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July 29, 2004

By Electronic Mail and U.S. Postal Service

Mr. William Johnson
Office of Air Quality Planning and Standards
Mail Drop C539-02
U.S. Environmental Protection Agency
109 TW Alexander Drive
Research Triangle Park, NC 27711

Dear Mr. Johnson:

Kowa American Corp. (Kowa or the Company) requests the U.S. Environmental Protection Agency (EPA or the Agency) to exempt the chemical, dimethyl carbonate (DMC) [CAS RN 616-38-6], from the Agency's definition of the term, *volatile organic compound* (VOC). This exemption would allow DMC to be used in the U.S. without regulation as a potential precursor to tropospheric ozone under the requirements at 40 CFR 51.100(s).

Our request for VOC exempt status on DMC is based on its exceptionally low potential to generate ozone in the troposphere. Its maximum incremental reactivity (MIR) value, estimated at 0.06, is perhaps one of the lowest measured MIR values of any liquid chemical in commercial production. We enclose here a study by Dr. William Carter, *Investigation of the Atmospheric Ozone Formation Potential of Selected Carbonates:*

Final Report to Exxon Mobil Chemical Company.[1] Dr. Carter is recognized as one the most respected and well known ozone-formation researchers in the world.

Dr. Carter's work was sponsored by ExxonMobil Corp. which has placed this study in the public domain. Dr. Carter's research used *state of the art* environmental chamber experiments and computer model calculations to determine that the ozone formation potential of DMC is well below the reactivity of the benchmark compound, ethane. As the Agency is aware, ethane is used for VOC exemption determinations on both gram and molar bases. The specific MIR values reported by Dr. Carter show that DMC is 20% and 60% lower than ethane on gram and mole bases, respectively.

	DMC	**Ethane**
grams ozone / grams VOC	0.06	0.31
Grams ozone / moles VOC	5.4	9.3

In his paper Dr. Carter concludes the following:[2]

> Based on the mechanism developed for this work, the ozone impact for dimethyl carbonate was calculated to be very low. It was calculated to be no more than ~4% of the ozone as an equal mass of the mixture representing VOC emissions from all sources, and no more than about 30% that of an equal mass of ethane. Its ozone impact was lower than that of ethane even when computed on a molar basis. Therefore, if ethane is used as the standard for defining negligible reactivity for VOC exemption purposes, then this compound could appropriately be exempted on this basis.

Separately, we also enclose the study, *Potential Ozone Creation Potentials (POCP) for Oxygenated Volatile Organic Compounds*.[3] This paper discusses a kinetic mechanism for the ozone creation potential of DMC. The author states that "highly oxygenated VOCs tend to be inefficient ozone producers…This is particularly the case for dimethyl

[1] Carter, W.P.L., et al., November 17, 2000. *Investigation of the Atmospheric Ozone Formation Potential of Selected Carbonates: Final Report to ExxonMobil Chemical Company*.
[2] Id. at p. 42.
[3] Jenkin, M., Hayman, G., 1998. *Photochemical Ozone Creation Potentials for Oxygenated Volatile Organic Compounds: Sensitivity to Variations in Kinetic and Mechanistic Parameters*. Atmospheric Environment, 33, 1275-1293.

carbonate, which has the lowest POCP of all oxygenated VOCs."[4] The author attributes this very low POCP to two things. First, there are a limited number of oxidation steps required to form CO_2. And second, the main oxidative intermediates, such as diformylcarbonate, are very unreactive toward ozone formation. On this latter point, he specifically states that DMC's "intermediate oxidation products…are also very unreactive, thereby further inhibiting ozone formation."[5]

Because of DMC's negligible photochemical reactivity, the compound does not meet EPA's definition of a VOC either on a gram or mole basis. As a result, DMC should be made immediately available to industry in the U.S. as a VOC exempt compound to help companies meet the ever increasing regulation under federal and state VOC control plans. Kowa further notes that DMC is not identified as a hazardous air pollutant (HAP) or ozone depleting substance.

The Company understands that EPA also takes into account factors beyond a chemical's photoreactivity. Specifically, the Agency is also interested in a chemical's toxicity, worker safety, and environmental fate when evaluating exemption petitions. DMC's profile in these endpoints is highly favorable and represents an environmentally friendly compound. An internet search on DMC reveals a large number of articles and patent references that describe the substance as a *green chemical* with very favorable safety health, and environmental properties.[6, 7] These references characterize DMC as a highly desirable replacement for a number of chemicals including dimethyl sulphate, methyl chloride, MEK, MIBK, n-butanol, xylene.[8, 9]

Dimethyl carbonate can be made by a number of synthesis routes. Historically, the substance was made primarily via the phosgene process. This older technology has given way to more advanced and environmentally favorable technologies that use methanol and carbon dioxide or carbon monoxide.[10]

We enclose our material safety data sheet (MSDS) on DMC which shows that the compound has a favorable toxicity profile.[11] See MSDS at Sections 11 and 12. DMC has

