

U.S. ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 51

[FRL-5082-2]

Air Quality: Revision to Definition  
of Volatile Organic Compounds - Exclusion of Volatile  
Methyl Siloxanes and Parachlorobenzotrifluoride

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This action revises EPA's definition of volatile organic compounds (VOC) for purposes of preparing State implementation plans (SIP's) to attain the national ambient air quality standards (NAAQS) for ozone under title I of the Clean Air Act (Act) and for the Federal implementation plan (FIP) for the Chicago ozone nonattainment area. This revision adds parachlorobenzotrifluoride (PCBTF) and volatile methyl siloxanes (VMS) to the list of compounds excluded from the definition of VOC on the basis that these compounds have negligible contribution to tropospheric ozone formation.

EFFECTIVE DATES: The EPA is publishing this action without prior proposal because the Agency views this as a noncontroversial amendment and anticipates no adverse comments. However, in a separate document in this Federal Register publication, the EPA is proposing to

approve the definition revision should adverse or critical comments be filed or a request for a public hearing be made. Thus today's final action will be effective on [insert date 60 days after publication in the Federal Register] unless notice is received by [insert date 30 days after publication in the Federal Register] that someone wishes to submit adverse or critical comments or request a public hearing. If the effective date is delayed for this action due to the need to provide for public comment, timely notice will be published in the Federal Register.

ADDRESSES: Comments should be submitted in duplicate (if possible) to: Air and Radiation Docket and Information Center (6102), Attention: Docket No. A-93-47, U.S. Environmental Protection Agency, 401 M Street, SW, Washington, DC 20460. Comments should be strictly limited to the subject matter of this rule, the scope of which is discussed below.

PUBLIC HEARING: If anyone contacts EPA requesting a public hearing, it will be held at Research Triangle Park, North Carolina. Persons wishing to request a public hearing, wanting to attend the hearing or wishing to present oral testimony should notify Mr. William

Johnson, Air Quality Management Division (MD-15), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone (919) 541-5245. The EPA will publish notice of a hearing, if a hearing is requested, in the Federal Register. Any hearing will be strictly limited to the subject matter of the rule, the scope of which is discussed below.

This action is subject to the procedural requirements of section 307(d)(1)(B), (J), and (U) of the Act, and 42 U.S.C. 7607(d)(1)(B), (J), and (U).

Therefore, EPA has established a public docket for this action, A-93-47, which is available for public inspection and copying between 8 a.m. and 4 p.m., Monday through Friday, at EPA's Air and Radiation Docket and Information Center, Room M-1500, 401 M Street, SW, Washington, DC 20460. A reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: William Johnson, Office of Air Quality Planning and Standards, Air Quality Management Division (MD-15), Research Triangle Park, NC 27711, phone (919) 541-5245.

SUPPLEMENTARY INFORMATION:

I. Background

On September 28, 1992, the Occidental Chemical

Corporation (also known as OxyChem) petitioned EPA to take all necessary and appropriate action to exclude parachlorobenzotrifluoride (also known as 4-chlorobenzotrifluoride, PCBTF,  $C_7H_4F_3Cl$  (CAS number 98-56-6)) from regulation as a precursor to tropospheric ozone. In support of their petition, Occidental Chemical Company submitted two reports: "Loss Processes for 4-Chlorobenzotrifluoride Under Atmospheric Conditions," by Roger Atkinson, Sara M. Aschmann, Arthur M. Winer and James N. Pitts, Jr., University of California at Riverside, October 1984; and "Tropospheric Lifetime Estimates for Several Aromatic Compounds," by David Nelson and Robert Brown, Aerodyne Research, Inc., May 1992. In addition, Occidental Chemical Company submitted a copy of an October 18, 1985 Federal Register notice (50 FR 42216) which announced a decision by EPA not to require further testing of parachlorobenzotrifluoride for health effects, environmental effects, and chemical fate under the Toxic Substances Control Act.

On December 11, 1992, Dow Corning Corporation petitioned EPA to take several actions that would have the effect of exempting VMS under the Act as precursors

to tropospheric ozone. The VMS are organic compounds whose basic molecular structure is built on a backbone of alternating silicon and oxygen atoms, formed into either a ring or linear chain containing from two to seven silicon atoms. Methyl groups (and no other functional groups, as defined here) are attached to this central backbone, their numbers varying with the size and shape of the molecule. Compounds covered by the designation VMS in this proposal are cyclic, branched, or linear, completely methylated siloxanes, including the compounds listed in Table 1. Symbols shown in the table, such as MM and D<sub>4</sub>, are commonly accepted abbreviations for the longer chemical name shown beside each.

