

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

**Draft Staff Report for
Proposed Amended Rule 102 - Definition of Terms**

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EXECUTIVE SUMMARY

The United States Environmental Protection Agency (U.S. EPA) revised the federal volatile organic compound (VOC) definition to exclude methyl formate, dimethyl carbonate, and propylene carbonate based on the compounds' negligible photochemical reactivity. These compounds are not classified as hazardous air pollutants under the federal Clean Air Act. Staff has reviewed the relevant documents provided by the U.S. EPA, California Air Resources Board (CARB) and industry, and is now proposing to amend Rule 102 – Definition of Terms by adding methyl formate, dimethyl carbonate, and propylene carbonate to the list of VOC exempt compounds in the rule.

Besides having negligible reactivity, methyl formate has other desirable properties in that it has negligible ozone depleting potential (ODP) and a very low or zero global warming potential (GWP). Dimethyl carbonate and propylene carbonate are not classified as ozone depleting substances. Staff also considered the potential health effects in evaluating these compounds for exemption.

Proposed Amended Rule (PAR) 102 may potentially eliminate approximately 238 tons per year of VOC emissions, and an additional 171 tons per year of global warming compound emissions just from foam manufacturing operations.

BACKGROUND

The U.S. EPA revises the definition of VOCs for purposes of preparing State Implementation Plans (SIPs) to attain national ambient air quality standards for ozone under the Clean Air Act. The U.S. EPA lists chemical compounds that are excluded from the VOC definition based on the compound's negligible contribution to the formation of tropospheric ozone (commonly known as smog). Smog is formed when VOCs react photochemically with nitrogen oxides in the atmosphere. However, different VOCs have different reactivity levels, i.e., they do not react to form ozone at the same rate or do not form ozone to the same extent. There are VOCs that react slowly, and changes in their emissions have limited effects on local or regional ozone pollution episodes. As a result, EPA's policy has been to exclude organic compounds with negligible reactivity level from the regulatory definition of VOCs, and helps states focus emission control efforts on VOCs that significantly increase ozone concentrations.

In determining negligible reactivity, the U.S. EPA compares the reactivity of a given organic compound to that of ethane. Compounds with reactivity levels lower than, or equal to, ethane under the assumed conditions may be deemed negligibly reactive, while compounds that are more reactive than ethane continue to be considered reactive VOCs, and therefore subject to control requirements.

The U.S. EPA uses three primary methods when comparing reactivity of a specific compound to that of ethane. The first method is based on the reaction rate constant (k_{OH}) of the compound with the hydroxyl (OH) radical in the air. This reaction is the initial step in a series of chemical reactions in the formation of ozone. If the reaction is slow, the compound will likely not form ozone at a fast rate.

Two other methods for comparing reactivity levels are based on maximum incremental reactivities (MIR) expressed either on a reactivity per gram basis or on a reactivity per mole basis. The MIR values are more recently developed measures of photochemical reactivity and

consider not only the initial reaction step but also includes the complete ozone forming activity of a specific organic compound. MIR values are 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).

During the past years, the U.S. EPA has revised the definition of VOCs to exclude several organic compounds from the definition of VOC based on their negligible contribution to ozone formation. In November 2004, the U.S. EPA delisted methyl formate in response to a petition from Foam Supplies, Inc. to exclude the compound from the definition of VOC. The U.S. EPA's decision to delist methyl formate was based on the compound's slightly lower k_{OH} value and reactivity rate at less than half that of ethane.

Effective February 2009, two additional organic compounds were added to the list of VOC exempt compounds, i.e., dimethyl carbonate and propylene carbonate, on the basis that these compounds are less photochemically reactive than ethane and, thus, have negligible contribution to tropospheric ozone formation. Kowa American Corporation petitioned the U.S. EPA seeking an exemption for dimethyl carbonate from the regulatory definition of VOC, while Huntsman Corporation submitted the exemption petition for propylene carbonate.

The following section provides a more detailed discussion on the three compounds exempted by the U.S. EPA from the VOC definition.

MATERIAL DESCRIPTION

Methyl Formate

Methyl Formate, also called methyl methanoate, is the methyl ester of formic acid and has the following molecular formula: $HCOOCH_3$. It is a clear liquid with a pleasant, ether-like odor, and is very soluble in water and miscible with most organic solvents. The compound is not classified as a hazardous air pollutant under the federal Clean Air Act.

