabolism of dimethyl carbonate, not the external air concentrations of the chemicals. We did not find any informative studies of formate by ingestion. Nonetheless, we briefly describe the inhalation studies below.

Animal Toxicity of Formic Acid

Amdur (1960) exposed guinea pigs (n=7-16/level) by inhalation to 0.34, 1.0, 2.8, 6.6, 13.5, or 42.5 ppm formic acid for 1 hour. The LOAEL was 42.5 ppm and the NOAEL was 13.5 ppm for overt respiratory irritation (measured by decreased breaths per minute), but more subtle adverse effects on lung function were measured at all the lower concentrations.

NTP (1992) conducted 2- and 13-week toxicity studies in male and female F344/N rats and $B6C3F_1$ mice exposed by whole body inhalation exposure to formic acid vapors.

In 2-week studies, groups of 5 F344/N rats and 5 $B6C3F_1$ mice of each sex were exposed 6 hours/day, 5 days/week for two weeks, to 0, 31, 62.5, 125, 250, or 500 ppm. Deaths occurred in animals exposed to 500 ppm (rats and mice) and 250 ppm (1 female mouse).

In 13-week studies, F344/N rats and B6C3F1 mice (10 animals/group/sex) were exposed to 0, 8, 16, 32, 64, and 128 ppm formic acid 6 hours/day, 5 days/week. One male and one female mouse in the 128 ppm groups died. Body weight gain was significantly decreased in mice exposed to 64 and 128 ppm.

In both the 2-week and 13-week studies, microscopic lesions of squamous metaplasia, necrosis, and inflammation in the respiratory and olfactory epithelia were detected in rats and mice. These were observed at 62.5 ppm and above after 2 weeks, but only at 128 ppm after 13 weeks. NTP concluded that the effects of formic acid were consistent with those of other irritants administered by inhalation. The no-observed-adverse-effect level (NOAEL) for respiratory injury was 32 ppm in rats and mice. There was no significant evidence of systemic toxicity.

Formate inhibits cytochrome c oxidase activity in the electron transport chain in intact mitochondria and in submitochondrial particles. The inhibition increases with decreasing pH, indicating that HCOOH may be the inhibitory species. Formate is permeable through the inner mitochondrial membrane (Nicholls, 1976) and could inhibit oxidative phosphorylation.

In genetic toxicity tests *in vitro* with *Salmonella typhimurium*, formic acid was not mutagenic either with or without metabolic activation (NTP, 1992).

5 Derivation of Acute Screening Level (1-hour exposure) for Dimethyl Carbonate

Study	Bevan and Beyer, 1995; Exxon, 1992
Study population	Pregnant female CD-1 mice
Exposure method	Inhalation of 0, 300, 1000, or 3000 ppm
Exposure duration	6 hours/day on gestation days 6 to 15
Critical effects	Fetal malformations
NOAEL	1000 ppm
Extrapolation to 1 hour	not done with developmental study (see below)
Interspecies uncertainty factor	
Toxicokinetic UF_{A-k}	2 (default)
Toxicodynamic UF_{A-d}	√10 (default)
Intraspecies uncertainty factor	
Toxicokinetic UF_{H-k}	10 (default)
Toxicodynamic UF_{H-d}	√10 (default)
Cumulative uncertainty factor	200
Acute Screening Level	5 ppm (18 mg/m^3; 18,000 μg/m^3)

The acute screening level for dimethyl carbonate is based on a developmental study in which pregnant mice were exposed 6 hours per day for 10 days. However, the resulting acute screening level is a level not to be exceeded in any one hour period. The acute screening level was developed using methodology published in 2008 (OEHHA, 2008). The methodology was modified from earlier methodology (OEHHA, 1999) due to a mandate to specifically insure that infants and children are protected from the adverse effects of chemicals. Because of the limited data available on dimethyl carbonate, default values were used for the uncertainty factors (UF).

The default interspecies UF_{A-k} of 2 was used for residual toxicokinetic differences in studies of non- primate species using the human equivalent concentration (HEC) approach. In this case the HEC adjustment factor was 1 since fetal malformations occur internally. The default interspecies UF_{A-d} of √10 was applied to compensate for the absence of data on pharmacodynamic differences between rodents and humans. The default intraspecies UF_{A-k} of 10 was used since there was no information on dimethyl carbonate metabolism at different stages of human development. The default interspecies UF_{A-d} of √10 was applied to compensate for the absence of data on pharmacodynamic differences among humans to the effects of dimethyl carbonate.

