SACRAMENTO METROPOLITAN
AIR QUALITY MANAGEMENT DISTRICT

STAFF REPORT

Proposed Amendments To

Rule 101 – General Provisions and Definitions

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EXECUTIVE SUMMARY

Since Rule 101, General Provisions and Definitions, was last amended on September 3, 1998, the United States Environmental Protection Agency (EPA) has revised the federal definition of volatile organic compound (VOC) in Title 40, Part 51 of the Code of Federal Regulations several times to include additional compounds that negligibly contribute to the formation of ozone. The following eight compounds were added to the list:

- 1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane (n-$C_3F_7OCH_3$ or HFE-7000)
- 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl) hexane (HFE-7500)
- 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea)
- methyl formate ($HCOOCH_3$)
- 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane (HFE-7300)
- propylene carbonate
- dimethyl carbonate
- tertiary butyl acetate (TBAc)

After reviewing each of the above compounds, Staff is proposing to amend Rule 101 to include HFE-7000, HFE-7500, HFE-7300, methyl formate, dimethyl carbonate and propylene carbonate to the list of exempt compounds. These compounds will not adversely impact human health or the environment. However, at this time, Staff is not proposing to exempt HFC-227ea or TBAc until more information becomes available to adequately determine whether or not these compounds will adversely impact human health or the environment.

In addition, Staff is proposing minor changes to add the common names for two compounds already included in Rule 101: HFE-7100 for 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane ($C_4F_9OCH_3$) and HFE-7200 for 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane ($C_4F_9OC_2H_5$).

BACKGROUND

Ground level ozone is a secondary pollutant formed from photochemical reactions of nitrogen oxides (NOx) and VOCs in the presence of sunlight. Ozone is a strong irritant that adversely affects human health and damages crops and other environmental resources. As documented by the EPA in the most recent Criteria Document for ozone[1], both short-term and long-term exposure to ozone can irritate and damage the human respiratory system, resulting in:

- decreased lung function;
- development and aggravation of asthma;
- increased risk of cardiovascular problems such as heart attacks and strokes;
- increased hospitalizations and emergency room visits; and
- premature deaths.

The District is currently designated as a nonattainment area for both the state and federal ozone standards. Since VOCs are a precursor to ozone, one of the strategies to control ozone pollution is to reduce VOC emissions from existing stationary sources by establishing more

[1] "Air Quality Criteria for Ozone and Related Photochemical Oxidants", U.S. EPA, February 2006.

stringent VOC emission limits. One method for complying with low VOC emission limits is through the use of organic compounds with negligible reactivity for ozone formation, also known as exempt compounds. Exempt compounds are listed in Rule 101.

Rule 101 was last amended on September 3, 1998. Since then, EPA has revised the federal definition of VOC[2] four times to add eight chemical compounds to the list of exempt compounds. This list consists of chemical compounds that are excluded from the federal VOC definition based on the compound's negligible contribution to the formation of ground level ozone.

Different organic compounds have different levels of reactivity. Some organic compounds do not react to form ozone at the same rate or to the same extent as other organic compounds. EPA has a policy to exempt organic compounds from the definition of VOC if the compounds have negligible levels of reactivity. By exempting non-reactive compounds, EPA helps states and air districts focus their efforts on organic compounds that significantly increase ozone concentrations.

EPA compares the reactivity of a compound to the reactivity levels of ethane. Compounds with reactivity levels less than or equal to the reactivity levels of ethane may be deemed negligibly reactive and exempted from the federal definition of VOC. EPA uses three methods to determine if a compound is negligibly reactive. The first method is based on the reaction rate constant of hydroxyl radical (known as K_{oh}) in the air. This reaction is the first step in a series of chemical reactions in the formation of ozone. If this reaction is slow (smaller K_{oh} value), then the compound will not likely form ozone at a fast rate. The other two methods are based on the maximum incremental reactivity (MIR) expressed either on a reactivity per gram basis (grams of ozone formed per gram of VOC) or on a reactivity per mole basis (grams of ozone formed per mole of VOC). The MIR methods consider the activities from all steps in the ozone formation process from a specific organic compound as opposed to just the first step of the chemical reaction.

Table 1 lists the eight compounds that EPA has added to their exempt list and compares the reactivity levels of each compound to that of ethane. It is apparent that propylene carbonate, dimethyl carbonate, and tertiary butyl acetate (TBAc) were exempted using the MIR methods, since the respective K_{oh} value of each compound was greater than the K_{oh} value of ethane.

[2] 40 CFR 51.100(s).

Table 1: Exempt Compounds

Federal Register Reference	EPA Exempt Compound	K_{oh}	MIR (mole basis)	MIR (mass basis)
	Ethane	**2.40×10^{-13}**	**8.12**	**0.27**
69 FR 69290	1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane ($n\text{-}C_3F_7OCH_3$ or HFE-7000)	1.20×10^{-14}	ND	ND
69 FR 69290	3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2(trifluoromethyl) hexane (HFE-7500)	2.20×10^{-15}	ND	ND
69 FR 69290	1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea)	1.09×10^{-15}	ND	ND
69 FR 69290	methyl formate ($HCOOCH_3$)	2.27×10^{-13}	ND	0.053
72 FR 2193	1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane (HFE-7300)	1.50×10^{-14}	ND	ND
74 FR 3437	propylene carbonate	6.90×10^{-13}	27.56	0.27
74 FR 3437	dimethyl carbonate	3.49×10^{-13}	5.04	0.056
69 FR 69298	tertiary butyl acetate (TBAc)	4.25×10^{-12}	27.88	0.24

ND = Not Determined

Compounds exempted from the federal VOC definition are not automatically exempted from District rules and regulations. The District considers a number of factors, including potential uses, impact on human health, and environmental concerns before adding federally-exempt compounds to Rule 101.

LEGAL MANDATES

Federal Mandates:

The District is designated “severe” nonattainment for the federal 8-hour ozone standard. In February 2009, the districts of the Sacramento Federal Nonattainment Area adopted an attainment plan to achieve the federal 8-hour ozone standard by 2018.

Clean Air Act (CAA) section 172(c)(1) specifies that State Implementation Plans for nonattainment areas must include “reasonably available control measures” (RACM), including “reasonably available control technology” (RACT), for sources of emissions.

The proposed amendments to Rule 101 will allow manufacturers and sources more flexibility in developing and using low VOC products that may ultimately lead to feasible, lower VOC emission limits.

State Mandates:

The District is designated "serious" nonattainment for the state ozone standard. The California Clean Air Act requires areas designated as "serious" to adopt control measures required in Section 40919 of the California Health and Safety Code (HSC).

- California HSC Section 40919 requires districts with serious nonattainment for ozone to adopt Best Available Retrofit Control Technology (BARCT) for all existing permitted sources. BARCT means an emission limitation that is based on the maximum degree of reduction achievable, taking into account environmental, energy, and economic impacts by each class or category of sources[3].
- Transport Mitigation Emission Control Requirements: Title 17, Section 70600 of the California Code of Regulations requires that districts within the areas of origin of transported air pollutants, as identified in Section 70500(c), include sufficient emission control measures (including "all feasible measures" and BARCT) in their attainment plans for ozone to mitigate the impact of pollution sources within their jurisdictions on ozone concentrations in downwind areas commensurate with the level of contribution. An upwind district must comply with the transport mitigation planning and implementation requirements set forth in this section regardless of its attainment status, unless the upwind district complies with the requirements of Section 70601.

The proposed amendments to Rule 101 will allow manufacturers and sources more exempt compounds to use in meeting VOC limits, and this may lead to more stringent and feasible BARCT requirements.

PROPOSED AMENDMENTS

Staff is proposing to amend Rule 101 to incorporate the following compounds into the list of exempt compounds in Section 204:

- 1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane (n-$C_3F_7OCH_3$ or HFE-7000)
- 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl) hexane (HFE-7500)
- Methyl formate
- 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane (HFE-7300)
- Dimethyl carbonate
- Propylene carbonate

Each compound is discussed in detail below:

1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane (n-$C_3F_7OCH_3$ or HFE-7000): On November 29, 2004, EPA exempted this compound from the federal definition of VOC because the K_{oh} value of HFE-7000 is less than the K_{oh} value of ethane. HFE-7000 may be used as a refrigerant or as an aerosol propellant. This compound is classified as a hydrofluoroether (HFE). In general, HFEs have an ozone depletion potential (ODP) of zero and may be acceptable substitutes for some chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). HFE-7000 is listed

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[3] California Health and Safety Code Section 40406.

as an acceptable replacement for trichlorofluoromethane (CFC-11) and 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) in EPA's Significant New Alternative Policy (SNAP) program[4]. The SNAP program evaluates and regulates substitutes for ozone-depleting chemicals that are being phased out under the stratospheric ozone protection provisions of the federal Clean Air Act. Both CFC-11 and CFC-113 are currently on the District's list of exempt compounds in Rule 101. HFE-7000 is estimated to have a global warming potential (GWP) between 140 and 400. The GWP of HFE-7000 is low compared to CFC-11 (GWP of 4000) and CFC-113 (GWP of 5000).