Table 1

## Volatile Methyl Siloxanes

Linear VMS

CAS Number	Chemical Name	Formula
107-45-0	Hexamethyldisiloxane (MM)	$C_6H_{18}OSi_2$
107-51-7	Octamethyltrisiloxane (MDM)	$C_8H_{24}O_2Si_3$
141-62-8	Decamethyltetrasiloxane (MD <sub>2</sub> M)	$C_{10}H_{30}O_3Si_4$
141-63-9	Dodecamethylpentasiloxane (MD <sub>3</sub> M)	$C_{12}H_{36}O_4Si_5$
107-63-9	Tetradecamethylhexasiloxane (MD <sub>4</sub> M)	$C_{14}H_{42}O_5Si_6$
63148-62-9	Dimethyl silicones and siloxanes (MD <sub>x</sub> M)	

Cyclic VMS

541-05-9	Hexamethylcyclotrisiloxane (D <sub>3</sub> )	$C_6H_{18}O_3Si_3$
556-67-2	Octamethylcyclotetrasiloxane (D <sub>4</sub> )	$C_8H_{24}O_4Si_4$
541-02-6	Decamethylcyclopentasiloxane (D <sub>5</sub> )	$C_{10}H_{30}O_5Si_5$
540-97-6	Dodecamethylcyclohexasiloxane (D <sub>6</sub> )	$C_{12}H_{36}O_6Si_6$
69430-24-6	Cyclopolydimethylsiloxanes (D <sub>x</sub> )	

Branched VMS

17928-28-8	1,1,1,3,5,5,5-Heptamethyl3-	
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	[(trimethylsilyl)oxyl]-	
	trisiloxane (M <sub>3</sub> T)	C <sub>10</sub> H <sub>30</sub> O <sub>3</sub> Si <sub>4</sub>
3555-47-3	1,1,1,5,5,5-Hexamethyl-3,3,-	
	bis[(trimethylsilyl)oxy]-	
	trisiloxane (M <sub>4</sub> Q)	C <sub>12</sub> H <sub>36</sub> O <sub>4</sub> Si <sub>5</sub>
-- -- --	Pentamethyl[(trimethylsilyl)oxy]-	
	cyclotrisiloxane (MD <sub>3</sub> )	C <sub>8</sub> H <sub>24</sub> O <sub>4</sub> Si <sub>4</sub>

Based on the results of reactivity studies demonstrating that VMS do not contribute to tropospheric ozone formation, Dow Corning Corporation requested that EPA do the following:

1. Amend EPA's general regulatory definition of VOC appearing in 40 CFR 51.100(s) (see 57 FR 3945, February 3, 1992) so as expressly to exclude VMS from the term "VOC" by final regulatory action.

2. In taking action on any currently-pending or future proposal to approve State VOC regulations as part of a SIP, clarify that EPA lacks authority to approve or enforce VOC regulations to the extent that they apply to VMS or otherwise regulate VMS as precursors to tropospheric ozone.

3. In taking any future proposed or final regulatory action to amend or promulgate VOC regulations

for the purpose of reducing tropospheric ozone (e.g., any action pursuant to section 183(e) of the Act to control VOC in consumer and commercial products), take such action and make such statements as may be necessary to ensure that such regulations will not apply to VMS.

4. Take such other actions and make such other statements as may be necessary to implement the exemption of VMS from regulation as precursors to tropospheric ozone.

In support of its requests, Dow Corning submitted supporting information and documentation to demonstrate that VMS:

1. Do not contribute to the formation of tropospheric ozone, and in some situations inhibit the formation of tropospheric ozone;

2. Do not deplete stratospheric ozone;

3. Are generally nontoxic to humans and the environment;

4. Are used in personal care products and other consumer products;

5. Have potential uses as substitutes for chlorofluorocarbons in a number of specified



applications; and,

6. Have a wide variety of applications and potential applications as substitutes for other VOC.

The petition included a number of reports on smog chamber reactivity studies on VMS and other supporting information. A copy of this material is included in the docket for this rulemaking.