The acute screening level of 18,000 μg/m^3 is somewhat more than half that for methanol (28,000 μg/m^3).

6 Derivation of Chronic Screening Level for Dimethyl Carbonate

No data are available on long term inhalation of dimethyl carbonate. However, since one mole of dimethyl carbonate is degraded to two moles of methanol plus one mole of carbon dioxide, a chronic screening level can be based on the chronic REL for methanol as a surrogate, assuming 100% conversion to methanol occurs during metabolism. The derivation of OEHHA's chronic REL for methanol, done by an earlier methodology (OEHHA, 2000), follows:

Methanol Chronic Reference Exposure Level

Study	Rogers *et al.* (1993)
Study population	Pregnant mice
Exposure method	Inhalation of 0, 300, 1000, or 3000 ppm
Exposure duration	7 hours/day on gestation days 6 to 15
Critical effects	Abnormal cervical ribs, exencephaly, cleft palate
NOAEL	1000 ppm
Benchmark Concentration (BMC_{05})	305 ppm
Average experimental exposure	89 ppm at BMC_{05} (305 ppm x 7/24)
Human equivalent concentration	89 ppm at BMC_{05} (gas with systemic effects, based on RGDR = 1.0 using default assumption that lambda (a) = lambda (h))
Subchronic uncertainty factor	1
LOAEL uncertainty factor	1
Interspecies uncertainty factor	3
Intraspecies uncertainty factor	10
Cumulative uncertainty factor	30
Chronic Methanol Reference Exposure Level	3 ppm (4 mg/m^3; 4,000 μg/m^3)

Since, as noted above, one mole of dimethyl carbonate gives rise to two moles of methanol, it is reasonable to extrapolate from the methanol REL of 3 ppm to an interim chronic screening level for dimethyl carbonate of 1.5 ppm. This is equivalent to $1.5 \times 3.68 \times 10^3 = 5500$ μg/m^3. The chronic REL for methanol is derived from a developmental study in which the critical exposures were over a relatively short timescale, rather than a long-term study. However, unlike the situation for dimethyl carbonate, there are several long-term studies of other endpoints in both rodents and primates which confirm that the developmental endpoint is the most sensitive (see Section 5 and the toxicity summary for the methanol chronic REL [OEHHA, 2008]). The REL thus derived is therefore protective against these other effects, which included liver toxicity and neurological or neuromuscular effects. Use of the methanol REL as an indirect basis for the dimethyl carbonate screening level is thus the preferred option, although alternatively it could be argued that a screening level based on the developmental toxicity data for dimethyl carbonate should be similarly protective of chronic effects.

7 Data Gaps

Data gaps of concern to OEHHA staff include:

1. No lifetime inhalation study of dimethyl carbonate is available. The longest inhalation study available in the open literature is an abstract of a 10 day developmental toxicity study in mice (Bevan and Beyer, 1995). This is a serious data gap for a high production volume chemical.

2. A substantial developmental toxicity study with group sizes of 30-32 pregnant female mice was reported, but no multigenerational studies or other investigations addressing reproductive toxicity in either sex were available.

3. There are no data in neonatal animals of the effects of dimethyl carbonate or formic acid exposure. OEHHA has a mandate to determine if our health values adequately protect infants and children.

4. There are very few data on genotoxicity of dimethyl carbonate itself. This is a source of concern which is partially alleviated by the fact that the first metabolite, methanol, is not genotoxic. The subsequent metabolites include formate, which is not genotoxic, and formaldehyde which is. The genotoxicity of formaldehyde when it is generated internally is probably only important in high dose situations, in view of its role in intermediary metabolism and the generally negative profile of various compounds of which it is a metabolite, including methanol.

8 Conclusion

There are no carcinogenicity or long-term toxicity data on dimethyl carbonate. There is no human evidence for carcinogenicity of methanol, the primary metabolite of dimethyl carbonate (along with carbon dioxide), despite a long history of human exposure. There is also a robust database on toxicity of methanol in animals, but only limited evidence for carcinogenicity. One study (Soffritti et al., 2002) found possible evidence of carcinogenicity with high oral (drinking water) does of methanol, although the results of this study are considered equivocal by some analysts. Inhalation studies in rats and mice (NEDO, 1985) were negative, and supporting evidence (including genotoxicity tests) is also generally negative.