In a report titled "Risk Screen on the Use of Substitutes for Ozone-Depleting Substances", EPA assessed the potential health impacts of including HFE-7000 in EPA's SNAP Program[5]. The study screened the potential risks to workers for occupational exposure and to the general public from exposure of ambient air releases of HFE-7000. EPA determined that the exposure of HFE-7000 to workers and the general population is expected to be below the level of concern for non-cancer risk. In addition, according to the final rule to exempt four compounds from the definition of VOC as published in the Federal Register[6], HFE-7000 is very similar in structure, toxicity, and atmospheric properties to other HFE compounds such as $C_4F_9OCH_3$ (HFE-7100) and $C_4F_9OC_2H_5$ (HFE-7200). In March 2008, CARB conducted an Environmental Impact Assessment of Selected Halogenated Chemicals, where HFE-7100 and HFE-7200 were among the seven compounds that were evaluated. CARB determined that HFE-7100 and HFE-7200 are not chemical carcinogens to humans and have an acute and chronic Hazard Index of less than 1[7], which indicates no adverse human health effects are expected to occur. Staff expects HFE-7000 to have low health impacts, similar to that of HFE-7100 and HFE-7200.

Staff is proposing to exempt HFE-7000 from the District's definition of VOC because this compound would not have an adverse impact on human health or the environment. In addition, this compound may have significant benefits to stratospheric ozone depletion and global warming concerns.

3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl) hexane (HFE-7500): On November 29, 2004, EPA exempted this compound from the federal definition of VOC because the K_{oh} value of HFE-7500 is less than the K_{oh} value of ethane. HFE-7500 may be used as a refrigerant. Similar to HFE-7000, this compound is classified as a HFE and has an ODP of zero. In EPA's SNAP program, HFEs, as a class, have been identified as possible substitutes for CFCs. HFE-7500 is estimated to have a GWP of 100. The GWP of HFE-7500 is low compared to CFCs. In general, CFCs have very high GWPs, usually greater than 1,000.

The Product Specification Sheet published by 3M stated that HFE-7500 has a very low overall toxicity. The Product Specification Sheet also indicated that the compound will cause minimal irritation to the skin and eyes when in contact with the material, and in a 28-day oral toxicity study, no adverse effects were observed. In addition, according to the final rule to exempt four

[4] "Protection of Stratospheric Ozone: Notice 16 for Significant New Alternatives Policy Program," Federal Register, Volume 67, March 2, 2002, p. 13272 – 13278.
[5] "Risk screen on the use of substitutes for ozone-depleting substances," U.S. EPA, August 21, 2003.
[6] "Air Quality: Revision to Definition of Volatile Organic Compounds – Exclusion of Four Compounds," Federal Register, Volume 69, November 29, 2004, p. 69290 – 69298.
[7] "Environmental Impact Assessment of Selected Halogenated Chemicals," CARB, March 2008, p. 18 – 19.

compounds from the definition of VOC as published in the Federal Register[8], HFE-7500 is very similar in structure, toxicity and atmospheric properties to other HFE compounds such as HFE-7100 and HFE-7200. As previously discussed, HFE-7100 and HFE-7200 are not expected to adversely impact human health, and Staff expects that HFE-7500 will have similarly low impacts on human health.

Staff is proposing to exempt HFE-7500 from the District's definition of VOC because this compound would not have an adverse impact on human health or the environment. In addition, this compound may have significant benefits to stratospheric ozone depletion and global warming concerns.

Methyl formate ($HCOOCH_3$): On November 29, 2004, EPA exempted this compound from the federal definition of VOC because the K_{oh} value of methyl formate is less than the K_{oh} value of ethane. This compound is used to manufacture formamides and formic acid. Because of its high vapor pressure, it may be used as a component for quick-drying finishes. It is also used as a blowing agent in foam manufacturing processes, where it may be a replacement for butane, pentane, and some HCFCs. Butane and pentane are VOCs with much higher reactivity than methyl formate. In general, HCFCs have ODPs ranging from 0.01 to 0.1 and GWPs ranging from 93 to 2000. Methyl formate has a negligible ODP and a very low or zero GWP.

In a May 19, 2008 letter to all Air Pollution Control Officers, CARB shared the results of its analysis prepared with assistance from the Office of Environmental Health Hazard Assessment (OEHHA). Methyl formate is hydrolyzed in the body to methanol and formic acid. Methanol can be enzymatically oxidized to formaldehyde. Because of its metabolites, methyl formate may be considered toxic. It can cause irritation to the eyes, skin, lungs, and at high exposure levels, it may cause pulmonary damage. After a review of methyl formate and its metabolites, OEHHA derived an interim acute non-cancer reference exposure level (REL) of 11,400 ug/m^3 that is considered to be protective of nearby receptors. No data were available on long term inhalation exposure of methyl formate, so a chronic REL could not be developed. Also, OEHHA determined that there is no evidence of carcinogenicity for methanol, despite a robust database on its toxicity and a long history of human exposure. In a memo to CARB, OEHHA concluded that at doses likely to be achieved in environmental exposures by inhalation, the toxicity concern appears to be minor. Based on OEHHA's conclusions, CARB recommended that methyl formate should be exempted from the definition of VOC, based on its low reactivity and the positive environmental benefits that may result if methyl formate displaces the use of other foam-blowing agents. CARB also recommended that the districts consider the impacts of exempting methyl formate, including the substances that it will likely replace the amount and nature of use, and the estimated population exposures and indoor exposure resulting from use.

The uses of methyl formate are as a foam blowing agent and as a component in quick-drying finishes. Currently, the District does not have any foam blowing operations, which are typically large operations. If, in the future, a foam blowing plant is proposed in the District, it would undergo extensive reviews under the District's permitting process, which includes a toxics review. These reviews will ensure that the operation complies with local, state, and federal rules and regulations, and that the risk to the public is acceptable.

[8] "Air Quality: Revision to Definition of Volatile Organic Compounds – Exclusion of Four Compounds," Federal Register, Volume 69, November 29, 2004, p. 69290 – 69298.

Additionally, if methyl formate is exempted from the District's VOC definition, its use as a component in quick-drying finishes may increase. It is necessary to ensure that in these applications, the increased use of methyl formate does not result in an unacceptable toxic risk. As such, Staff calculated the maximum emission of methyl formate that will cause adverse impact to human health. Generally, a hazard index of less than 1 is not considered to be a significant concern to human health at a nearby receptor. Staff used the Bowman Environmental Engineering Short Term (BEEST) for Windows modeling program, version 9.63, to determine the unit emission rate concentration from a point source (emissions exhausted from a stack) and volume source (emissions vented from a building) necessary to reach an acute hazard index of 1. The specific details and modeling assumptions are summarized in Appendix B and the modeling results are shown in the following table.

Table 2: Acute Impacts for Methyl Formate

Source Type	Unit Emission Rate 1-hour Conc. (ug/m^3)/(g/s)	Acute Hazard Index	Acute REL (ug/m^3)	Emission Rate (g/s)	Hourly MF Emissions (lb/hour)
Point	1,080	1	11,400	10.5	83.6
Volume	21,700	1	11,400	0.53	4.16

Emission Rate, g/s = (Acute REL, ug/m^3)/(Unit Emission Rate Conc. (ug/m^3)/(g/s))
Hourly emissions, lb/hr = emission rate, g/s * 0.0022 lb/g * 3600 s/hr

To ensure that the hazard index is less than 1, the hourly emission rate of methyl formate from a point source should be less than 83.6 pounds per hour. To assess the significance of the hourly emissions, Staff compared the calculated hourly emissions to actual VOC emissions from the largest coating facility in District. According to the 2009 Emission Inventory, the largest coating facility, which is a point source, emits approximately 15,000 pounds of VOC per year. Assuming that the facility operates 8 hours per day, 5 days per week, and 52 weeks per year, the average hourly VOC emission for the facility would be approximately 7.2 pounds per hour. From this comparison, Staff can conclude that it is very unlikely that methyl formate emissions will be greater than 83.6 pounds per hour from a point source within the District, even if 100% of the VOC is replaced by methyl formate.