The predominant industrial use of methyl formate is in the manufacture of formamide, dimethylformamide, and formic acid. Because of methyl formate's high vapor pressure, it is commonly used as a component of the solvent system for quick-drying coatings. It is also used in the manufacture of pharmaceuticals, and as a blowing agent in foam manufacturing. The U.S. EPA's decision to exempt methyl formate as a VOC was based on the compound's low ozone forming potential (reactivity). Scientific studies indicate that the compound's reaction rate constant (k_{OH}) with the OH radical in the air is $2.27 \times 10^{-13} \text{ cm}^3/\text{molecule}/\text{sec}$, which is slightly lower than ethane's k_{OH} value of $2.4 \times 10^{-13} \text{ cm}^3/\text{molecule}/\text{sec}$. Further evidence of methyl formate's low reactivity, as reported in Dr. William Carter's 2007 research report titled "Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales," shows an MIR value of 0.053 gram of ozone formed per gram of VOC. This is less than the MIR value of 0.27 for ethane, which is the benchmark compound for exemption purposes. Because of methyl formate's low or negligible reactivity compared to ethane, it is not expected to have a meaningful contribution to ozone formation.

Besides having negligible reactivity, methyl formate has other desirable properties in that it has negligible ozone depleting potential (ODP) and a very low or zero global warming potential (GWP). The GWP refers to the amount of global warming caused by a substance. It is the ratio of the warming caused by a substance to the warming caused by a similar mass of carbon dioxide.

Methyl formate is a suitable replacement for hydrocarbon blowing agents used in polyurethane and polystyrene foam manufacturing. Polyurethane foam products include rigid insulating foam (used in refrigerators) and flexible foam (used in furniture). Polystyrene foams are commonly used in manufacturing food containers. Some of the substances that the compound may replace for foam blowing include high GWP hydrofluorocarbons such as HFC-134a, HFC-152a, and HFC-245fa, and other VOC blowing agents such as butane and pentane. Replacing these compounds will help achieve overall reduction in VOC emissions and Greenhouses Gases.

In assessing a chemical compound for possible delisting as VOC in Rule 102, staff not only evaluates its environmental benefits but also determines potential health risks associated with the use of such compound. In response to petitions for VOC exempt status and requests from some air districts, the California Air Resources Board, in conjunction with the Office of Environmental Health Hazard Assessment (OEHHA), conducted an environmental impact assessment of methyl formate particularly on possible health effects associated with inhalation exposure to the compound.

Methyl formate is rapidly hydrolyzed in the body to methanol and formic acid. Methanol is enzymatically oxidized to formaldehyde, which is then rapidly oxidized to formic acid. These metabolites were also considered by OEHHA in assessing toxicity of methyl formate. Formaldehyde and methanol are listed as toxic air contaminants in AQMD Rule 1401, and formaldehyde is a known carcinogen.

OEHHA's assessment indicates that the use of methyl formate as substitute for more reactive blowing agents would increase exposure by inhalation of workers and the general public near facilities using the compound. The report also indicates that methyl formate is expected to be less irritating to mucous membranes than its metabolites, formaldehyde or formic acid. In addition, OEHHA's toxicity assessment finds that methyl formate has no carcinogenicity or long-term toxicity data. Similarly, there is no evidence of carcinogenicity for methanol despite a vast database on toxicity and long history of human exposure. On the other hand, formaldehyde is carcinogenic by inhalation, but it has not been determined whether internal levels of dissolved or bound formaldehyde produced by intermediary metabolism or by methanol oxidation are associated with cancer.

OEHHA's toxicity assessment concluded that for methyl formate's intended use as substitute blowing agent in foam manufacturing, the health concern is the internal levels of methanol and formic acid (or formate ion) in solution due to metabolism of methyl formate, and not the external air concentrations of the chemicals. Further, OEHHA, in a memorandum to CARB on the health effects of exposure to methyl formate, dated March 14, 2008, concluded that "at dose levels likely to be achieved in environmental exposures by inhalation, these concerns appear to be minor."

There is no chronic Reference Exposure Level (REL) or cancer potency values due to lack of data on long-term health effects. However, OEHHA has estimated an interim acute REL of 11,400 $\mu\text{g}/\text{m}^3$ (4.7 ppm) for methyl formate, which is much greater than the acute REL for formaldehyde (55 $\mu\text{g}/\text{m}^3$), and less than half that of methanol (28,000 $\mu\text{g}/\text{m}^3$). OEHHA's

estimated interim REL for methyl formate, however, has not undergone external peer review nor has it been approved by the Scientific Review Panel on Toxic Air Contaminants. According to OEHHA's report, formaldehyde's low acute REL reflects its reactivity which causes sensory effects and tissue damage at the point of contact with the respiratory system and the eyes.