Exposure to workers and the general public near facilities in California using dimethyl carbonate will occur if it is exempted. Dimethyl carbonate is an ester and would be expected to be less irritating to mucous membranes than formaldehyde or formic acid. In the present application the concern is the internal levels of methanol and its metabolites formaldehyde and formic acid (or formate ion) in solution due to metabolism of dimethyl carbonate, rather than the external air concentrations of the chemicals. The proposed acute screening level of 18, 000 $\mu g/m^3$ and chronic screening level of 5500 $\mu g/m^3$ are expected to be protective of anticipated adverse health effects, including the developmental toxicity observed in the key study (Bevan and Beyer, 1995; Exxon, 1992) reported for dimethyl carbonate.

These screening levels have not undergone public and peer review. It should be noted that large data gaps exist for dimethyl carbonate.

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APPENDIX D

Analysis of Potential Risks from Use of Dimethyl Carbonate (DMC), Methyl Formate (MF), and Tertiary-Butyl Acetate (TBAc)

February 21, 2013

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San Joaquin Valley
Unified Air Pollution Control District

Date: October 24, 2012

To: Lisa Van de Water, Air Quality Specialist

From: Glenn Reed, Senior Air Quality Specialist

Subject: Analysis of Potential Risks from Use of Dimethyl Carbonate (DMC), Methyl Formate (MF), and tert-Butyl Acetate (tBAC)

The U.S. Environmental Protection Agency (EPA) has exempted DMC, MF, and tBAC from the definition of “volatile organic compounds” or “VOCs”. The San Joaquin Valley Unified Air Pollution Control District (the “District”) conditionally exempted tBAC and MF previously. The District’s Strategies and Incentives Department (SI) asked the Permit Services Department (PSD) to perform an analysis to determine the potential risks from exempting DMC.

On February 14, 2011, PSD personnel reported the results of the initial risk analysis. That analysis was based on a recent Risk Management Review for a surface coating operation. That analysis assumed that the coating operation occurred in a spray booth. Two scenarios were assumed for the booth’s stack. First, the stack was modeled with a vertical release. Second, it was assumed that there is a cap on the stack.

During the course of reviewing that analysis, an issue arose concerning operations that are not permitted. In accordance with Rule 2020, surface coating operations that use less than 1 quart of surface coating per day or less than 8 gallons per year are exempt from permitting. To analyze the risk from unpermitted sources, the following assumptions were made:

- No spray booth would be used. Emissions were modeled as a volume source.
- Receptors would be located at a minimum distance of 25 m from the volume source.
- For acute risk, the entire 1 quart per day would be used within an hour and all the solvent would evaporate within that hour.
- The only constituent of the coating would be the compound of interest.
- Two types of coating were analyzed: 1) a high solids coating with a solvent content of 47 percent by volume and 2) a water-based coating with a solvent content of 5 percent by volume. These two coatings were selected from the information in the Air Resource Board’s Draft Report on the 2005 Architectural Coatings Survey. These data are for nonflat – high gloss coatings.
- All solvent in these two coating options were assumed to be replaced with DMC, TBAC, or MF.

The following table summarizes the results:

Risk Estimates	Acute Risk for 1 Quart in 1 Hour	
	47 Percent VOC Solvent-Based Coating	**5 Percent VOC Water-Based Coating**
Dimethyl Carbonate	0.52	0.06
Methyl Formate	0.67	0.07
tert-Butyl Acetate	0.39	0.04

At an annual usage rate of 8 gallons per year, the maximum chronic hazard index for DMC would be 0.0002 and the cancer risk for tBAC would be 0.3 in a million.

Permit Services concludes from this analysis that an unpermitted source using any of these three compounds in reasonably anticipated ways would not pose an unacceptable risk.

Further, if usage rates of coatings containing these compounds exceed the limits in Rule 2020, a permit would be required. The District performs Risk Management Reviews for all operations that require a permit and would therefore regulate individual project risk as a part of the permitting process.