For a volume source, the estimated maximum concentration is located approximately 10 meters from the emission source, which is considered the worst-case scenario. To ensure that the hazard index is less than 1, the hourly emission rate of methyl formate from a volume source should be less than 4.16 pounds per hour. Volume sources are usually small operations; however, as a worst-case estimate, Staff assumed that the largest coating facility in the District is a volume source. As previously determined, the average hourly emission from the largest coating facility is 7.2 pounds of VOC per hour. Since methyl formate is used as one of multiple components, its emissions from quick-drying finishes depend on the percentage of methyl formate used in the products. To exceed the hazard index of 1, methyl formate emissions would need to be 58% of the total VOC emissions to emit 7.2 pounds of VOC per hour. Based on CARB's Environmental Impact Assessment of tertiary-butyl acetate, the total emissions of xylene, toluene, or MEK from coating operations are 61% to 80% of the total VOC emissions[9]. Methyl formate, a much faster evaporating compound with a vapor pressure of 476 mm Hg at 20°C, would not be a suitable replacement for compounds such as xylene, toluene, and MEK that are slower evaporating VOCs with vapor pressures ranging from 9 mm Hg at 20°C to 79

[9] "Environmental Impact Assessment of Tertiary-Butyl Acetate" CARB, January 2006, p. 30.

mm Hg at 20°C[10]. Assuming methyl formate is used to replace compounds other than xylene, toluene, or MEK, methyl formate emissions would only be as high as 39% of the total VOC emissions, which is less than the emissions needed to exceed the hazard index of 1.
Staff also reviewed the most recent inspection reports available and found that the largest quarterly emission from a coating volume source in 2010 was 989 pounds of VOC per quarter. Assuming that the facility operates 8 hours per day, 5 days per week, and 13 weeks per quarter, the average hourly VOC emission for the facility would be approximately 1.9 pounds per hour, which is less than emissions needed to exceed the hazard index of 1 even if 100% of the VOC is replaced by methyl formate.

In addition, according to the American Coating Association, the use of methyl formate in coatings is a small fraction of solvents used in a coating because methyl formate is flammable and dries too quickly[11]. Therefore, Staff can conclude that it is very unlikely that methyl formate emissions will be greater than 4.16 pounds per hour at a coating operation volume source within the District.

Staff is proposing to exempt methyl formate from the District's definition of VOC because it is unlikely to cause adverse impacts to human health or the environment.

1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane (HFE-7300): On January 18, 2007, EPA exempted this compound from the federal definition of VOC because the K_{oh} value of HFE-7300 was less than the K_{oh} value of ethane. HFE-7300 may be used in a variety of applications, including heat transfer, lubricant deposition, electronic testing and cleaning applications. Similar to HFE-7000 and HFE-7500, this compound is classified as a HFE and has an ODP of zero. Under EPA's SNAP program, HFEs, as a class, have been identified as possible substitutes for CFCs. According to EPA's analysis, HFE-7300 could be used to reduce GHG by substituting for other compounds with higher GWP, such as replacing CFCs.

The Product Specification Sheet published by 3M indicates that HFE-7300 has low toxicity. In addition, according to the final rule to exempt HFE-7300 from the definition of VOC as published in the Federal Register[12], HFE-7300 is very similar in structure, toxicity and atmospheric properties to other HFE compounds such as HFE-7100 and HFE-7200. As previously discussed, HFE-7100 and HFE-7200 are not expected to adversely impact human health, and Staff expects that HFE-7300 will have similarly low impacts on human health.

Staff is proposing to exempt HFE-7300 from the District's definition of VOC because this compound would not have an adverse impact on human health or the environment. In addition, this compound may have significant benefits to stratospheric ozone depletion concerns.

Dimethyl carbonate: On January 21, 2009, EPA exempted this compound from the federal definition of VOC based on the MIR methods. The MIRs of dimethyl carbonate on a mass and mole basis were lower than those of ethane. This compound is used as a co-solvent in paints,

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[10] Center for Disease Control and Prevention, http://www.cdc.gov/niosh/npg/default.html, (accessed on 9/21/2011).
[11] E-mail correspondence with David Darling, American Coating Association, September 21, 2011
[12] "Air Quality: Revision to Definition of Volatile Organic Compounds – Exclusion of HFE-7300," Federal Register, Volume 72, January 18, 2007, p. 2193 – 2196.

sealants, adhesives, and as a multi-purpose and thinning solvent. Dimethyl carbonate may also be used as a niche or specialty solvent in industrial coating/sealant applications. For some cleaning applications, dimethyl carbonate may be used as a substitute for isopropyl alcohol. This compound has an ODP and GWP of zero.

In December of 2009, OEHHA completed a toxicity assessment on dimethyl carbonate. Dimethyl carbonate is hydrolyzed to carbon dioxide and methanol in the body via esterase. Methanol is metabolized to formaldehyde, which is further oxidized to formic acid. Because of its metabolites, dimethyl carbonate may be considered toxic. To be protective of nearby receptors from the use of dimethyl carbonate, OEHHA derived an interim acute REL of 18,000 ug/m^3 and chronic REL of 5,500 $ug/'m^3$. OEHHA has determined that there is no evidence of carcinogenicity for methanol, the primary metabolite of dimethyl carbonate, despite a robust database on its toxicity and a long history of human exposure. OEHHA has also determined that the proposed interim acute and chronic RELs are expected to be protective of anticipated effects, including developmental toxicity observed in a key study reported for dimethyl carbonate. Additionally, in OEHHA's memo to CARB[13], OEHHA finds that the exposure to the general public near facilities using dimethyl carbonate will occur, and, at dose levels likely to be achieved by inhalation from the general public, the toxicity impact from the use of this compound appears to be relatively minor.

According to Kowa American Corporation, a manufacturer and distributor of chemical compounds, dimethyl carbonate may be substituted for fast evaporating compounds used in paints, sealants, adhesives and multi-purpose and thinning solvents. Dimethyl carbonate may replace other non-exempt compounds such as xylene, toluene, methyl ethyl ketone (MEK) and hexane that have been identified as Toxic Air Contaminants by CARB. Dimethyl carbonate may replace non-exempt compounds like ethyl acetate or isopropanol. Dimethyl carbonate may also be a better alternative to some exempt compounds such as acetone and methyl acetate. Because of the low flash point of acetone and methyl acetate, using dimethyl carbonate in coating formulations helps lower the risk of fires or explosions. Acetone and methyl acetate have flash points of -20 °C and -10 °C, respectively, whereas dimethyl carbonate has a flash point of 17 °C.

If dimethyl carbonate is exempted from the District's definition of VOC, its use in the potential applications discussed above may increase. To ensure that the increased uses of dimethyl carbonate do not adversely impact human health, Staff calculated the maximum usages for dimethyl carbonate that would result in hazard indices less than 1 using the same dispersion methodology used for methyl formate. The specific details and modeling assumptions are summarized in Appendix B, and the modeling results are shown in Table 3 for acute impacts and Table 4 for chronic impacts.

[13] "Revised Assessment of Health Effects of Exposure to Dimethyl Carbonate, A Chemical Petitioned for Exemption from VOC Rules," Memorandum from OEHHA to Air Resources Board, December 8, 2009.

Table 3: Acute Impacts for Dimethyl Carbonate

Source Type	Unit Emission Rate 1-hour Conc. (ug/m^3)/(g/s)	Acute Hazard Index	Acute REL (ug/m^3)	Emission Rate (g/s)	Hourly DMC Emission (lb/hour)
Point	1,080	1	18,000	16.6	132
Volume	21,700	1	18,000	0.83	6.58

Emission Rate, g/s = (Acute REL, ug/m^3)/(Unit Emission Rate Conc. (ug/m^3)/(g/s)
Hourly emissions, lb/hr = emission rate, g/s * 0.0022 lb/g * 3600 s/hr

The maximum hourly emission rate for dimethyl carbonate for a point source to ensure that the acute hazard index is less than 1 is 132 pounds per hour. As previously determined, the largest coating facility in the District emits an average of 7.2 pounds of VOC per hour. Staff can conclude that it is unlikely for point source facility to emit more than 132 pounds of dimethyl carbonate per hour.