Based on OEHHA's assessment of exposures, as well as positive environmental benefits of using methyl formate, CARB, in a letter to air pollution control officers, dated May 19, 2008, recommends that air districts consider this compound for exemption in the definition of VOC, but also to remain vigilant about possible adverse effects as its uses increase.

In addition to OEHHA's toxicity evaluation, AQMD staff performed health risk analysis (HRA), as part of CEQA's environmental assessment, on the use of methyl formate as a foam blowing agent at both polyurethane and polystyrene foam manufacturing facilities. AQMD staff estimated methyl formate's Tier 1 screening value for acute hazard index (HIA) to be 5.7 pounds per hour (lb/hr), based on OEHHA's interim REL value, using the same methodology when adding a compound to Rule 1401, and worst-case scenario assumptions.

A Tier 1 HRA was performed using AQMD's 2005/2006 Annual Emissions Reporting (AER) data as well as manufacturer's estimated average foam blowing agent emissions for a typical polyurethane foam manufacturing facility. Based on this information, the screening value of 5.7 lb/hr would not be exceeded.

For the four known polystyrene foam manufacturing facilities in the South Coast Air Basin, daily emissions from the blowing agent are higher and would exceed the Tier 1 HIA screening value of 5.7 lb/hr; thus, staff conducted a Tier 2 and Tier 3 HRA to identify acute hazard index for these facilities. Using the shortest screening receptor distance of 25 meters, staff's analysis indicated that polystyrene foam manufacturing facilities would not exceed an HIA significance threshold of 1.0.

Based on the HRAs conducted for foam manufacturing facilities, staff concluded that methyl formate's use as replacement blowing agent is not expected to generate significant adverse acute non-cancer health risk impact.

Table 1 summarizes the physical and chemical properties of methyl formate, including the two compounds currently classified as VOCs (pentane and butane) and three HFCs that may be replaced with methyl formate. Health data including OSHA's Permissible Exposure Limits (PEL), OEHHA/ARB-approved acute and chronic exposure levels, and carcinogenicity are also summarized.

Table 1 – Physical and Chemical Properties for Methyl Formate and Currently Used Conventional Blowing Agents

	Conventional Blowing Agents					Proposed Compound
	HFC 134a	HFC 152a	HFC 245fa	Pentane	Butane	Methyl Formate
Appearance	Clear colorless gas	Clear colorless gas	Clear colorless gas	Clear colorless liquid	Clear colorless liquid	Clear colorless liquid
Odor	Slight ether	Slight ether	No odor warning properties	Mild pleasant, gasoline like	Mercaptan odor	Ethereal sweet odor
Molecular Formula	CH ₂ H ₂ F ₄	CH ₃ CH F ₂	CF ₃ CH ₂ CHF ₄	C ₅ H ₁₂	C ₄ H ₁₀	HCOOCH ₃
Molecular Weight	102.03 g/mole	66.05 g/mole	134 g/mole	72.15 g/mole	58.12 g/mole	60.05 g/mole
Density	1.21 g/ml	0.91 g/mL	1.35 g/mL	2.48 g/mL	2.11 g/mL	0.98 g/mL
Boiling Point	-26.5 °C (-15.7°F)	-25 °C (-13 °F)	15.3 °C	36.1 °C (97 °F)	15.5 °C (31.1 °F)	32 °C (89.7 °F)
Melting Point	-101 °C	-117 °C	Not determined	-130 °C (-202 °F)	-138.4 °C (-217.0 °F)	-100 °C
Vapor Pressure	4960 mmHg @ 25 °C	4500 mmHg @ 25 °C	921 mmHg @ 20 °C	426 mmHg @ 20 °C	1557 mmHg @ 20 °C	585.7 mmHg @ 25 °C
Solubility in Water	Soluble	Soluble	Soluble	Soluble	Insoluble	Soluble
Solvent Solubility	Not available	Not available	Not available	Miscible with most organic solvents	Not available	Miscible with most organic solvents
NFPA ^A Flammability Rating	0	4	0	4	4	4
Lower Explosive Limit	None per ASTM E681	3.9%	None	1.5%	1.6%	5%
Upper Explosive Limit	None per ASTM E681	16.9%	None	7.8%	8.4%	23%
Flash Point	No flashpoint	-50 °C (-58 °F)	No flashpoint	-49 °C (-56.2 °F)	Less than -117 °F	-19 °C (-2.2 °F)
OSHA PEL	None	None	None	1000 ppm	None	100 ppm
Acute REL ^B	None	None	None	None	None	11,400 ug/m ³
Chronic REL ^B	None	None	None	None	None	None
Carcinogenic	No	No	No	No	No	No

^A National Fire Protection Agency^B OEHHA/ARB Approved Risk Assessment Health Values

Dimethyl Carbonate

This organic compound, also known as carbonic acid dimethyl ester, is a colorless, fast-evaporating solvent that is used as a methylating agent and reaction solvent in chemical processing. It is also used as solvent for lithium ion batteries. It is highly flammable, with a flash point of 64 °F (closed cup). Despite its relatively low flashpoint, dimethyl carbonate represents a more favorable alternative to two commonly used VOC-exempt solvents: acetone and methyl acetate, which have lower flashpoints.

