Dr. Souad A. Benromdhane

Health and Environmental Impacts Division
Risks and Benefits Group
HEID, OAQPS, U.S. EPA
Mail Drop C539-07
U. S. Environmental Protection Agency
109 TW Alexander Drive
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Dear Dr. Benromdhane,

The Chemours Company requests the U.S. Environmental Protection Agency (EPA or Agency) to exempt the Methyl-Perfluoroheptene-ethers (MPHE), from the Agency's definition of the term, *volatile organic compound* (VOC). This exemption would allow MPHE to be used in the U.S. without regulation as a potential precursor to tropospheric ozone under the requirements in 40 CFR 51.100(s). MPHE has very low potential to generate ozone in the troposphere. Its maximum incremental reactivity (MIR) value is estimated at 0.022 which is 92% lower than the MIR of ethane.

Attached please find, the petition and a summary of data from the peer-reviewed scientific literature on the atmospheric reactivity of MPHE and the propensity of this molecule to contribute to tropospheric ozone formation. MPHE was developed to replace metals and electronics precision cleaning solvents or aerosols, heat transfer fluids and carrier fluids with higher global warming potential or GWP (>700 GWP). MPHE has zero direct ozone depletion potential (ODP) and a GWP of 2.5 on a 100 year time horizon (Jubb et al). A toxicological assessment indicating low acute toxicity of MPHE is attached. Chemours has established an internal occupational exposure limit (AEL - Acceptable Exposure Limit) of 500 ppm (8- and 12- hour TWA) for this substance which is similar to currently commercial precision cleaning solvents with Occupational Exposure Limits ranging from 100 ppm to 1000 ppm.

The Premanufacture Notice (PMN # P-12-0425) and a SNAP applications have been approved under the Significant New Alternatives Policy program (see Docket EPA-HQ-OAR-2003-0118).

Please contact me if you have any questions about this request or need further clarification.

Sincerely,

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Via Federal Express with attachments

PETITION TO EXEMPT

METHYL-PERFLUOROHEPTENE-ETHERS (MPHE)

FROM EPA REGULATION AS A VOLATILE ORGANIC COMPOUND (VOC)

Report prepared for U. S. Environmental Protection Agency by

The Chemours Chemical Company

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Summary

The Chemours Chemical Company submits this petition requesting that EPA modify the definition of volatile organic compound (VOC) found at 40 CFR 51.100 (s) to exempt methyl-perfluoroheptene-ethers (MPHE) from regulation as a VOC. This exemption would allow MPHE to be used in the U.S. without regulation as a potential precursor to tropospheric ozone under the requirements in 40 CFR 51.100(s). MPHE has very low potential to generate ozone in the troposphere.

MPHE is a hydrofluoro-olefin (HFO) based fluorinated fluid with a low Global Warming Potential (GWP) that extends Chemours existing Vertrel® specialty solvent product line. HFOs are the next generation solvent molecules that exhibit an application profile similar to HFCs, but with a significantly lower GWP. MPHE Pre-Manufacture Notice (PMN # P-12-0425) and SNAP applications have been approved by the EPA, see Docket EPA-HQ-OAR-2003-0118 at www.regulations.gov.

We present data from peer-reviewed scientific literature on the atmospheric reactivity of methyl-perfluoroheptene-ethers (MPHE) isomers and the propensity of this mixture to contribute to tropospheric ozone formation. We show that MPHE is expected to have an ozone impact significantly less than that of ethane on a mass basis and, in keeping with previous rulings, should be exempt from regulation as a VOC ozone precursor.

Chemours Company kindly requests expedited consideration and ruling on this petition. The specialty solvent market place and customers urgently need access to low GWP substitute options to replace high ODP and GWP solvents being phased out by regulations. MPHE was developed to replace HFCs & PFCs with higher GWP (>700 GWP). MPHE has zero direct ozone depletion potential (ODP) and a GWP of 2.5, a 100 year time horizon (Jubb et al).

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Attachments

1. Introduction

Tropospheric ozone is formed in the reactions of volatile organic compounds (VOCs) and oxides of nitrogen in sunlight. A multitude of man-made and natural VOCs are currently emitted into the atmosphere, each reacting at different rates and via different reaction pathways. The contribution to ozone formation of a given quantity of any VOC is primarily determined by its atmospheric reactivity. U.S. EPA has issued exemptions for VOCs with ozone impacts expected to be less than those associated with ethane [1, 2].