For a volume source, the estimated maximum concentration is located approximately 10 meters from the emission source, which would be considered a worst-case scenario. The maximum hourly emission rate for a volume source to ensure that the acute index is less than 1 is less than 6.58 pounds per hour. As a potential solvent component in paint, sealant, and adhesive, dimethyl carbonate may replace xylene, toluene, and MEK. Based on CARB's Environmental Impact Assessment of tertiary-butyl acetate, the total emissions of xylene, toluene and MEK are as high as 80% of the total VOC emissions from coatings[14]. Assuming that 100% of xylene, toluene and MEK are replaced by dimethyl carbonate, the VOC emissions and the emissions from dimethyl carbonate from coating facility would need to be more than 8.2 pounds of VOC per hour to exceed the acute hazard index of 1. As previously determined, the largest coating facility in the District emits an average of 7.2 pounds of VOC per hour. Therefore, Staff can conclude that it is unlikely that a volume source would emit more than 6.58 pounds of dimethyl carbonate per hour.

Table 4: Chronic Impacts for Dimethyl Carbonate

Source Type	Unit Emission Rate Annual Conc. (ug/m^3)/(g/s)	Chronic Hazard Index	Chronic REL (ug/m^3)	Emission Rate (g/s)	Annual DMC Emission (lb/year)
Point	95.1	1	5,500	57.8	954,000
Volume	1,880	1	5,500	2.93	48,300

Emission Rate, g/s = (Acute REL, ug/m^3)/(Unit Emission Rate Conc. (ug/m^3)/(g/s)
Annual emissions, lb/year = emission rate, g/s * 0.0022 lb/g * 3600 s/hr * 8 hr/day * 5 day/wk * 52 wk/yr

The maximum emission rate for dimethyl carbonate for a point source to ensure that the chronic hazard index is less than 1 is 57.8 grams per second. Based 8 hours per day, 5 days a week, and 52 weeks per year of operation, the emission rate is equivalent to 954,000 pounds per year. For a volume source, the estimated maximum concentration is located approximately 10 meters

[14] "Environmental Impact Assessment of Tertiary-Butyl Acetate" CARB, January 2006, p. 30.

from the emission source, which would be considered a worst-case scenario. The maximum emission rate for a volume source is 2.93 grams per second, which is equivalent to 48,300 pounds of dimethyl carbonate per year. As previously determined, the largest coating facility in the District emits approximately 15,000 pounds of VOC per year according to the 2009 Emission Inventory. Therefore, Staff can conclude that it is highly unlikely for a facility to use amounts that would result in a chronic hazard index greater than 1.

Staff is proposing to exempt dimethyl carbonate from the District's definition of VOC because it will not cause adverse impact to human health or the environment.

Propylene carbonate: On January 21, 2009, EPA exempted this compound from the federal definition of VOC based on the MIR method. The MIR of propylene carbonate on a mole basis was lower than that of ethane. This compound has been used in adhesives, paint strippers, and as a solvent for aerial pesticide applications. This compound is also used in cosmetics, lip liners, baby lotions, shampoos, special purpose lubricants, general purpose degreasers, rubberized coatings, and painting products. It is allowed to be used in cosmetic products at concentrations up to 20%. It also has an ODP and a GWP of zero.

In June of 1998, EPA completed a study entitled, "Environmental Profile for Propylene Carbonate," which evaluated the environmental impacts of using propylene carbonate. This study found that propylene carbonate causes mild skin and eye irritation but it is not known to be a reproductive toxin, a mutagen, or a carcinogen. The study also concluded that propylene carbonate poses minimal risk to workers and residential populations based on the low order of toxicity, low rate of skin absorption, low volatility and low environmental persistence. No acute or chronic RELs have been assigned to propylene carbonate. However, as noted in the EPA study, rats exposed to very high aerosol concentrations (up to 10^6 ug/m^3) over a 90-day period showed no significant signs of toxic effects, except for some swelling around the eyes at the higher concentrations.

Staff is proposing to exempt propylene carbonate from the District's definition of VOC because this compound would not have an adverse impact on human health or the environment. In addition, this compound may have significant benefits to stratospheric ozone depletion and global warming concerns.

Minor Changes to Rule 101

Staff is proposing minor changes that add the common names for two compounds already included in Rule 101: HFE-7100 for 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane ($C_4F_9OCH_3$) and HFE-7200 for 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane ($C_4F_9OC_2H_5$).

EPA EXEMPT COMPOUNDS NOT RECOMMENDED FOR DISTRICT EXEMPTION

In addition to the compounds discussed above, EPA has exempted HFC-227ea and TBAc from the federal definition VOC. Staff, however, is not proposing to incorporate these compounds into the District's list of exempt compounds either because Staff does not have adequate information to evaluate these compounds, or has concerns regarding the adverse impact to human health or the environment. Staff may recommend exempting these compounds in the future when more information becomes available and/or additional health and environmental assessment has been completed. Each compound is discussed below.

1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea): On November 29, 2004, EPA exempted this compound from the federal definition of VOC because the K_{oh} value of HFC-227ea is less than the K_{oh} value of ethane. This compound may be used as a fire suppressant or aerosol propellant. This compound is classified as a hydrofluorocarbon (HFC). In general, HFCs have an ODP of zero, and this compound may be an acceptable substitute for CFCs. Some HFCs have high GWPs. HFC-227ea has GWP of 3800 and could be used to replace other compounds with either higher or lower GWPs. In various fire suppression applications, HFC-227ea may be used as a replacement for Halon 1301, with a GWP (6900) that is higher than HFC-227ea or Halon 1211, with a GWP (1300) that is lower than HFC-227ea.

HFC-227ea is listed as a potent greenhouse gas and would contribute to global warming if used as a replacement for compounds with lower GWPs. This compound could potentially have an adverse impact on the environment. Furthermore, Staff has not received a request to exempt this compound and does not recommend it for exemption at this time.

Tertiary butyl acetate (TBAc): On November 29, 2004, EPA exempted TBAc from the federal definition of VOC in Title 40, Part 51 of the Code of Federal Regulation for the purpose of complying with VOC emission limitations or VOC content requirements. However, EPA maintained TBAc as a VOC for the purposes of all recordkeeping, emissions reporting, photochemical modeling, and emissions inventory requirements. This compound may be used in a variety of coatings, cleaning solvents, and degreasers.

In 2006, CARB, with assistance from the Office of Environmental Health Hazard Assessment (OEHHA), conducted an environmental impact assessment of TBAc. CARB determined that the increased use of TBAc is not expected to increase depletion of stratospheric ozone or contribute to global warming. CARB also concluded that TBAc could pose a potential cancer risk to humans because TBAc metabolizes to tertiary butyl alcohol (TBA). TBA is a potential carcinogen that may result in a cancer risk to humans. Because TBAc may be a carcinogen, OEHHA developed an interim inhalation unit risk factor for TBAc of 4×10^{-7} $(ug/m^3)^{-1}$. CARB recommended that the air districts determine whether the use of TBAc in certain products would pose an unacceptable exposure.

Staff calculated the maximum emissions of TBAc that will cause adverse impact to human health. Generally, a cancer risk of less than 10 in a million per facility for a nearby receptor is below the threshold of significance and considered acceptable based on SMAQMD threshold of significance for the California Environmental Quality Act (CEQA). Staff used the BEEST for Windows modeling program, version 9.63, to determine the unit emission rate concentration from a point source and volume source necessary to reach a cancer risk of 10 in a million. The specific detail and modeling assumptions are summarized in Appendix B and the modeling results are shown in the following table.