Dimethyl carbonate is not identified as a hazardous air pollutant under the federal Clean Air Act nor is it classified as an ozone depleting substance. Effective February 20, 2009, the U.S. EPA excluded dimethyl carbonate from the definition of VOC based on its low potential to generate ozone in the troposphere. The report by Dr. Carter shows much lower MIR values for dimethyl carbonate than ethane, as summarized in Table 2 below.

Table 2 – Comparison of MIR Values for Dimethyl Carbonate and Ethane

MIR	Dimethyl Carbonate	Ethane
gram ozone/gram VOC	0.056	0.27
Gram ozone/mole VOC	5.04	8.12

Based on dimethyl carbonate's low MIR values, the U.S. EPA concluded that the compound is negligibly reactive, and excluded it from the VOC definition.

A VOC-exempt dimethyl carbonate may be used as a paint, sealant and adhesive co-solvent, and may provide use as multipurpose and thinning solvent. Because of its solubility properties, dimethyl carbonate may be useful as a co-solvent in acrylics, urethane and alkyd systems, and potentially replace alcohols, ketones, esters and glycol ethers. Dimethyl carbonate may likely be used as a niche or specialty solvent in industrial coating/sealant applications as well as may be incorporated in waterborne coatings and adhesives because of its partial miscibility in water.

For some cleaning applications, dimethyl carbonate may be used to replace isopropyl alcohol (IPA) although the compound is less polar than IPA. Because of its high boiling point, it is not expected to be used in vapor degreasing. In spite of its relatively low flash point, dimethyl carbonate may still be a better alternative to acetone and other fast evaporating organic solvents in cold batch cleaning applications. In addition, the compound has solubility and other properties that might make it a replacement for trichloroethylene in solvent cleaning operations. Because of the compounds drawbacks such as low flash point and relatively high cost, Kowa American estimates that potential volume of use in California would only be 2 million pounds per year.

Given the potential applications of the compound, inhalation is expected to be the primary pathway of exposure due to evaporation of the solvent. This exposure would be similar to any other paint, sealant and adhesive solvent it is intended to replace. There may also be some minor dermal exposure from coatings splattering or careless mixing operations. Oral exposure

is rare and is limited to accidental ingestion.

Data from Kowa American indicates that dimethyl carbonate is primarily metabolized in the body by de-esterification or hydrolysis by carboxyl esterase enzymes to produce methanol and carbon dioxide. At this time, CARB and OEHHA have not conducted an assessment of the health effects of exposure to dimethyl carbonate, although both agencies have done extensive research on methanol toxicity as part of the methyl formate VOC exemption petition. The AQMD has initiated a request with OEHHA to evaluate any health concerns from the use of dimethyl carbonate.

No exposure guidelines have been established for dimethyl carbonate by OSHA, ACGIH, or NIOSH. However, Kowa American recommends an occupational exposure level of 200 ppm over an 8-hour TWA based on the exposure limit established by OSHA and ACGIH for methanol, which is the primary metabolite of dimethyl carbonate.

Based on information provided by Kowa American, dimethyl carbonate is reported to have low acute toxicity, low irritancy, and no mutagenicity. However, one teratology study conducted by Exxon in 1992 indicates maternal and developmental toxicity on mice at high (3000 ppm) inhalation exposure level. No observed effects were reported at 1,000 ppm exposure level. Such results are consistent with the teratology effect levels of methanol. There are no data available on the chronic effects/carcinogenicity of dimethyl carbonate.

Staff conducted an HRA for dimethyl carbonate using the Tier 1 screening level for methanol, which is the primary metabolite of dimethyl carbonate. Four different-sized solvent cleaning facilities with different amounts of solvent usage were screened to project future health risk analysis for solvent cleaning operations impacts from methanol.

In determining emissions to be used in the screening evaluation, staff assumed a one-to-one replacement ratio of methanol for the currently used solvents. The estimated emissions were then doubled based on the two-to-one stoichiometric ratio of dimethyl carbonate to methanol. Using the most conservative receptor distance (25 meters) for screening purposes, staff's health risk screening evaluation for methanol indicated that emissions from the solvent cleaning facilities did not exceed the non-carcinogenic (acute/chronic) emissions thresholds, and therefore, are not considered significant. The results are shown in Table 3.

