CHEMSERVICE
GERMANY

Polychlorotrifluoroethylene (HORIBA S-316) within the framework of the Montreal Protocol

EC No.: 618-336-7

CAS No.: 9002-83-9

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for

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1. Background

Chemservice was charged to identify the likelihood if the substance Polychlorotrifluoro-ethylene (PCTFE, CAS 9002-83-9, HORIBA S-316) is being included in the list of ozone depleting substances (ODS) according to the criteria and requirements of the Montreal Protocol[1]. The purpose of this report is to identify the likelihood if PCTFE is will be classified as an ODS and whether this substance will be affected by an extension of the Montreal Protocol's substance lists in the future.

The ozone layer of the Earth's stratosphere absorbs a portion of the radiation from the sun, preventing it from reaching the planet's surface. Most importantly, it absorbs the portion of UV light called UVB. UVB has been linked to many harmful effects, including skin cancers, cataracts and harm to some crops and marine life. When chlorine and bromine atoms come into contact with ozone in the stratosphere, they destroy ozone molecules. One chlorine atom can destroy over 100,000 ozone molecules before it is removed from the stratosphere. Ozone can be destroyed more quickly than it is naturally created. Some compounds release chlorine or bromine when they are exposed to intense UV light in the stratosphere. These compounds contribute to ozone depletion, and are called ozone-depleting substances (ODS). Fluorinated gases are also persistent greenhouse gases, but they don't react readily with ozone.

Ozone-depleting substances are man-made chemicals that damage the ozone layer. ODS include chlorofluorocarbons (CFCs), hydrofluorochlorocarbons (HCFCs), halons, and certain other gases. Due to their high chemical stability and low flammability, ODS were used in a wide range of industrial and consumer applications in Europe until recently. Specifically, these applications include refrigeration and air conditioning, fire extinguishing, solvents for cleaning, aerosol propellants, and foam blowing agents. In developing countries and emerging markets, the use of ODS in all these applications is still common and widespread.

The ozone depletion potential (ODP) of a chemical compound is the relative amount of degradation to the ozone layer it can cause, with trichlorofluoromethane (R-11 or CFC-11) being fixed at an ODP of 1.0 as a reference. Precisely, ODP of a given substance is defined as the ratio of global loss of ozone due to the given substance to the global loss of ozone due to CFC-11 of the same mass. ODP can be estimated from the molecular structure of a given substance.

The *"Montreal Protocol on Substances that Deplete the Ozone Layer"*[2] was signed in 1987 and, following sufficient country ratification, entered into force in 1989. The Protocol has been successful in establishing legally binding controls for developed and developing nations on the production and consumption of halogen source gases known to cause ozone depletion.

2. Ozone depleting substances (ODS) controlled under the Montreal Protocol

In 1989, the Montreal Protocol on Substances that Deplete the Ozone Layer entered into force. Its objective is to protect the stratospheric ozone layer by phasing out the production of ozone-depleting substances. The Montreal Protocol was signed in September 1987 by 24 Governments and the Commission of the European Community. The protocol covers over 200 individual substances with a high ozone-depleting potential (ODP), including:

- chlorofluorocarbons (CFCs)
- halons
- carbon tetrachloride (CTC)
- 1,1,1-Trichloroethane (TCA)

[1] http://ozone.unep.org/en/treaties-and-decisions/montreal-protocol-substances-deplete-ozone-layer
[2] http://www.environment.gov.au/protection/ozone/montreal-protocol

- hydrochlorofluorocarbons (HCFCs)
- hydrobromofluorocarbons (HBFCs)
- bromochloromethane (BCM)
- methyl bromide (MB)

all of which are referred to as “controlled substances”.