Several toxicity studies for multiple routes of exposure exist for parachlorobenzotrifluoride. In laboratory animals, kidney and liver effects have been documented. More importantly, eye and nasal irritation were observed during inhalation exposures. However, it is not expected to have ecological effects. There is a lack of data concerning carcinogenicity in humans and animals. Of the volatile methyl siloxanes, only the D4 has been studied extensively. Mild liver effects (inhalation exposure) and testicular effects (dietary exposure) were observed in laboratory animals. The D4 compound is known to produce adverse immunological effects when injected, but it is not known if the same effect can be elicited by inhalation exposure. These compounds are not included on the 112(b)(1) list of hazardous air pollutants and are not regulated by any

program. Our best judgment at this time is that the known toxic effects of the pollutants do not warrant alteration of a decision to remove them from the VOC list nor warrant addition to the 112(b)(1) list. If additional data were to alter this judgment, or if petitioned, the Agency would further consider the need to add either or both compounds to 112(b)(1).

If VMS and PCBTF are accepted as having negligible photochemical reactivity, exempting them from regulation as ozone precursors could contribute to the achievement of several important environmental goals. For example, they might be used as a substitute for several compounds (e.g., methyl chloroform) that are listed as hazardous air pollutants (HAP) under section 112 of the Act.

Another area of concern is finding substitutes for ozone depleting substances (ODS) which are active in depleting the stratospheric ozone layer. Under the London Amendments to the Montreal Protocol on substances that deplete the ozone layer ("Montreal Protocol"), the United States agree to phase out production and consumption of certain chlorofluorocarbons (CFC) by the year 2000 and methyl chloroform by 2005 (see 58 FR 15016 (March 18, 1993)). In 1990, Congress added title VI to

the Act in part to provide for the implementation of this phaseout (see 42 U.S.C. 7671 et seq.). The 1990 Amendments specified an initial list of Class I and Class II ODS, authorizing EPA to add compounds to both lists depending on a given compound's potential to contribute to stratospheric ozone depletion, ( Id. 7671a.) The 1990 Amendments further required phaseout of the production and consumption of Class I ODS by 2000, methyl chloroform by 2002, and Class II ODS by 2030 (see 42 U.S.C. 7671c, 7671d). At the fourth meeting, in 1992, of the parties to the Montreal Protocol in Copenhagen, Denmark, the parties adjusted the phaseout schedules of Class I substances under the Montreal Protocol to phase out Class I CFC and methyl chloroform by 1996. In 1993, EPA proposed to accelerate the phaseout of Class I CFC and methyl chloroform in order to discontinue use of these compounds after January 1, 1996 (see 58 FR 15022).

As a result of these phaseout deadlines, there is a need to develop substitutes for ODS. The EPA has listed several VMS compounds as ozone-depleting substance substitutes under the program known as the "Significant New Alternatives Policy" (SNAP) program, (59 FR 13044, March 18, 1994). Within the context of the SNAP rule,

substitutes are "acceptable" if they are technically feasible to be used as an alternative to an ODS for particular uses and give reduced overall risk to human health and the environment compared to the ODS they replace. In the SNAP rule, EPA listed several volatile siloxanes as acceptable substitutes for metal cleaning, electronics cleaning, and precision cleaning (59 FR 13134). The SNAP program lists benzotrifluorides as "pending decisions" for use in aerosols and adhesives, coatings, and inks (59 FR 13145). The Agency has not yet completed reviews of data for these benzotrifluoride compounds, but plans to issue a SNAP determination for these substitutes in the next set of listing decisions (59 FR 13118).

In these areas of concern, toxic air emissions and depletion of stratospheric ozone, adding these compounds to the list of negligibly-reactive VOC may provide support for the EPA's pollution prevention efforts. By enacting the Pollution Prevention Act of 1990, Congress established as a national policy that "pollution should be prevented or reduced at the source whenever feasible" (42 U.S.C. 13). An important part of EPA's pollution prevention strategy is encouraging companies to use

substitutes in their production processes that are more environmentally benign than the substances they currently use. For example, in its blueprint for a comprehensive national pollution prevention strategy, ((56 FR 7849 (February 26, 1991))), the EPA recognized that the definition of pollution prevention

includes a "switch to non-toxic or less toxic substitutes" ( Id. at 7854).