Table 3 – Methanol Health Risk (commercial/industrial)

Facility	Solvent Usage (gal/yr)	Solvent Density (lb/gal)	TAC Wt Fraction	Emissions (lb/yr)	Table 1-A Screening Emissions (lb/yr) ^a	Emissions (lb/hr)	Table 1-A Screening Emissions (lb/hr) ^a	Adjusted Emissions for Dimethyl Carbonate (2X), lb/hr
Facility A	75	6.61	1	496	132,000	0.24	14	0.48
Facility B	420	6.61	1	2,775	132,000	1.33	14	2.66
Facility C	1274	6.61	1	8,418	132,000	4.05	14	8.10
Facility D	100	6.61	1	661	132,000	0.32	14	0.64

^a SCAQMD, Risk Assessment Procedures for Rules 1401 and 212, August 2000, Attachment G, Table 1A, 25 meters.

Emissions, lb/yr = Solvent Usage, gal/yr x Solvent Density, lb/gal x TAC Wt Fraction

Emissions, lb/hr = (Emissions, lb/yr)/(260 day/year)/(8 hour/day)

Staff used a similar health risk screening approach in evaluating dimethyl carbonate in an area source application as architectural coating and related cleanup solvent for the coating equipment. Potential dimethyl carbonate quantities used in paint (10%) as well as in cleanup solvent (100%) were screened for a single family dwelling to project future health risk impacts. The results are presented below in Table 4.

Table 4 – Methanol Health Risk (residential/architectural coatings)**Single Family Home DMC Usage from Paint**

Avg. Single Family Home Size (sq ft)	Conversion, (sq ft wall)/ (sq ft footprint)	Paint Usage (sq wall/ gal)	Paint Usage (gal/home)	Avg. DMC Content	DMC Usage from Paint, gal/home
1,800	2.7	180	27	0.1	2.7

URBEMIS2007 values for single family home size, conversion from area footprint to wall area and paint usage in gallons per wall area were used.

Total DMC Usage

DMC Usage from Paint (gal/home)	DMC Usage from Solvent (gal/home)	Total DMC Usage (gal/home)
2.7	5	7.7

Tier I - Health Risk Evaluation

Total DMC Usage (gal/home)	DMC to Methanol Conversion	Methanol Density, (lb/gal)	Methanol Usage (lb/day)	Methanol Usage (lb/hr)	Table 1-A Screening Methanol Emissions (lb/hr) ^a	Significant
7.7	2	6.61	102	12.7	14	No

^a SCAQMD, Risk Assessment Procedures for Rules 1401 and 212, August, 2000, Attachment G, Table 1A, 25 meters

Based on the health risk screening evaluation conducted for methanol, the estimated emissions per hour did not exceed the Tier 1 non-carcinogenic (acute/chronic) emissions thresholds, and, therefore, are not considered significant.

Table 5 below summarizes the physical and chemical properties of dimethyl carbonate, including the properties of five compounds that may be replaced with dimethyl carbonate. Health data including OSHA's Permissible Exposure Limits (PEL), OEHHA/ARB-approved acute and chronic exposure levels, and carcinogenicity are also summarized.

Table 5 – Physical and Chemical Properties for Dimethyl Carbonate and Currently Used Compounds

	Currently Used Compounds					Proposed Compound
	Acetone	Ethylene Glycol	Isopropanol	Methyl Acetate	Methyl Ethyl Ketone	Dimethyl Carbonate
Appearance	Colorless clear liquid	Colorless clear liquid	Clear colorless liquid	Colorless clear liquid	Colorless clear liquid	Clear colorless liquid
Odor	Ethereal	Odorless	Rubbing alcohol odor	Fragrance like	Sharp mint-like odor	Pleasant odor
Molecular Formula	C ₃ H ₆ O	HOCH ₂ CH ₂ OH	(CH ₃) ₂ CHOH	CH ₃ COOCH ₃	CH ₃ COCH ₂ CH ₃	(CH ₃) ₂ CO 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
Density	2 g/mL	2.14 g/mL	2.1 g/mL	2.8 g/mL	2.5 g/mL	1.07 g/mL
Boiling Point	56.2 °C	197.6 °C	82 °C	57 °C	80 °C	90 °C
Melting Point	-95.35 °C	-13 °C	-89 °C	-98.05 °C	-86 °C	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
Solubility in Water	Soluble	Soluble	Miscible in water	Soluble	Soluble	Soluble