Chemours is planning to produce a mixture of reactive, partially fluorinated methyl heptene ethers (MPHE, comprising a mixture of ethers each having the structural formula ($CH_3OC_7F_{13}$). The manufacture and use of MPHE will result in new atmospheric emissions and such use would normally be subject to VOC regulations aimed at reducing ozone formation. The regulatory status of MPHE is summarized in attachment 1. We will show that each molecular component of the MPHE mixture is likely to have an ozone impact significantly less than that of ethane on a mass basis and, in keeping with previous rulings, MPHE should be exempt from regulation as a VOC ozone precursor.

2. What is MPHE?

MPHE is a mixture of structural and stereo isomers with the formula $C_7F_{13}OCH_3$, and consist of methyl ethers attached to perfluoronated heptenes. The isomers vary by the olefin (double bond) being either on the 2 or 3 position and the methyl ether being on the 2, 3, 4 or 5 position

3. Basis for MPHE VOC exemption

a. Atmospheric Chemistry of MPHE (Attachment 5)

The atmospheric chemistry of MPHE was examined in experiments performed by Jubb *et al.* [3]. **The atmospheric fate of MPHE is dominated by reaction with tropospheric OH radicals, and the rate coefficients for the reaction of the components of MPHE with OH lie in the range of *k* (296K) = ~0.1 to 2.9 × 10^{-13} cm^3 molecule^{-1} s^{-1} with corresponding atmospheric lifetimes due to loss by reaction with OH in the range of 4 to 111 days**. For comparison, the rate coefficient for the reaction of ethane with OH is about 2.4 x 10^{-13} cm^3 molecule^{-1} s^{-1}.

b. Ozone Impact of MPHE: Maximum Incremental Reactivity (Attachment 5 & 6)

Reactivity-based VOC regulations require means to quantify ozone impacts for VOCs. The most common approach is to use the “incremental reactivity” of the VOC, which is defined as the change in ozone caused by adding a small amount of the VOC to the emissions in an ozone pollution episode, divided by the amount of VOC added. Incremental reactivities depend on both the chemical properties of the VOC being studied, as well as the specifics of the ozone episode studied. Urban air-sheds vary considerable from one region to another and the incremental reactivities likewise vary considerably in different cities. For regulatory purposes, a useful reactivity scale will summarize this variability on a simple quantity. The most widely used scale is the Maximum Incremental Reactivity (MIR) scale of carter [4], attachment 4a.

A full MIR analysis of MPHE has been performed [5] and the reactivity in the MIR scale was found to be 0.022 grams per gram VOC, which is about 8% of that calculated for ethane (0.28 grams per gram VOC).

c. Ozone Impact of MPHE: Photochemical Ozone Creation Potential

Reactivity-based VOC regulations require means to quantify ozone impacts for VOCs. The Photochemical Ozone Creation Potential (POCP) is a well-tested scale for assessing the ozone production associated with releases of a given VOC. We have estimated the POCP for the components of MPHE using the methods given by Derwent and Jenkin [5] and Jenkin [7].

The POCP method described by Derwent *et al.* [8] uses a photochemical air quality model to calculate the total additional ozone formed over about five days after a given release of a volatile organic compound (attachment 4b). The POCP scale is relative to the POCP for ethene which is defined as 100. These are quite challenging calculations and it is fortunate that Derwent *et al.* [6] and Jenkin [7] have developed a simplified procedure which uses fundamental molecular properties to provide estimated POCPs *via* the expression:

$$\varepsilon^{POCP} = \alpha_1 \gamma_S \gamma_R^{\beta} (1 - \alpha_2 n_C)$$

In this expression, ε^{POCP} is the estimated POCP and α_1, α_2, and β are constants. The term η_C is the number of carbon atoms, γ_S is a structure based ozone formation index given by

$$\gamma_S = \frac{28 n_B}{6M}$$

where n_B and M are the total number of C=C and C-H bonds and the molecular weight of the VOC molecule respectively. γ_R is a reactivity based ozone formation index given by

$$\gamma_R = \frac{6 k_{OH}}{n_B k_{OH}^{ethene}}$$

where k_{OH} is the rate coefficient for reaction of the VOC with OH radicals at 298 K and 760 Torr of air, and k_{OH}^{ethene} is the rate coefficient for reaction of ethene with OH radicals at 298 K and 760 Torr of air (k_{OH}^{ethene} = 8.64×10^{-12} cm^3 $molecule^{-1}$ s^{-1}). Jenkin [7] showed this approach can be used to estimate excellent POCPs for compounds spanning a wide range of reactivity.