Within the European Union (EU), the use and trade of “*controlled substances”* is regulated by Regulation (EC) No 1005/2009 (known as the ODS Regulation) (EC, 2009)[3]. This regulation stipulates that each company producing controlled substances, importing them into and/or exporting them out of the EU, as well as feedstock users, process agent users and destruction facilities, must report its activities concerning controlled substances annually. The ODS Regulation also encompasses five additional substances that are not covered by the Montreal Protocol but have an ozone depleting potential. (these are referred to as ”*new substances*”). Producers, importers and exporters have to report their activities for new substances. These new substances are halon 1202, methyl chloride (MC), ethyl bromide (EB), trifluoro iodomethane (TFIM) and *n*-propyl bromide (n-PB). Both production and consumption of HCFCs (defined as production + imports – exports) are to be phased out by 1 January 2020 in developed countries and by 1st January 2030 in developing countries, following the specified reduction schedules. Additionally, 0.5 % and 2.5 % of base years consumption is allowed for servicing the refrigeration and air conditioning equipment existing at the phase-out date in developed and developing countries, respectively, until 31 December 2030 and 31 December 2040. Although HCFCs have their ozone depletion potentials (ODPs) in the range of 0.01-0.52, i.e. very low as compared to ODPs of chlorofluorocarbons (CFCs) which were replaced by HCFCs, their overall effect on ozone layer depletion is quite high because of the large quantities which are still consumed globally.

While the global HCFC phase-out process is progressing, the most common alternatives to HCFCs that have zero ODP values – hydrofluorocarbons (HFCs), unsaturated HFCs (HFOs), hydrocarbons (HCs), ammonia or CO2 – are gradually being phased in. Due to their specific features like non-flammability, chemical inertness, relatively low cost and excellent performance as refrigerants, foam blowing agents, aerosol propellants or solvents, HFCs have become the major replacements for HCFCs over the last decade. However, the great disadvantage of HFCs is that the most commonly-used HFC substances and blends are powerful greenhouse gases which have very high global warming potentials (GWPs), several thousand times greater than the GWP of CO2.

Accordingly, the Parties to the Montreal Protocol agreed in October 2016 the Kigali Amendment which extended the list of controlled substances to include 18 HFCs (hydrofluorocarbons, see chapter below). The Amendment also established phase-down schedules for HFC production and consumption (defined as production + imports – exports of HFCs expressed in CO2 equivalents). The Parties decided that there will be two different phasedown schedules established for two groups of Article 5 Parties: Group 1 – countries which will follow the more ambitious HFC phase-down timeline and Group 2 – countries which, due to specific national circumstances will follow a different schedule.

Under the US EPA Clean Air Act[4] ozone depleting substances are split into two groups. Class I ODS, such as chlorofluorocarbons (CFCs), and Class II ODS, such as hydrochloro-fluorocarbons (HCFCs). Class I substances are defined with having an ODP of 0.2 or higher, and include halons, chlorofluorocarbons (CFCs), methyl chloroform, carbon tetrachloride, and methyl bromide. Class II substances have an ozone depletion potential (ODP) less than 0.2 and are all hydrochlorofluorocarbons (HCFCs). The actual list of ODS is shown in Annex I of this report.

[3] https://eur-lex.europa.eu/legal-content/DE/TXT/?uri=CELEX%3A32009R1005
[4] https://www.epa.gov/ozone-layer-protection/ozone-depleting-substances

3. Modification and update procedure of the ODS lists

The Montreal Protocol provides two mechanisms by which the substance list can be modified:

Amendments

Amendments are the broad-based mechanism, they change the text of the Montreal Protocol and must be adopted by a two-thirds majority and then ratified by the Member States. In the meantime, the regulatory requirements have been constantly modified and supplemented by the six Amendments of London (1990), Copenhagen (1992), Vienna (1995), Montreal (1997), Beijing (1999) and Kigali (2016). The recent amendments to the Montreal Protocol agreed in Kigali (2016), go beyond the protection of the ozone layer and pursuing the objective of climate protection, which includes global warming potential of substances (GWP). Adding a new OPS is a very lengthy and administrative procedure and needs to be ratify by each participating party.