Table 5 – Physical and Chemical Properties for Dimethyl Carbonate and Currently Used Compounds (continued)

	Currently Used Compounds					Proposed Compound
	Acetone	Ethylene Glycol	Isopropanol	Methyl Acetate	Methyl Ethyl Ketone	Dimethyl Carbonate
Solvent Solubility	Not available	Slightly soluble	Not available	Easily soluble in methanol, diethyl ether	Miscible with most organic solvents	Miscible with most organic solvents
NFPA ^A Flammability Rating	3	1	3	3	3	3
Lower Explosive Limit	2.5%	3.2%	2.0%	3.1%	1.4%	4.2%
Upper Explosive Limit	12.8%	36%	12.7%	16%	11.4%	12.9%
Flash Point	-20 °C	111 °C	12 °C	-10 °C	-9 °C	18 °C
OSHA PEL	1000 ppm	None	400 ppm	200 ppm	200 ppm	200 ppm ^B
Acute REL ^C	None	None	3,200 ug/m ³	None	13,000 ug/m ³	28,000 ^B ug/m ³
Chronic REL ^C	None	400 ug/m ³	7,000 ug/m ³	None	None	4,000 ^B ug/m ³
Carcinogenic	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

Propylene Carbonate

Propylene carbonate 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 has been used in adhesives, paint strippers, and as a solvent for aerial pesticide application. Propylene carbonate is also used in more than 1,300 individual cosmetic products such as mascara, lip gloss, foundation, sunscreen, lip liner, deodorant, anti-aging and concealers. Other known application of propylene carbonate includes special purpose lubricant, general purpose degreasers for industrial use, rubberized coatings, and non-flat aerosol paint products. Propylene carbonate may also be used as tail solvent because of its slow evaporation rate, and in certain solvent cleaning applications.

Huntsman Corporation submitted a petition to the U.S. EPA requesting VOC exempt status for propylene carbonate based on its low reactivity relative to ethane. More recent data from Dr. Carter's study indicates the reactivity values for propylene carbonate, as summarized in Table 6.

Table 6 – Comparison of MIR Values for Propylene Carbonate and Ethane

	Propylene Carbonate	Ethane
gram ozone/gram VOC	0.27	0.27
gram ozone/mole VOC	27.56	8.12
k_{OH} (cm ³ /molecule-sec)	6.9×10^{-13}	2.4×10^{-13}

From the above data, propylene carbonate has a higher k_{OH} value than ethane, meaning it initially reacts more quickly in the atmosphere than ethane. Further, a molecule of propylene carbonate is more reactive than ethane based on MIR value calculated as gram ozone/mole VOC. However, a gram of propylene carbonate is less reactive or creates less ozone than ethane. Propylene carbonate has a molecular weight that is over three times that of ethane; thus, it requires 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 value for propylene carbonate being equal to or less than that of ethane, the U.S. EPA concluded that propylene carbonate is negligibly reactive and has low potential to generate ozone in the troposphere. Effective February 20, 2009, the U.S. EPA delisted the compound from the definition of VOC. In addition, propylene carbonate qualifies as non-VOC under CARB's Consumer Products Regulation because of its low vapor pressure.

Propylene carbonate 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, propylene carbonate has low acute toxicity. However, prolonged contact with the skin as well as eye contact may cause irritation. No data is available on health effects caused by chronic exposure to the chemical. In addition, there is no established airborne occupational exposure limit for propylene carbonate. The AQMD has initiated a request with OEHHA to evaluate any health concerns from the use of propylene carbonate. However, based on its current uses in consumer products, propylene carbonate is not expected to generate significant adverse health effects due to exposure to sensitive populations.

Table 7 summarizes the physical and chemical properties of propylene carbonate, including five compounds that with propylene carbonate. Health data including OSHA's Permissible Exposure Limits (PEL), OEHHA/ARB-approved acute and chronic exposure levels, and carcinogenicity are also summarized.