Table 5: TBAc Emissions Impact on Nearby Receptors

Source Type	Unit Emission Rate Annual Conc. $(ug/m^3)/(g/s)$	Inhalation Unit Risk Factor $(ug/m^3)^{-1}$	Cancer Risk (per 10^6 Cases)	Emission Rate (g/s)	Annual TBAc Emissions (lb/year)
Point	95.1	4×10^{-7}	10	0.26	4,340
Volume	1,880	4×10^{-7}	10	0.01	220

Emission Rate, g/s = Cancer Risk/[(Unit Emission Rate $(ug/m^3)/(g/s)$ * (Inhalation Unit Risk Factor $(ug/m^3)^{-1}$]
Annual emissions, lb/year = emission rate, g/s * 0.0022 lb/g * 3600 s/hr * 8 hr/day * 5 day/wk * 52 wk/yr

For a coating operation, a point source facility is a facility that sprays paint inside a spray booth and the emissions are exhausted through a stack. The maximum emission rate for TBAc from a point source to ensure that the cancer risk is less than 10 in a million is 0.26 grams per second. This emission rate is equivalent to 4,340 pounds per year, assuming the operation is 8 hours per day, 5 days per week, and 52 weeks per year. In CARB's Environmental Impact Assessment of Tertiary-butyl Acetate, CARB determined that TBAc may be used to replace xylene, toluene, and MEK in coatings. The total emissions of xylene, toluene and MEK are as high as 80% of the total VOC emissions from coatings[15]. Assuming that 100% of xylene, toluene and MEK are replaced by TBAc, the VOC emissions, including TBAc emissions, from the coating facility would need to be more than 5,425 pounds per year to exceed the cancer risk of 10 in a million.

As previously determined, the largest coating facility in the District emits approximately 15,000 pounds of VOC per year. In addition, according to District permit database, there are many other point source coating facilities that have the potential to emit more than 5,425 pounds of VOC per year.

The use of TBAc in coatings or as solvents may not occur in a paint spray booth. A volume source technique in the BEEST model evaluates these facilities where coating or solvent use does not occur in a spray booth, and the emissions are exhausted through ground level openings in the building, e.g. doors and windows, not through an exhaust stack. The maximum emission rate for a volume source to ensure that the cancer risk is less than 10 in a million is 0.01 grams per second, which is equivalent to 220 pounds of TBAc per year assuming the operation is 8 hours per day, 5 days per week, and 52 weeks per year. If TBAc is assumed to replace 80% of the VOC, the VOC emissions, including TBAc, would need to be more than 275 pounds per year to exceed the cancer risk of 10 in a million.

[15] "Environmental Impact Assessment of Tertiary-Butyl Acetate" CARB, January 2006, p. 30.

To assess the significance of the emissions from a volume source, Staff compared the calculated annual TBAc emissions to District's exemption threshold for coating operations. Rule 201 – General Permit Requirements exempts coating operations that use less than 1 gallon per day of coating materials and solvents from the requirement to obtain a permit. The analysis considered an unpermitted facility without a spray booth using the amount of coatings allowed under the exemption, (just under) 1 gallon per day, for 5 days per week and 52 weeks per year. This is equivalent to 260 gallons of coatings per year. At 260 gallons per year, a volume source would need to use coatings with an average VOC content of 1.1 pounds per gallon or more to emit VOC emissions that would exceed the cancer risk threshold. For comparison purposes, the average VOC content for automotive refinishing coatings is 4.5 pounds per gallon[16]. Since TBAc can be used in a variety of coatings and solvents, Staff can conclude that it is likely the average VOC content of coatings and solvents could be more than 1.1 pounds per gallons.

Staff concludes that TBAc may be emitted in quantities that would exceed a cancer risk of 10 in a million and may potentially cause an adverse impact to receptors near facilities using TBAc. At this time, Staff is proposing that TBAc not be an exempt compound for all uses in the District. Instead, Staff will evaluate TBAc on a rule-by-rule basis to determine the need to exempt TBAc and the potential health impact of TBAc to nearby receptors. If TBAc is needed to formulate compliant products and the health impact is less than significant, Staff may consider exempting TBAc within specific prohibitory rules.

To date, no studies have been conducted to assess the carcinogenicity of TBAc itself, only its metabolite, TBA. If future studies of TBAc demonstrate lower cancer risk than that used in this analysis, Staff may reconsider a general exemption of TBAc.

SOCIOECONOMIC IMPACT ANALYSIS

The provisions of Section 40728.5 of the California Health and Safety Code require, in part, that:

> *"Whenever a district intends to propose the adoption, amendment, or repeal of a rule or regulation that will significantly affect air quality or emissions limitations, that agency shall, to the extent that data are available, perform an assessment of the socioeconomic impacts of the adoption, amendment, or repeal of the rule or regulation...This section does not apply to the adoption, amendment, or repeal of any rule or regulation that results in any less restrictive emissions limit if the action does not interfere with the district's adopted plan to attain ambient air quality standards, or does not result in any significant increase in emissions."*

The proposed amendments to Rule 101 update the District's list of exempt compounds to include six compounds that were exempted by EPA. These amendments do not establish emission limitations, and because these compounds have negligible reactivity, their exemption will not significantly affect air quality. The proposed amendments will not interfere with the District's adopted plan to attain the ambient air quality standards. Therefore, the provisions of Section 40728.5 of the Health and Safety Code do not apply to the proposed amendments to Rule 101, and a socioeconomic impact analysis is not required.

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[16] Ibid, p. 36.

PUBLIC COMMENTS

Staff held a public workshop to discuss the proposed amendments on September 16, 2010. A public notice for the workshop was mailed to interested and potentially affected parties, including all permitted stationary sources (except for gas stations and dry cleaners), industry associations, coating manufacturers and suppliers, and all persons who have requested to receive rulemaking notices. The notice was also published in the "Our Region" section of the Sacramento Bee and posted on the District web site. The draft rule and staff report were available for public review prior to the public workshop.

Staff received comments and questions concerning Rule 101 at the workshop, as well as written comments from chemical manufacturers and distributors, coating manufacturers and distributors, and a coating association. CARB and EPA reviewed the proposed amendments, and EPA had an editorial comment. All comments and responses to comments are included in Appendix C.

Several written comments were received requesting Staff to consider an exemption for TBAc as a VOC. Some comments further requested that if Staff was unwilling to grant a full exemption for TBAc, then exempt TBAc with the same permitting requirement proposed for dimethyl carbonate and methyl formate. Staff had initially proposed to exempt dimethyl carbonate and methyl formate with restrictions that required a facility to submit a permit application if the facility would use more than 1 gallon of dimethyl carbonate or methyl formate. Staff is no longer proposing to add these additional permitting requirements for dimethyl carbonate and methyl formate because Staff performed a health risk assessment and determined that it is unlikely that the use of these compounds would adversely impact human health. Staff performed a health risk assessment for TBAc and determined that the use of TBAc may impact human health at nearby receptors at the facilities using TBAc. Furthermore, TBAc is a potential carcinogen, whereas dimethyl carbonate and methyl formate are not. Therefore, Staff is not proposing to exempt TBAc as a VOC in Rule 101 but will evaluate TBAc on a rule-by-rule basis as rules are adopted or amended so that an evaluation of the need of the exemption and health impacts can be assessed. Staff may reconsider an exemption at a later time when CARB or OEHHA has determined that TBAc will not adversely impact human health.

ENVIRONMENTAL REVIEW AND COMPLIANCE

California Public Resources Code Section 21159 requires an environmental analysis of the reasonably foreseeable methods of compliance. Proposed amendments to Rule 101 will add six organic compounds to the list of exempt compounds and will not establish emission limitations; however, these compounds may be used to comply with VOC limits in other District rules. Staff reviewed the six compounds and determined that the compounds have negligible or zero ODPs. Also, each compound either has a low GWP or would be used to replace other organic compounds with higher GWPs. Where the compounds have toxicity concerns, Staff performed health risk assessments to ensure that the potential increased use of the compounds will not cause an adverse impact to nearby receptors. The proposed amendments will not cause any other significant adverse effects on the environment and will not increase emissions; therefore, Staff has concluded that no environmental impacts will be caused by the proposed amendments.

Staff finds that the proposed rule amendments are exempt from CEQA because it can be seen with certainty that there is no possibility that the activity in question may have a significant adverse effect on the environment[17].