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[4] Id. at p. 1284.
[5] Id. at p. 1288.
[6] Rivetti, F., Tundo, P.T. (Ed.s), 2000. Green Chemistry: Challenging Perspectives. Oxford University Press., 201-219.
[7] Tundo, P.T., Selva, M., 2002. *The Chemistry of Dimethyl Carbonate*. Acc. Chem. Res., 35, 706-716.
[8] Rivetti, F., 2000. *The Role of Dimethyl Carbonate in Replacement of Hazardous Chemicals*. Comptes Rendus de L'Academie des Sciences, Serie IIc: Chimie, 3(6), 497-503.
[9] World Intellectual Property Organization patent assigned to Exxon Chemical Patents, Inc. *Environmentally Preferred Solvents and Fluid Blends with Low Reactivity for Ozone Formation*. International Publication No. WO/99/57217. Note: Kowa includes this patent for technical reference. Any potential users of DMC must determine if their use of the compound infringes on any patents or other intellectual property.
[10] *Developments in Dimethyl Carbonate Production Technologies*. Chemsystems Report, http://www.chemsystems.com/newsletters/perp/May200099s6abs.cfm.
[11] Kowa American Corp., Dimethyl Carbonate Material Safety Data Sheet, June 8, 2004.

very low acute toxicity when tested via oral, dermal, inhalation routes of exposure. In addition, the compound was not found to be irritating to the skin and only slightly irritating to the eyes. DMC was also found to be non-mutagenic in *in vitro* testing. DMC was also evaluated in one inhalation teratology study in mice at doses of 0, 300, 1,000, or 3,000 ppm during gestation. Developmental effects were noted only at the very high dose level of 3,000 ppm; however, no effects were noted at 1,000 ppm or the two lowest doses.[12]

Workers generally respond favorably to DMC since the compound is only a non-irritating or slightly irritating chemical. In addition, the compound does not have an objectionable odor to workers or neighbors. Environmental fate data show DMC to be readily biodegradable, have a low potential to bioaccumulate, and have low toxicity to fish, daphnia, or bacteria. (Environmental modeling suggests that that the material may possibly be harmful to algae.)

Recent work by Katrib et al. evaluated the degree to which DMC is deposited back to earth. The author's study shows that DMC's loss process in the atmosphere is by photolysis during which the compound's wet deposition back to Earth is negligible.[13]

DMC is flammable with a flashpoint of 63 ºF (16 ºC). However, even with this flashpoint, DMC still represents a safer alternative to two existing VOC exempt solvents widely used in the U.S., acetone and methyl acetate, both with flashpoints of 15 ºF.

We believe customers would prefer and, therefore, adopt DMC immediately as a replacement for acetone and possibly methyl acetate. Such a change would result in slightly less flammable products. More importantly, the use of DMC would reduce ambient ozone air pollution since the compound has one-seventh and one-fifth the ozone reactivity of acetone on gram and molar bases, respectively. Another advantage of DMC is that the compound is partially water soluble. As such, the material can be used in water borne paints and adhesives as an alternative to many HAPs including those listed under the glycol ethers category.

We ask EPA to consider this exemption request on an expedited basis. We believe the very low reactivity values and very favorable toxicity and environmental fate profiles of DMC would greatly enhance industrial companies' ability to comply with VOC restrictions present in federal and state pollution prevention plans. We particularly note that the current program to expand VOC restrictions in the northeast states in January 2005 warrants the swift action by EPA.

Kowa proposes that after the Agency's preliminary review of this application, EPA immediately issue a proposed rule in the Federal Register. There are numerous

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[12] Bevan, C, Beyer, B., 1995. *Developmental Toxicity Evaluation of Dimethylcarbonate by Inhalation in CD-1 Mice*. International Toxicologist, 7(1): AB# 74-P-2.

[13] Katrib, Y. et al., 2002. *Atmospheric Loss Processes of Dimethyl and Diethyl Carbonate*. Journal of Atmospheric Chemistry, 43:151-174.

organizations that are reviewing requests for VOC exemptions, and we believe that these groups are in a position to identify any issues of concern regarding DMC. The merits of exempting DMC as a VOC would be well received by U.S. industry, environmental groups, and both federal and state air pollution regulators.

For all questions and comments regarding this request, please contact Mr. Mark Smith of Kowa at (212) 303-7800. Thank you for your assistance in this matter.

Sincerely,

Mark K. Smith
Sales Manager

cc: D. Sanders, EPA
R. Stallings, EPA

Enclosures:

- *Investigation of the Atmospheric Ozone Formation Potential of Selected Carbonates: Final Report to ExxonMobil Chemical Company* (Carter, et al.)
- *Photochemical Ozone Creation Potentials for Oxygenated Volatile Organic Compounds: Sensitivity to Variations in Kinetic and Mechanistic Parameters* (Jenkin and Hayman)
- *Atmospheric Loss Processes of Dimethyl and Diethyl Carbonate* (Katrib, et al.), pp. 151-152
- *The Chemistry of Dimethyl Carbonate* (Tundo and Selva)
- *The Role of Dimethyl Carbonate in Replacement of Hazardous Chemicals* (Riveti)
- *Developments in Dimethyl Carbonate Production Technologies* (Chemsystems), abstract only
- Dimethyl Carbonate Material Safety Data Sheet (Kowa American Corp.)