Attachments:

A. *Basic Coating Data*
B. *Table of Results—Solvent-Based Coating*
C. *Table of Results—Water-Based Coating*

Attachment A Basic Coating Data

Basic Coating Data

Average Composition of Solvent-Based (SB) and Water-Based Architectural
(Percent by Volume)

Component	**SB**	**WB**
Solids	53	35
Water	0	60
Exempt	0	0
VOCs	47	5

		Emissions (g/sec)			
		Solvent-Based		**Water-Based**	
Specific Gravities		**Hourly**	**Annual**	**Hourly**	**Annual**
Dimethyl Carbonate	1.069	0.131951	0.005498	0.014037	0.000585
Methyl Formate	0.866	0.106894	0.004454	0.011372	0.000474
tert-Butyl Acetate	0.98	0.120966	0.00504	0.012869	0.000536

Non-Flat: High Gloss

All data are taken from Table 8-1of the 2005 Architectural Coatings Survey, (Draft Report), California Air Resources Board, September 2006.

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Attachment B Table of Results—Solvent-Based Coating

Substitution of VOCs in Solvent-Based Coating

Urban Dispersion Coefficients

	1-Hour	**Annual**	
Max concentration at 1 g/s	29772	1192	
Specific Gravities			
Dimethyl Carbonate			1.069
Methyl Formate			0.866
tert-Butyl Acetate			0.98
Emission Rates (g/s)			
Dimethyl Carbonate	0.131951	0.005498	
Methyl Formate	0.106894	0.004454	
tert-Butyl Acetate	0.120966	0.00504	
Max concentration at 1 qt/day			
Dimethyl Carbonate	3928.456	6.553585	
Methyl Formate	3182.454	5.309078	
tert-Butyl Acetate	3601.391	6.007964	
Risk Values	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	18000	4000	
Methyl Formate	11400		
tert-Butyl Acetate	22000		4.00E-07
Risk Estimates	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	0.218248	0.001638	
Methyl Formate	0.279163		
tert-Butyl Acetate	0.1637		2.40E-06

Rural Dispersion Coefficients

	1-Hour	**Annual**	
Max concentration at 1 g/s	71048	1492	
Specific Gravities			
Dimethyl Carbonate			1.069
Methyl Formate			0.866
tert-Butyl Acetate			0.98
Emission Rates (g/s)			
Dimethyl Carbonate	0.131951	0.005498	
Methyl Formate	0.106894	0.004454	
tert-Butyl Acetate	0.120966	0.00504	
Max concentration at 1 qt/day			
Dimethyl Carbonate	9374.881	8.202977	
Methyl Formate	7594.619	6.645256	
tert-Butyl Acetate	8594.372	7.520035	
Risk Values	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	18000	4000	
Methyl Formate	11400		
tert-Butyl Acetate	22000		4.00E-07
Risk Estimates	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	0.520827	0.002051	
Methyl Formate	0.666195		
tert-Butyl Acetate	0.390653		3.01E-06

Spray Booth with Uncapped Stack

	1-Hour	**Annual**	
Max concentration at 1 g/s	3875	63	
Specific Gravities			
Dimethyl Carbonate			1.069
Methyl Formate			0.866
tert-Butyl Acetate			0.98
Emission Rates (g/s)			
Dimethyl Carbonate	0.131951	0.005498	
Methyl Formate	0.106894	0.004454	
tert-Butyl Acetate	0.120966	0.00504	
Max concentration at 1 qt/day			
Dimethyl Carbonate	511.3401	0.34408	
Methyl Formate	414.2381	0.27874	
tert-Butyl Acetate	468.7683	0.315433	
Risk Values	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	18000	4000	
Methyl Formate	11400		
tert-Butyl Acetate	22000		4.00E-07
Risk Estimates	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	0.028408	8.6E-05	
Methyl Formate	0.036337		
tert-Butyl Acetate	0.021308		1.26E-07

Spray Booth with Capped Stack

	1-Hour	**Annual**	
Max concentration at 1 g/s	7618	351	
Specific Gravities			
Dimethyl Carbonate			1.069
Methyl Formate			0.866
tert-Butyl Acetate			0.98
Emission Rates (g/s)			
Dimethyl Carbonate	0.131951	0.005498	
Methyl Formate	0.106894	0.004454	
tert-Butyl Acetate	0.120966	0.00504	
Max concentration at 1 qt/day			
Dimethyl Carbonate	1005.153	1.932323	
Methyl Formate	814.277	1.565381	
tert-Butyl Acetate	921.4682	1.771447	
Risk Values	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	18000	4000	
Methyl Formate	11400		
tert-Butyl Acetate	22000		4.00E-07
Risk Estimates	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	0.055842	0.000483	
Methyl Formate	0.071428		
tert-Butyl Acetate	0.041885		7.09E-07