FINDINGS

Finding	Finding Determination
Authority: The District must find that a provision of law or of a state or federal regulation permits or requires the District to adopt, amend, or repeal the rule.	The District is authorized to adopt and amend Rule 101 by California Health and Safety Code (HSC) Sections 40001, 40702, and 41010. [HSC Section 40727(b)(2)].
Necessity: The District must find that the rulemaking demonstrates a need exists for the rule, or for its amendment or repeal.	The proposed amendments to Rule 101 are necessary to incorporate six compounds exempted by EPA into the District's definition of VOC. This will give manufacturers and sources more flexibility in formulating and using products with low VOC limits. [HSC Section 40727(b)(1)].
Clarity: The District must find that the rule is written or displayed so that its meaning can be easily understood by the persons directly affected by it.	Staff has reviewed the proposed rule amendments and determined that they can easily be understood by the affected parties. In addition, the record contains no evidence that the persons directly affected by the rule cannot understand it. [HSC Section 40727(b)(3)].
Consistency: The rule is in harmony with, and not in conflict with or contradictory to, existing statutes, court decisions, or state or federal regulations.	The proposed amendments to the rule do not conflict with and are not in contradictory to existing statutes, court decisions, or state or federal regulations. [HSC Section 40727(b)(4)].
Non-Duplication: The District must find that either: 1) The rule does not impose the same requirements as an existing state or federal regulation; or (2) that the duplicative requirements are necessary or proper to execute the powers and duties granted to, and imposed upon the District.	The proposed amendments to the rule do not duplicate any existing state or federal laws or regulations. [HSC Section 40727(b)(5)].
Reference: The District must refer to any statute, court decision, or other provision of law that the District implements, interprets, or makes specific by adopting, amending or repealing the rule.	Health and Safety Code Sections 40001, 40702, and 41010. [HSC Section 40727(b)(6)].
Additional Informational Requirements: In complying with HSC Section 40727.2, the District must identify all federal requirements and District rules that apply to the same equipment or source type as the proposed rule or amendments.	The amendments to Rule 101 incorporate additional compounds into the list of exempt compounds and will not require limits on VOC emissions. Therefore, a written analysis of federal regulations and other District rules is not required. [HSC Section 40727.2(g)].

[17] State CEQA Guidelines, Section 15061(b)(3).

REFERENCES

3M Company. “Product Information: 3M Novec 7300 Engineered Fluid.” September 2009

3M Company. “Product Information: 3M Novec 7500 Engineered Fluid.” September 2009

American Coating Association, e-mail from David Darling, American Coating Association, to Kevin J. Williams, SMAQMD, September 21, 2011.

California Air Resources Board. “Environmental Impact Assessment of Tertiary-Butyl Acetate.” January 2006.

California Air Resources Board. “Environmental Impact Assessment of Selected Halogenated Chemicals.” March 2008.

California Air Resources Board. Letter to Air Pollution Control Officers regarding methyl formate assessment. May 19, 2008.

Kowa American Corporation. Dimethyl Carbonate Information Request submitted to U.S. Environmental Protection Agency. Modified January 2010.

Office of Environmental Health Hazard Assessment. Memorandum to Air Resources Board, “Revised Assessment of Health Effects of Exposure to Dimethyl Carbonate, A Chemical Petitioned for Exemption from VOC Rules”. December 8, 2009.

San Joaquin Valley Unified Air Pollution Control District. Final Draft Staff Report: Proposed Amendments to Rule 1020 (Definitions). December 18, 2008

South Coast Air Quality Management District. Final Staff Report for Proposed Amended Rule 102 – Definition of Terms. September 2009.

U.S. Environmental Protection Agency. 40 CFR Part 51.100(s)(1) Definition of Volatile Organic Compound.

U.S. Environmental Protection Agency. “Environmental Profile for Propylene Carbonate”, EPA/600/R-98/068. June 1998.

U.S. Environmental Protection Agency. Federal Register, 67 FR 13272: “Protection of Stratospheric Ozone: Notice 16 for Significant New Alternatives Policy Program.” March 22, 2002.

U.S. Environmental Protection Agency. “Risk Screen on the Use of Substitutes for Ozone-Depleting Substances: Aerosols and Solvents.” August 21, 2003.

U.S. Environmental Protection Agency. Federal Register, 69 FR 69290: “Air Quality: Revision to Definition of Volatile Organic Compounds – Exclusion of Four Compounds.” November 29, 2004.

U.S. Environmental Protection Agency. Federal Register, 69 FR 69298: “Revision to Definition of Volatile Organic Compounds – Exclusion of t-Butyl Acetate.” November 29, 2004.

U.S. Environmental Protection Agency. “Air Quality Criteria for Ozone and Related Photochemical Oxidants”, EPA 600/R-05/004aF. February 2006.

U.S. Environmental Protection Agency. Federal Register, 72 FR 2193: “Air Quality: Revision to Definition of Volatile Organic Compounds – Exclusion of HFE-7300.” January 18, 2007.

U.S. Environmental Protection Agency. Federal Register, 74 FR 3437: “Air Quality: Revision to Definition of Volatile Organic Compounds – Exclusion of Propylene Carbonate and Dimethyl Carbonate.” January 21, 2009.

Appendix A

SUMMARY OF PROPOSED AMENDMENTS

Rule 101 – General Provisions and Definitions

EXISTING SECTION	NEW SECTION	CHANGE
204.45	Same	Added common name, HFE-7100, for this compound.
204.47	Same	Added common name, HFE-7200, for this compound.
New	204.50	Added HFE-7000 to the list of exempt compounds.
New	204.51	Added HFE-7500 to the list of exempt compounds.
New	204.52	Added methyl formate to the list of exempt compounds
New	204.53	Added HFE-7300 to the list of exempt compounds.
New	204.54	Added propylene carbonate to the list of exempt compounds.
New	204.55	Added dimethyl carbonate to the list of exempt compounds
204.50	204.56	Section renumbered.

APPENDIX B
HEALTH RISK ASSESSMENT

Point Source Modeling Parameters

Emission Rate:	1 gram per second
Release Type:	Default
Stack Height:	20 feet
Stack Temperature:	140° Fahrenheit
Exit Diameter:	2.83 feet
Exit Velocity:	31.8 feet per second
Flow Rate:	12,000 cubic feet per minute
Building Height:	14 feet
Land:	Urban

Point Source BEEST for Windows Output

Max Annual Concentration:	95.09 (ug/m^3)/(g/s)
Max 1-hour Concentration:	1,081.5 (ug/m^3)/(g/s)

Volume Source Modeling Parameters

Emission Rate:	1 gram per second
Building Dimensions:	24 feet x 24 feet x 12 feet (length x width x height)
Release Height:	10 feet
Horizontal Dim:	5.58 feet (length/4.3)
Vertical Dim:	5.58 feet (height/2.15)
Elevation:	0 feet
Land:	Urban

Volume Source BEEST for Windows Output

Max Annual Concentration:	1,878 (ug/m^3)/(g/s)
Max 1-hour Concentration:	21,708 (ug/m^3)/(g/s)

Hazard Index

$$\text{Hazard Index} = \frac{\text{Concentration (ug/m}^3\text{)/(g/s) * Emission Rate (g/s)}}{\text{Reference Exposure Level (ug/m}^3\text{)}}$$

Cancer Risk

Cancer Risk = Inhalation Unit Risk Factor (ug/m^3)$^{-1}$ * Concentration (ug/m^3)/(g/s)) * Emission Rate (g/s)

Methyl Formate

Density: 8.17 lb/gal
Acute Reference Exposure Level (REL): 11,400 ug/m^3

Calculating the maximum emission rate (ER) from a point source to have an acute hazard index (HI) of 1:

ER = (HI * REL)/1-hour Conc.
ER = (1 * 11,400 ug/m^3)/(1,081.5 (ug/m^3)/(g/s))
ER = 10.5 g/s

Hourly Emission = ER * 0.0022 lb/g * 3600 s/hr
Hourly Emission = 10.5 g/s * 0.0022 lb/g * 3600 s/hr
Hourly Emission = 83.6 lb/hr

Calculating the maximum emission rate from a volume source to have an acute HI of 1:

ER = (HI * REL)/1-hour Conc.
ER = (1 * 11,400 ug/m^3)/(21,708 (ug/m^3)/(g/s))
ER = 0.53 g/s

Hourly Emission = ER * 0.0022 lb/g * 3600 s/hr
Hourly Emission = 0.53 g/s * 0.0022 lb/g * 3600 s/hr
Hourly Emission = 4.16 lb/hr

Dimethyl Carbonate

Density: 8.92 lb/gal
Acute Reference Exposure Level (REL): 18,000 ug/m^3
Chronic Reference Exposure Level (REL): 5,500 ug/m^3

Calculating the maximum emission rate from a point source to have an acute HI of 1:

ER = (HI * Acute REL)/1-hour Conc.
ER = (1 * 18,000 ug/m^3)/(1,081.5 (ug/m^3)/(g/s))
ER = 16.6 g/s

Hourly Emission = ER * 0.0022 lb/g * 3600 s/hr
Hourly Emission = 16.6 g/s * 0.0022 lb/g * 3600 s/hr
Hourly Emission = 132 lb/hr

