

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

**Preliminary 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 physical and chemical properties of methyl formate are summarized in the following table.

Table 1 – Physical and Chemical Properties of Methyl Formate

Description	Colorless liquid; pleasant odor
Molecular Formula	$HCOOCH_3$
Molecular Weight	60.05 g/mol
Density	0.98 g/mL
Boiling Point	32 °C (89.7 °F)
Melting Point	-100 °C
Vapor Pressure	585.7 mmHg @ 25 °C
Solubility in Water	Soluble
Solvent Solubility	Miscible with most organic solvents
Flash Point	-19 °C (-2.2 °F)

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.

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. The table below summarizes the physical and chemical properties of dimethyl carbonate.

Table 2 – Physical and Chemical Properties of Dimethyl Carbonate

Appearance	Clear colorless liquid
Odor	Pleasant odor
Molecular Formula	$(\text{CH}_3)_2\text{CO}_3$
Molecular Weight	90.08 g/mol
Density	1.07 g/mL
Boiling Point	90 °C (194 °F) @ 760 mmHg

Vapor Pressure	55 mmHg @ 25 °C
Solubility in Water	13.9 g/100 g water
Solvent Solubility	Miscible with most organic solvents
Flash Point	18°C (64.4 °F)

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 3 below.

Table 3 – 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. Teratology study indicates effects 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.

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. A summary of the compound's physical and chemical properties is shown in the following table.

Table 4 – Physical and Chemical Properties of Propylene Carbonate

Appearance	Colorless liquid
Odor	Odorless
Molecular Formula	C ₄ H ₆ O ₃
Molecular Weight	102.09 g/mol
Density	1.25 g/mL
Boiling Point	240 °C (464 °F)
Vapor Pressure	0.03 mmHg @ 20 °C
Flash Point	132 °C (269.6 °F)

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 5.

Table 5 – 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 x 10 ⁻¹³	2.4 x 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.

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

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 gases 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 unknown. Because of its cost and other properties, dimethyl carbonate is expected to remain very much as a niche solvent. For propylene carbonate, it will be difficult to quantify its potential use on coatings formulations or on other likely applications mentioned in the previous section.

COST

There is no additional cost to industry as a result of the proposed amendment to Rule 102.

CALIFORNIA ENVIRONMENTAL QUALITY ACT (CEQA)

Staff is evaluating the proposed project, and pursuant to CEQA and AQMD Rule 110, appropriate CEQA documentation will be prepared for PAR 102.