**Table 7 – Physical and Chemical Properties for Propylene Carbonate
and Currently Used Compounds**

	Currently Used Compounds					Proposed Compound
	Acetone	Ethylene Glycol	Isopropanol	Methyl Acetate	Methyl Ethyl Ketone	Propylene Carbonate
Appearance	Colorless clear liquid	Colorless clear liquid	Clear colorless liquid	Colorless clear liquid	Colorless clear liquid	Colorless clear liquid
Odor	Ethereal	Odorless	Rubbing alcohol	Fragrance like	Sharp mint-like odor	Odorless
Molecular Formula	C ₃ H ₆ O	HOCH ₂ CH ₂ OH	(CH ₃) ₂ CHOH	CH ₃ COOCH ₃	CH ₃ COCH ₂ CH ₃	C ₄ H ₆ O ₃
Molecular Weight	58.08 g/mole	62.07 g/mole	60.09 g/mole	74.08 g/mole	72.11 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	1.25 g/mL
Boiling Point	56.2 °C	197.6 °C	82 °C	57 °C	80 °C	240 °C
Melting Point	-95.35 °C	-13 °C	-89 °C	-98.05 °C	-86 °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	0.03 mmHg (@ 20 °C)
Solubility in Water	Soluble	Soluble	Miscible in water	Soluble	Soluble	Soluble
Solvent Solubility	Not available	Slightly soluble	Not available	Easily soluble in methanol, diethyl ether	Miscible with most organic solvents	Not available
NFPA ^A Flammability Rating	3	1	3	3	3	1
Lower Explosive Limit	2.5%	3.2%	2.0%	3.1%	1.4%	1.21%
Upper Explosive Limit	12.8%	36%	12.7%	16%	11.4%	5.35%
Flash Point	-20 °C	111 °C	12 °C	-10 °C	-9 °C	132 °C
OSHA PEL	None	None	3,200 ug/m ³	None	13,000 ug/m ³	None
Acute REL ^B	None	400 ug/m ³	7,000 ug/m ³	None	None	None
Chronic REL ^B	No	No	No	No	No	No
Carcinogenic	No	No	No	No	No	No

^A National Fire Protection Agency

^B OEHHA/ARB Approved Risk Assessment Health Values

LEGISLATIVE AUTHORITY

The California Legislature created the South Coast Air Quality Management District (AQMD) in 1977 (The Lewis-Presley Air Quality Management Act, Health and Safety Code Section 40400 et seq.) as the agency responsible for developing and enforcing air pollution control rules and regulations in the South Coast Air Basin (Basin). By statute, the AQMD is required to adopt an Air Quality Management Plan (AQMP) demonstrating compliance with all state and federal ambient air quality standards for the Basin [California Health and Safety Code Section 40460(a)]. Furthermore, the AQMD must adopt rules and regulations that carry out the AQMP [California Health and Safety Code Section 40440(a)].

RULE PROPOSAL

Staff is proposing to amend Rule 102 by expanding the definition of Group I VOC-exempt compounds to include methyl formate, dimethyl carbonate, and propylene carbonate. Similar to other Group I exempt compounds in Rule 102, methyl formate is not toxic, not an ozone depleter or global warming compound. Propylene carbonate is not a hazardous air pollutant or an ozone depleting compound, and is already a VOC-exempt compound under CARB's Consumer Products Regulation based on its low vapor pressure. In addition, dimethyl carbonate is neither a toxic nor an ozone depleting substance, and is suited for inclusion under Group I exempt compounds.

EMISSIONS INVENTORY AND REDUCTIONS

Based on 2006/2007 AER data and industry input, replacement of hydrocarbon blowing agents used in foam manufacturing with a VOC-exempt methyl formate would potentially reduce VOC emissions by approximately 238 tons per year or about 0.65 ton/day. In addition, the use of methyl formate as substitute for global warming VOC-exempt compounds, such as HCFC-22 and HFC-152a, would potentially reduce greenhouse gas emissions by 171 tons per year (0.47 ton/day).

The emissions impact in the South Coast Air Basin of exempting dimethyl carbonate and propylene carbonate is difficult to quantify at this time. Although manufacturers have expressed interest in both compounds as potential replacement in coatings and other product formulation, a high degree of uncertainty exists for the potential penetration of the use of dimethyl carbonate and propylene carbonate; therefore, additional VOC emission reductions are not included.

COST AND SOCIOECONOMIC IMPACTS

There is no additional cost to users of the three compounds proposed for exemption since use of these compounds is strictly voluntary. However, PAR 102 allows flexibility by providing with additional options in meeting AQMD's strict VOC requirements. Furthermore, PAR 102 would lower emission fees for facilities and manufacturers opting to use any of these proposed exempt compounds.

In conclusion, PAR 102 would result in savings to the affected facilities, and therefore, would not have any adverse socioeconomic impacts.

CALIFORNIA ENVIRONMENTAL QUALITY ACT (CEQA)

The AQMD, as lead agency, has prepared a Draft Environmental Assessment (EA) for Proposed Amended Rule 102 – Definition of Terms, pursuant to CEQA Guidelines §15070, §15071, and §15252. The Draft EA finds that there will be no significant adverse environmental impacts from implementing the proposed project. Pursuant to CEQA Guidelines §15073, the Draft EA was circulated for a 30-day public review period, which began on July 28, 2009, and closes on August 26, 2009. After the close of the public review period, all comments received will be addressed and responses will be included in the Final EA.