Calculating the maximum emission rate from a volume source to have an acute HI of 1:

ER = (HI * Acute REL)/1-hour Conc.
ER = (1 * 18,000 ug/m^3)/(21,708 (ug/m^3)/(g/s))
ER = 0.83 g/s

Hourly Emission = ER * 0.0022 lb/g * 3600 s/hr
Hourly Emission = 0.83 g/s * 0.0022 lb/g * 3600 s/hr
Hourly Emission = 6.58 lb/hr

Calculating the maximum emission rate from a point source to have a chronic HI of 1:

ER = (HI * Chronic REL)/Annual Conc.
ER = (1 * 5,500 ug/m^3)/(95.09 (ug/m^3)/(g/s))
ER = 57.8 g/s

Annual Emission = ER * 0.0022 lb/g * 3600 s/hr * 8hr/day * 5 days/wk * 52 wk/yr
Annual Emission = 57.8 g/s * 0.0022 lb/g * 3600 s/hr * 8hr/day * 5 days/wk * 52 wk/yr
Annual Emission = 954,000 lb/year

Calculating the maximum emission rate from a volume source to have a chronic HI of 1:

ER = (HI * Chronic REL)/Annual Conc.
ER = (1 * 5,500 ug/m^3)/(1,878 (ug/m^3)/(g/s))
ER = 2.93 g/s

Annual Emission = ER * 0.0022 lb/g * 3600 s/hr * 8hr/day * 5 days/wk * 52 wk/yr
Annual Emission = 2.93 g/s * 0.0022 lb/g * 3600 s/hr * 8 hr/day * 5 days/wk * 52 wk/yr
Annual Emission = 48,300 lb/year

Tertiary Butyl Acetate

Density of TBAc: 7.18 lb/gal
Inhalation Unit Risk Factor (URF) = 4 x 10^{-7} (ug/m^3)$^{-1}$

Calculating the maximum emission from a point source to have a cancer risk of less than 10 in a million:

ER = Cancer Risk/(URF*Annual Conc)
ER = (10 x10^{-6})/(4 x 10^{-7} (ug/m^3)$^{-1}$ * 95.09 (ug/m^3)/(g/s))
ER = 0.26 g/s

Annual TBAc Emission = ER * 0.0022 lb/g * 3600 s/hr * 8 hr/day * 5 days/wk * 52 wk/yr
Annual TBAc Emission = 0.26 g/s * 0.0022 lb/g * 3600 s/hr * 8 hr/day * 5 days/wk * 52 wk/yr
Annual TBAc Emission = 4340 lb/year

Assume: 80% of VOC is replaced by TBAc
Annual VOC Emission = 4340 lb/year / 80%
Annual VOC Emission = 5425 lb/year

Calculating the maximum emission from a volume source to have a cancer risk of less than 10 in a million:

ER = Cancer Risk/(URF*Annual Conc)
ER = (10 x10^{-6})/(4 x 10^{-7} (ug/m^3)$^{-1}$ * 1,878 (ug/m^3)/(g/s))
ER = 0.01 g/s

Annual TBAc Emission = ER * 0.0022 lb/g * 3600 s/hr * 8 hr/day * 5 days/wk * 52 wk/yr
Annual TBAc Emission = 0.01 g/s * 0.0022 lb/g * 3600 s/hr * 8 hr/day * 5 days/wk * 52 wk/yr
Annual TBAc Emission = 220 lb/year

Assume: 80% of VOC is replaced by TBAc
Annual VOC Emission = 220 lb/year / 80%
Annual VOC Emission = 275 lb/year

Calculating the District permitting threshold:

Permitting threshold = 1 gallon of coatings and solvents per day
Permitting threshold = 1 gallon/day * 5 days/wk * 52 wk/yr
Permitting threshold = 260 gallons/yr

Calculating the average VOC content to emit VOC emissions that exceed the cancer risk

Average VOC content = Annual VOC Emissions/Permitting threshold
Average VOC content = 275 lb/yr / 260 gallons/yr
Average VOC content = 1.1 lb/gallon

APPENDIX C
COMMENTS AND RESPONSES

Public Workshop for Rules 101, 451 and 459
September 16, 2010, 2:00 PM

Attendees:

Allen Cripe, CalTrans
Brad Gacke, SMUD
Brett Hayes, Hayes Brothers Collision
Brittany Marcotte, Nestle Waters North America
Bryon Theis, 3M
Cerlut Fre, Sherwin-Williams
Clifford Waters, Sherwin-Williams
Dale Schell, Jim's Color Corner
Dan Porreau, LyondellBasell
Danny Nunez, Finish Masters
Dave Fisher, Morrison Paint Supply
Dave Harshbarger, MAC's Distribution
David Luer, MAC's Distribution
David McClune, California Autobody Association
David Roznowski, LyondellBasell
Debra Wynne, Original Paint
Dennis Barkman, Colors On Parade
Deran Berggne, Jerry's Paint
Eric Cooc, Precision Autobody
George Contos, Blomberg Window
Glenn Galbaugh, DuPont Company
Grey Calhorn, Finish Master
Jason Kowen, Spies Hecker
Jeanette Duncan, Ellis & Ellis Sign Systems
Jeremy Tiner, Warehouse Paint

Jim Brett, CalTrans
Jim Cropper, CARB
Josh Cox, Jerry's Paint
June Livingston, BERC
Kelly Hitt, Nestle Waters North America

Kendall McCane, Jerry's Paint
Kevin Holley, MAC's Distribution
Kevin Thompson, Thompson Sales
Larry Medrano, PBE Inc
Lisa Dobeck, Caltrans
Mark McCleskey, Jerry's Paint
Mark Tavianini, CARB
Matt Stevens, Shanahan's Autobody
Mike Veney, Sherwin-Williams
Pat Newcomb, Jerry's Paint

Pat Stickle, Angel Warehouse
Peter Bezech, California Autobody Association
Phil Brown, PPG Industries
Rich Mott, Jerry's Paint
Rick Hays, MAC's Distribution
Robert Blair, Finish Mater
Shane Whitcomb, Ellis & Ellis Sign Systems
Stan Brecetu, 3M
Steve Nesbitt, PCL
Terry Klemin, Matrix
Todd Everitt, Valspar Refinish
Tom Walther, Jim's Color Corner
Vern Heffner, City of Sacramento Fleet Management

Oral Comments from the Public Workshop

Note: A combined workshop was held for proposed amendments to Rule 101, Rule 451 and Rule 459. Only comments pertaining to the proposed amendments to Rule 101 are shown below.

Comment #1 Lyondell supports the exemption of propylene carbonate in Rule 101.

Response: Thank you for your comment.

Comment #2 Lyondell objects to the unequal treatment of TBAc with regard to dimethyl carbonate and methyl formate. Lyondell requests that the proposed amendments exempt TBAc with the same restriction as for dimethyl carbonate and methyl formate.

Response: Staff is no longer proposing to add permitting restrictions to dimethyl carbonate and methyl formate because Staff has determined from health risk modeling that these compounds will not cause an adverse impact on human health. Staff has not changed its position on TBAc and is not proposing to exempt TBAc in Rule 101. Because TBAc is a potential carcinogen and may be used in a variety of applications, the decision to exempt TBAc would need to be looked at within each prohibitory rule. Most recently, Staff reviewed the potential impacts of exempting TBAc as a VOC in Rule 459, Automotive, Mobile Equipment, and Associated Parts and Components Coating Operations, and provided a limited exemption for TBAc.

Written Comments from Environmental Protection Agency dated 9/3/2010

Comment #3 Office of Air Quality Planning and Standards (OAQPS) plans to fix an editorial error in 40 CFR 51.100. The name of the compound should be 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane (HFE-7300), instead of (1) 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane (HFE-7300). The “(1)” should be removed.

Response: Staff has made the change in the proposed amendments to Rule 101.

Written Comments from LyondellBasell dated 8/31/2010

Comment #4 We support the addition of propylene carbonate to the list of exempt compounds.

Response: Thank you for your comment.

Comment #5 The staff report for Rule 101 cites CARB’s 2006 environmental impact assessment as the reason for not proposing the exemption of TBAc. CARB’s concern at the time was that TBAc could pose a potential cancer risk to humans because TBAc metabolized to TBA. Since CARB’s 2006 Environmental Impact Assessment on TBAc, several studies have confirmed that neither TBA nor TBAc are genotoxic, potential human carcinogens, or reproductive toxins.