## II. The EPA Response to the Petitions

The EPA is responding to these petitions by taking action in this notice to add PCBTF and VMS to the list of compounds appearing in 40 CFR 51.100(s) that are excluded from the definition of VOC. By this final action, PCBTF and VMS are excluded from the VOC definition.

The EPA's conclusions concerning the exclusion of PCBTF are based on the report "Loss Processes For 4-Chlorobenzotrifluoride Under Atmospheric Conditions," by Roger Atkinson et al. (University of California/Riverside), October 1984. This report along with other information was submitted by Occidental Chemical Corporation and has been placed in the docket for this action.

The Atkinson et al. report indicated that the  $k_{OH}$  reactivity of PCBTF ( $2.3 \times 10^{-13} \text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ) is somewhat lower than, but statistically indistinguishable from, that of ethane ( $2.7 \times 10^{-13} \text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ). Ethane is currently the most reactive of the compounds currently excluded as VOC due to negligible photochemical reactivity. It is conceivable, however, that there are other processes, e.g., photodissociation, reaction with ozone or with nitrogen trioxide ( $\text{NO}_3$ ) radicals, that might enhance the ozone-forming reactivity of PCBTF. Atkinson et al. explored to some extent these possibilities by studying experimentally the photodissociation of PCBTF and its reaction with ozone. They found a negligibly low rate of reaction with ozone and no measurable photolysis of PCBTF. The photolysis detection limit, however, was  $2.7 \times 10^{-6} \text{ sec}^{-1}$ , which is a rate somewhat higher than that of the reaction rate with hydroxyl radicals (OH) in typical mid-day urban atmospheres ( $1.4 \times 10^{-6} \text{ sec}^{-1}$ ). Thus, significant, though nonmeasurable, photodissociation of PCBTF in the atmosphere cannot be precluded. On the other hand, it is not known whether dissociation, even if it does occur, would enhance the ozone-forming reactivity of PCBTF. In

the absence of measurable photodissociation, Atkinson et al. could not obtain evidence on the nature and follow-up chemistry of the photodissociation products.

In summary, the evidence available indicates that:

(1) The  $k_{OH}$  reactivity of PCBTF is not higher than that of ethane, and (2) there is no evidence of processes (other than reaction with OH) that might increase the ozone-forming reactivity above that of ethane.

The EPA's decision concerning the exclusion of VMS as VOC is based on the following: "Investigation of the Ozone Formation Potential of Selected Volatile Silicone Compounds," by William P. L. Carter et al. (University of California/Riverside), November 1992; "Determination of the Atmospheric Lifetimes of Organosilicon Compounds," by Roger Atkinson et al. (University of California/Riverside), September 1990; and "Kinetics of the Gas Phase Reactions of a Series of Organosilicon Compounds with OH and NO<sub>3</sub> Radicals and O<sub>3</sub> at 297±2K," by R. Atkinson et al. (Environmental Science & Technology, 25, p.863, 1991). These reports were submitted, along with other materials by Dow Corning, in support of its petition. This information has been placed in the docket for this action.

The Atkinson et al. studies indicated that volatile methyl siloxanes have  $k_{OH}$  reactivities higher than that of ethane, and suggested that follow-up smog chamber studies should be conducted to determine their ozone-forming potentials. Such a chamber study is the subject of the Carter et al. report. Carter produced evidence for hexamethyldisiloxane (MM), octamethylcyclotetrasiloxane ( $D_4$ ), and decamethylcyclopentasiloxane ( $D_5$ ) that showed these siloxanes have negative ozone-forming potentials for commonly-occurring ambient conditions. However, the degradation pathways (mechanism) are still not well understood. Nevertheless, the investigators concluded that the ozone-forming reactivities of these siloxanes cannot be higher than that of ethane.