COMPARATIVE ANALYSIS

The proposed amendment to Rule 102 does not impose emission control requirements on any equipment or source and, therefore, the analysis required by the California Health and Safety Code §40727.2 cannot be performed.

DRAFT FINDINGS UNDER THE CALIFORNIA HEALTH AND SAFETY CODE

Before adopting, amending, or repealing a rule, the California Health and Safety Code requires the AQMD to adopt written findings of necessity, authority, clarity, consistency, non-duplication, and reference, as defined in Section 40727. The findings are as follows:

Necessity - The AQMD Governing Board has determined that a need exists to amend Rule 102 - Definition of Terms to incorporate new compounds delisted by U.S. EPA from the federal VOC definition.

Authority - The AQMD Governing Board obtains its authority to adopt, amend, or repeal rules and regulations from the California Health and Safety Code sections 39002, 40000, 40001, 40440, 40441, 40702, 41508, and 41700.

Clarity - The AQMD Governing Board has determined that the proposed amendment to Rule 102 - Definition of Terms is written or displayed so that its meaning can be easily understood by persons directly affected by it.

Consistency - The AQMD Governing Board has determined that Proposed Amended Rule 102 - Definition of Terms is in harmony with, and not in conflict with or contradictory to, existing federal or state statutes, court decisions, or regulations.

Non-Duplication - The AQMD Governing Board has determined that the proposed amendment to Rule 102 - Definition of Terms does not impose the same requirement as any existing state or federal regulation, and the proposed amended rule is necessary and proper to execute the powers and duties granted to, and imposed upon, the AQMD.

Reference - In adopting this regulation, the AQMD Governing Board references the following statutes which the AQMD hereby implements, interprets or makes specific: Health and Safety Code sections 40001, 40440, and 40702

PUBLIC COMMENTS AND RESPONSES

This section summarizes the comments received as a result of the Public Workshop conducted on July 9, 2009.

COMMENT: A study on dimethyl carbonate indicates that the chemical compound causes developmental toxicity in mice exposed by inhalation. The AQMD should delay the exemption for dimethyl carbonate until OEHHA performs toxicity evaluation of the compound.

RESPONSE: AQMD staff is aware of one teratology study that indicates certain developmental effects on mice exposed by inhalation to very high concentration (3,000 ppm) of dimethyl carbonate during gestation. In addition, the study found no effects for developmental toxicity at 1,000 ppm or below exposure levels. Given the manufacturer's recommended exposure level of 200 ppm and established exposure controls and personnel protection, staff believes that workers and the general public would not be subjected to undue risk at the expected level of exposure to dimethyl carbonate.

In order to further evaluate potential health impacts, AQMD staff conducted a health risk assessment for dimethyl carbonate using screening level for methanol, which is the primary metabolite of dimethyl carbonate. This methodology is similar to OEHHA's approach during its evaluation of the health effects from exposure to tertiary butyl acetate. Based on this assessment, AQMD staff has concluded that there are no significant adverse impacts associated with exempting dimethyl carbonate as a VOC. Therefore, staff, under the most conservative scenarios, modeled the risks based on Methanol's Acute and Chronic risk factors and found no concerns from uses at small and larger facilities, as well as area source uses.

COMMENT: AQMD staff needs to re-evaluate tertiary butyl acetate (TBAC) for inclusion in the list of VOC exempt compounds in Rule 102. New toxicological data is available on TBAC that will address health concerns previously raised by OEHHA.

RESPONSE: Staff has previously analyzed the risks from TBAC's primary metabolite, Tertiary Butanol, and determined that the risks may exceed threshold levels. Therefore, the AQMD has carefully carved out exemptions only in areas where the use of personal protective equipment is widespread, such as automotive refinishing and industrial maintenance coatings. Based on recent feedback from OEHHA staff, they still have concerns with the increased use of TBAC. Therefore, staff is not ready to propose TBAC for an exemption at this point. However, staff has committed to meet with CARB, OEHHA, and the manufacturer to continue discussions on the latest health studies presented by the manufacturer,

and plans to follow OEHHA's guidance in the future and propose another amendment to Rule 102, if necessary.

COMMENT: We support the proposed amendment to Rule 102. The proposed exemption may provide more options for industry in meeting AQMD's VOC requirements.

RESPONSE: Staff acknowledges the comment in support of the proposed amendment.