Response: Staff relied on the published toxicity evaluations from experts at OEHHA and CARB. Staff contacted OEHHA regarding the studies mentioned in the comment letter. According to OEHHA staff, these studies have not provided sufficient evidence demonstrating that the rodent tumor studies are not relevant to humans. Therefore, OEHHA still considers TBAc to be a potential human carcinogen. Staff will reconsider an exemption for TBAc when OEHHA or CARB has concluded that it will not cause an adverse impact to human health.

Meanwhile, Staff will consider an exemption for TBAc within specific prohibitory rules as they are adopted or amended. Staff will review the potential impacts and determine whether exempting TBAc would cause an adverse impact to human health.

Comment #6 DMC metabolizes to methanol, a chemical OEHHA has proposed to add to Prop 65 as a reproductive toxin, which in turn metabolizes to formaldehyde, a probable human carcinogen. Therefore, it is incongruous that staff would propose the exemption of dimethyl carbonate in Rule 101 but not TBAc, whose metabolite TBA is neither a listed carcinogen nor reproductive toxin.

Response: The Prop 65 list is a notification requirement regarding the use of compounds that are considered to be carcinogens or reproductive toxins. Methanol is proposed to be added to the Prop 65 list as a reproductive toxin; however, no action has been taken by OEHHA. Furthermore, OEHHA has concluded in a memo to CARB[18] that there is no evidence of carcinogenicity for methanol, the primary metabolite of dimethyl carbonate, despite a robust database on toxicity and a long history of human exposure. Also, according to OEHHA, formaldehyde, the metabolite for methanol, is carcinogenic by inhalation, but in the case of dimethyl carbonate exposure, formaldehyde would be formed inside the human body. This formation has not shown that the internal levels of dissolved or bound formaldehyde produced by intermediary metabolism or by methanol oxidation are associated with cancer. OEHHA further concluded that the proposed interim acute and chronic REL are expected to be protective of anticipated adverse health effects, including the developmental toxicity observed in the key study reported for dimethyl carbonate. Therefore, Staff expects that an exemption for dimethyl carbonate will not cause adverse impact on human health.

Comment #7 We believe that adding TBAc to Rule 101 with the same use restrictions (permit requirements) as dimethyl carbonate and methyl formate is consistent with the science, rulemakings in several other California counties and air districts, protective of human health, and provides the District with a mechanism to review potential risks on a case-by-case basis. We request that TBAc be added to the list of exempt compounds in Rule 101 with the same permitting requirements as dimethyl carbonate and methyl formate.

Response: See responses to comments #2 and #5.

[18] "Revised Assessment of Health Effects of Exposure to Dimethyl Carbonate, A Chemical Petitioned for Exemption from VOC Rules," Memorandum from OEHHA to Air Resources Board, December 8, 2009.

Written Comments from LyondellBasell in E-mail dated 9/1/2010

Comment #8 We object to the uneven handling of TBAc compared to dimethyl carbonate and methyl formate and request that TBAc also be added to the list of exempts in Rule 101 with the same permitting requirements.

Response: See response to comment #2.

Written Comments from Miami Chemicals dated 9/8/2010

Comment #9 Miami Chemical supports the proposed amendments to Rule 101.

Response: Thank you for your comment.

Written Comments from Kowa American Corporation dated 9/9/2010

Comment #10 Kowa American Corp would like to ask the SMAQMD to exempt the solvent dimethyl carbonate as a VOC. We feel dimethyl carbonate being VOC exempt will allow your local businesses a much greater degree of flexibility in meeting the more stringent VOC restrictions moving forward.

Response: Staff is proposing to exempt dimethyl carbonate from the District's definition of VOC in Rule 101.

Comment #11 We understand the District is contemplating having users of dimethyl carbonate apply for permits to use dimethyl carbonate. We think this would add an unnecessary amount of extra work for your air district.

Response: Staff has performed a health risk assessment and has determined that dimethyl carbonate will not cause an adverse impact on human health; therefore, Staff is no longer proposing to add permitting requirements for dimethyl carbonate.

Comment #12 If a permit is required, we would ask that: a sunset provision be included for the permit requirement, increase the permit to a larger amount (say for usages of more than 1,000 gallons per year) and allow contractors to use their permit across the air district instead of requiring one for each individual work site. We think these suggestions would make a permit process much easier for dimethyl carbonate users and for your District's employees.

Response: See response to comment #11.

Written Comments from American Coating Association (ACA) dated 9/9/2010

Comment #13 ACA supports the comments by Lyondellbasell and Kowa and suggests that propylene carbonate, TBAc, and dimethyl carbonate all be added to the list of exempt compounds without any restrictions since these compounds were exempted by the U.S. EPA, nearly every state in the U.S., and many California air districts based on their negligible contribution to tropospheric ozone formation.

Response: See responses to Comments #2, #4 through #8, and #10 through #12. Staff is proposing to add propylene carbonate and dimethyl carbonate to the list of exempt compounds in Rule 101. At this time, Staff is not proposing to exempt TBAc as a VOC because of its potential adverse impact on human health. Instead, Staff intends to review the impacts of TBAc on a rule-by-rule basis and where Staff determines it appropriate, include an exemption or limited exemption for TBAc.

Comment #14 If the District does not outright exempt TBAc, ACA suggests to be fair the District should exempt TBAc and include the same permit requirements as dimethyl carbonate and methyl formate in order to address any possible concerns with the use of TBAc.

Response: See response to Comment #2.

Written Comments from AkzoNobel Car Refinishes dated 9/16/2010

Comment #15 TBAc has been fully exempted as a VOC by the U.S. EPA and in the following California Air Pollution Control Districts: San Joaquin, Santa Barbara, Yolo-Solano APCD.

Response: U.S. EPA exempted TBAc as a VOC for the purpose of meeting VOC content limits or VOC emission limits, but EPA maintained its status as a VOC for the purposes of recordkeeping, emissions reporting, photochemical modeling, and emissions inventory requirements. At this time, Staff is not proposing to exempt TBAc in Rule 101 because of the potential adverse impact to human health but will assess the appropriateness of exempting it under specific rules. See response to Comment #5.

Comment #16 AkzoNobel suggests that the exemption for TBAc should be moved from Rule 459, Section 268, to Rule 101, Section 204, in order to clarify that the TBAc is VOC exempt and would eliminate the need for any further tracking use.

Response: See response to Comment #15. Regardless of where an exemption for TBAc would be allowed, District rules would include recordkeeping and tracking as required by the U.S. EPA exemption.

Written Comments from DuPont Performance Coatings dated 9/17/2010

Comment #17 We struggle to understand the conditional exemption of dimethyl carbonate and methyl formate. Like many of the other solvents exempted from consideration as a VOC, dimethyl carbonate and methyl formate would be incorporated into finished products. End-users may not have the capacity to track this required information, and we believe the provision is unnecessarily burdensome.

Response: See response to Comment #2. Staff is no longer proposing permitting requirements for dimethyl carbonate and methyl formate.

Comment #18 We struggle to understand the absence of an exemption for TBAc. Manufacturers need every tool to formulate coatings that meet ever-lowering VOC standards. TBAc is VOC-exempt in most States and some California Air Districts. This solvent is effective for a wide range of coatings types, and formulations for surface preparation. There is a critical and urgent need for safe, effective and affordable exempt solvents for use in the industry.

Response: Staff understands that TBAc may be used in a wide range of applications. As such, there is a potential for a significant increase in the use of TBAc within the District if it is exempted as a VOC. According to the information from CARB's Environmental Impact Assessment of Tertiary-Butyl Acetate, TBAc is a potential human carcinogen, and its increased use may potentially cause an adverse impact on human health. Staff intends to review the impacts of TBAc on a rule-by-rule basis and determine if there is a need to exempt TBAc and if the potential use of TBAc in specific applications will not cause adverse impacts on human health.

Comment #19 Because of their broad usefulness in formulation and demonstrated safety, we request that the District fully exempt all solvents currently exempted by U.S. EPA.

Response: Staff is not proposing the add TBAc and HFC-227ea to the list of exempt compounds because of the potential adverse impact to human health or the environment. Compounds exempted from the federal VOC definition are not automatically exempted from District rules and regulations. The District considers a number of factors, including potential uses, impact on human health, and environmental concerns before adding federally-exempt compounds to Rule 101.