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Attachment C Table of Results—Water-Based Coating

Substitution of VOCs in Water-Based Coating

Urban Dispersion Coefficients

	1-Hour	Annual	
Max concentration at 1 g/s	29772	1192	
Specific Gravities			
Dimethyl Carbonate			1.069
Methyl Formate			0.866
tert-Butyl Acetate			0.98
Emission Rates (g/s)			
Dimethyl Carbonate	0.014037	0.000585	
Methyl Formate	0.011372	0.000474	
tert-Butyl Acetate	0.012869	0.000536	
Max concentration at 1 qt/day			
Dimethyl Carbonate	417.9209	0.69719	
Methyl Formate	338.5589	0.564796	
tert-Butyl Acetate	383.1267	0.639145	
Risk Values	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	18000	4000	
Methyl Formate	11400		
tert-Butyl Acetate	22000		4.00E-07
Risk Estimates	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	0.023218	0.000174	
Methyl Formate	0.029698		
tert-Butyl Acetate	0.017415		2.56E-07

Rural Dispersion Coefficients

	1-Hour	Annual	
Max concentration at 1 g/s	71048	1492	
Specific Gravities			
Dimethyl Carbonate			1.069
Methyl Formate			0.866
tert-Butyl Acetate			0.98
Emission Rates (g/s)			
Dimethyl Carbonate	0.014037	0.000585	
Methyl Formate	0.011372	0.000474	
tert-Butyl Acetate	0.012869	0.000536	
Max concentration at 1 qt/day			
Dimethyl Carbonate	997.3278	0.872657	
Methyl Formate	807.9382	0.706942	
tert-Butyl Acetate	914.2949	0.800004	
Risk Values	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	18000	4000	
Methyl Formate	11400		
tert-Butyl Acetate	22000		4.00E-07
Risk Estimates	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	0.055407	0.000218	
Methyl Formate	0.070872		
tert-Butyl Acetate	0.041559		3.20E-07

Spray Booth with Uncapped Stack

	1-Hour	Annual	
Max concentration at 1 g/s	3875	63	
Specific Gravities			
Dimethyl Carbonate			1.069
Methyl Formate			0.866
tert-Butyl Acetate			0.98
Emission Rates (g/s)			
Dimethyl Carbonate	0.014037	0.000585	
Methyl Formate	0.011372	0.000474	
tert-Butyl Acetate	0.012869	0.000536	
Max concentration at 1 qt/day			
Dimethyl Carbonate	54.39788	0.036604	
Methyl Formate	44.06788	0.029653	
tert-Butyl Acetate	49.86897	0.033557	
Risk Values	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	18000	4000	
Methyl Formate	11400		
tert-Butyl Acetate	22000		4.00E-07
Risk Estimates	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	0.003022	9.15E-06	
Methyl Formate	0.003866		
tert-Butyl Acetate	0.002267		1.34E-08

Spray Booth with Capped Stack

	1-Hour	Annual	
Max concentration at 1 g/s	7618	351	
Specific Gravities			
Dimethyl Carbonate			1.069
Methyl Formate			0.866
tert-Butyl Acetate			0.98
Emission Rates (g/s)			
Dimethyl Carbonate	0.014037	0.000585	
Methyl Formate	0.011372	0.000474	
tert-Butyl Acetate	0.012869	0.000536	
Max concentration at 1 qt/day			
Dimethyl Carbonate	106.9311	0.205566	
Methyl Formate	86.62521	0.16653	
tert-Butyl Acetate	98.02853	0.188452	
Risk Values	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	18000	4000	
Methyl Formate	11400		
tert-Butyl Acetate	22000		4.00E-07
Risk Estimates	**Acute**	**Chronic**	**Cancer**
Dimethyl Carbonate	0.005941	5.14E-05	
Methyl Formate	0.007599		
tert-Butyl Acetate	0.004456		7.54E-08

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