Using this approach with the rate constants *k* (296K) obtained by Jubb *et al.* [3], one obtains POCP values for the individual components of the MPHE mixture that lie in the range of 0.9 to 4.8. For comparison Derwent *et al.* [6] found the POCP for ethane to be 12.3. Thus the estimated POCP values for the components of MPHE are approximately fourteen to three times smaller than that of ethane, and the ozone impact of the mixture MPHE is expected to be significantly less than that of ethane.

4. Toxicology and Environmental Fate (Attachment 2)

MPHE does not exhibit dermal sensitization, ocular irritation and genotoxicity. It also has low acute oral, inhalation and dermal toxicity potential with an internal occupational acceptable exposure limit of 500 ppm (8 – and 12-hour TWA). MPHE has low solubility in water and is inherently biodegradable therefore exhibits low acute and chronic aquatic toxicity, low terrestrial and microbial toxicity. See attachment 2 for MPHE detailed toxicology and environmental fate assessments.

5. Justification for expedited petition ruling

Regulations are phasing out products with Ozone Depletion Potentials (ODP) and high Global Warming Potentials (GWP). MPHE is an HFO based fluid with low GWP and Zero ODP which represents the next generation alternative technology. MPHE can be used to replace high GWP and high ODP industrial solvents. If the VOC exemption under the Federal Clean Air Act is granted, MPHE will be an effective substitute in the development of environmentally sustainable solutions that reduce ozone formation. MPHE has as excellent toxicity profile and is not classified as a hazardous substance or mixture according to the Occupational Safety and Health Administration (OSHA) Hazard Communications Standard 2012. The MPHE VOC exemption will help the precision cleaning, carrier fluids, thermal management and aerosol industries meet their sustainability goals since the use of MPHE as a low GWP and Zero ODP can significantly reduce their greenhouse gas emissions. Manufactures and customers are waiting for this VOC exemption ruling to introduce MPHE based products (already adopted in other global regions) to the North American market.

6. Use of MPHE

MPHE is used mainly for thermal management in heat transfer and is expected to be a 1 to 1 replacement of ODS substances. In the metal and electronics precision cleaning application, about 4% to 100% of MPHE blended with other chemicals is used to remove either highly fluorinated oils, hydrocarbon-based oils, grease, fluxes and non-volatile residues from industrial surfaces and parts. For aerosol applications, MPHE is expected to replace ODS substances at a ratio of 0.25 to 1 in non-flammable energized electrical contact cleaners for flux removal. In carrier fluid applications such as adhesives and coatings, MPHE is also expected to replace ODS substances in a ratio of 0.25 to 1. These applications rely on MPHE characteristics such as thermal properties, non-flammable, low environmental impact, dielectric properties, surface tension, vapor pressure, viscosity and low toxicity profile.

7. Conclusion

Based on the atmospheric chemistry and the ozone impact presented in this petition, Chemours respectively requests that EPA grant MPHE a VOC exemption.

8. References

1. **Dimitriades, B., *Scientific basis of an improved EPA policy on control of organic emissions for ambient ozone reduction.* Journal of the Air and Waste Management Association, 1999. 49(7): p. 831-838.**
2. **EPA, *Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans*, E.P. Agency, Editor 2005: Federal Register. p. 54046-54051.**
3. **Jubb, A.M., et al., *Methyl-Perfluoroheptene-Ethers (CH3OC7F13): Measured OH Radical Reaction Rate Coefficients for Several Isomers and Enantiomers and Their Atmospheric Lifetimes and Global Warming Potentials.* Environmental Science & Technology, 2014. 48(9): p. 4954-4962.**
4. **Carter, W.P.L., *Development of Ozone Reactivity Scales for Volatile Organic Compounds*. Journal of the Air & Waste Management Association, 1994. 44(7):p881-889.**
5. **Carter, W.P.L., *Estimation of the Ground -Level Atmospheric Ozone Formation Potential of Methyl Perfluoro Heptene Ethers Mixtures*, 2011: Riverside, California**
6. **Derwent, R.G., et al., *Photochemical ozone creation potentials for organic compounds in northwest Europe calculated with a master chemical mechanism.* Atmospheric Environment, 1998. 32(14–15): p. 2429-2441.**
7. **Jenkin, M.E., *Photochemical Ozone and PAN Creation Potentials: Rationalisation and Methods of Estimation* 1998, AEA Technology plc Culham, UK.**
8. **Derwent, R.G., M.E. Jenkin, and S.M. Saunders, *Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions.* Atmospheric Environment, 1996. 30(2): p. 181-199.**