### III. Final Action

Today's final action is based on EPA's review of the material in Docket No. A-93-47. The EPA is publishing this action without prior proposal because the Agency views this as a noncontroversial amendment and anticipates no adverse comments. However, in a separate document in this Federal Register publication, the EPA is proposing to approve the definition revision should adverse



or critical comments be filed or a request for a public hearing be made. The EPA hereby amends its definition of VOC at 40 CFR 51.100(s) to exclude PCBTF and VMS as VOC for ozone SIP and ozone control purposes. The revised definition will apply in the Chicago ozone nonattainment area pursuant to the 40 CFR 52.741(a)(3) definition of volatile organic material or volatile organic compound. States are not obligated to exclude from control as a VOC those compounds that EPA has found to be negligibly reactive. However, States should not include these compounds in their VOC emissions inventories for determining reasonable further progress under the Act (e.g., section 182(b)(1)) and may not take credit for controlling these compounds in their ozone control strategy. Further, these negligibly-reactive compounds may not be used for emissions netting (e.g., 40 CFR 51.166(b)(2)(c)), offsetting (40 CFR appendix S), or trading with reactive VOC (Emissions Trading Policy Statement, 51 FR 43814, December 4, 1986 and Economic Incentive Program Rules, 59 FR 16690, April 7, 1994).

In addition, corrections are made to the names of three compounds which have previously been exempted from the definition of VOC: 1,1,1-trichloro-2,2,2-

trifluoroethane (CFC-113) is changed to 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); chlorodifluoromethane (CFC-22) is changed to chlorodifluoromethane (HCFC-22); and trifluoromethane (FC-23) is changed to trifluoromethane (HFC-23). These changes are corrections to nomenclature only and are not substantive.

Pursuant to 5 U.S.C. 605(b), I hereby certify that this action will not have a significant economic impact on a substantial number of small entities because it relaxes current regulatory requirements rather than imposing new ones. The EPA has determined that this rule is not "significant" under the terms of Executive Order 12866 and is, therefore, not subject to Office of Management and Budget (OMB) review. This action does not contain any information collection requirements subject to OMB review under the Paperwork Reduction Act of 1980 (44 U.S.C. 3501 et seq.).

Assuming this rulemaking is subject to section 317 of the Act, the Administrator concludes, weighing the Agency's limited resources and other duties, that it is not practicable to conduct an extensive economic impact assessment of today's action since the rule promulgated

today will relax current regulatory requirements. Accordingly, the Administrator simply notes that any costs of complying with today's action, any inflationary or recessionary effects of the regulation, and any impact on the competitive standing of small businesses, on consumer costs, or on energy use, will be less than or at least not more than the impact that existed before today's action.

List of Subjects in 40 CFR Part 51

Environmental protection, Administrative practice and procedure, Air pollution control, Carbon monoxide, Intergovernmental relations, Lead, Nitrogen dioxide, Ozone, Particulate matter, Reporting and recordkeeping requirements, Sulfur oxides, Volatile organic compounds.

Dated: September 23, 1994.

Carol M. Browner,  
Administrator.

For reasons set forth in the preamble, part 51 of chapter I of title 40 of the Code of Federal Regulations is proposed to be amended as follows:

PART 51-REQUIREMENTS FOR PREPARATION, ADOPTION, AND SUBMITTAL OF IMPLEMENTATION PLANS.

1. The authority citation for part 51 continues to read as follows:

Authority: 42 U.S.C. 7410(a)(2), 7475(e), 7502(a) and (b), 7503, 7601(a)(1) and 7620.

2. Section 51.100 is amended by revising paragraph (s)(1) introductory text to read as follows:

§ 51.100 Definitions.

\* \* \* \* \*

(s) \* \* \*

(1) This includes any such organic compound other than the following, which have been determined to have negligible photochemical reactivity: methane; ethane; methylene chloride (dichloromethane); 1,1,1-trichloroethane (methyl chloroform); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); trichlorofluoromethane (CFC-11); dichlorodifluoromethane (CFC-12); chlorodifluoromethane (HCFC-22); trifluoromethane (HFC-23); 1,2-dichloro 1,1,2,2-tetrafluoroethane (CFC-114);

chloropentafluoroethane (CFC-115); 1,1,1-trifluoro 2,2-dichloroethane (HCFC-123); 1,1,1,2-tetrafluoroethane (HFC-134a); 1,1-dichloro 1-fluoroethane (HCFC-141b); 1-chloro 1,1-difluoroethane (HCFC-142b); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); pentafluoroethane (HFC-125); 1,1,2,2-tetrafluoroethane (HFC-134); 1,1,1-trifluoroethane (HFC-143a); 1,1-difluoroethane (HFC-152a); parachlorobenzotrifluoride (PCBTF); cyclic, branched, or linear completely methylated siloxanes; and perfluorocarbon compounds which fall into these classes:

\* \* \* \* \*

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