Adjustments

Adjustments are more limited: they can only update the estimates of ozone depletion potential or adjust the frame and schedule for regulated substances. By contrast, new substances can not be included in the protocol through adjustments. Also, adjustments are decided with two-thirds majority, however, no ratification is necessary. Six months after a Member State has been informed of a proposed adjustment, it becomes binding on it, even if it does not vote for the adjustment - this is unusual for international environmental law.

4. Conclusion and likelihood of inclusion of PCTFE in the ODS List

PCTFE (HORIBA S-316) or its monomer is not an identified ODS and to our knowledge not subject of discussions to be included. To clarify the probability that the substance PCTFE will be listed as an ODS within the framework of the Montreal Protocol, the following must be considered.

PCTFE is a viscous liquid polymer with a relative high boiling point of 132 °C, a low volatility and therefore it is nearly impossible that the substance reaches the stratosphere and cause ozone depleting harm. PCTFE is a polymeric-oligomeric substance and is reacted from monomer units of Chlorotrifluoroethylene (CTFE, CAS 79-38-9), which was registered under REACH[5]. According to the registration dossier[6] the substance is not classified as “Hazardous to the ozone layer” according to CLP Regulation EC No 1272/2008[7], which is supported by different literature references. CTFE is chemically unstable and decomposes mainly into hydrochloric acid (HCl) and hydrogen fluoride (HF). Therefore, Chlorotrifluoroethylene is shipped as a liquefied gas under its vapor pressure. The fact that CTFE has no ozone depleting potential can be applied to the polymer/oligomers as well.

In order to get the view of the German Competent Authority responsible for the Montreal Protocol implementation in Germany, a telephone consultation with the German Umweltbundesamt (UBA, Dresden) was held. According to the feedback from UBA, the extension of the Montreal Protocol’s List of ODSs is a very complex and lengthy procedure, which can sometimes take decades. Furthermore, since the substance concerned is a polymeric, liquid and not a volatile substance, the likelihood of inclusion in the ODS list is negligible.

However, during the evaluation we found, that the monomer CTFE (CAS 79-38-9) has been included in several material declaration lists driven by the Automotive industry, the Global

[5] https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32006R1907
[6] https://echa.europa.eu/de/registration-dossier/-/registered-dossier/13752
[7] https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32008R1272

Automotive Declarable Substance List (GADSL)[8]. Reason for Restriction and/or Declaration according to GADSL is the ozone-depleting potential, which to our assessment is incorrect. Moreover, it concerns only the monomer and not the polymer/oligomers. We would therefore recommend, that the Automotive industry is being contacted accordingly.

In conclusion, due to the missing physical-chemical properties of PCTFE and its monomer (CTFE), the inclusion of PCTFE (HORIBA S-316) in the list of ozone-depleting substances is unlikely to impossible, based on the currently available information.

[8] https://www.gadsl.org/

Annex I

Class I ODS

Class I ODS are divided into eight groups.

- Class I ODS listed in Groups 1 through 5 are identified in Title VI of the US Clean Air Act.
- Class I ODS listed in Groups 6 and 7, methyl bromide and hydrobromofluorocarbons, are identified in EPA's Accelerated Phaseout final rule.
- Class I ODS listed in Group 8, chlorobromomethane, is identified in EPA's Chlorobromo-methane Phaseout final rule.

Chemical Name	Lifetime, in years	ODP1 (Montreal Protocol)	ODP2 (WMO 2011)	GWP1 (AR4)	GWP2 (AR5)	CAS Number
Group I						
CFC-11 (CCl3F) Trichlorofluoromethane	45	1	1	4750	4660	75-69-4
CFC-12 (CCl2F2) Dichlorodifluoromethane	100	1	0.82	10900	10200	75-71-8
CFC-113 (C2F3Cl3) 1,1,2-Trichlorotrifluoroethane	85	0.8	0.85	6130	5820	76-13-1
CFC-114 (C2F4Cl2) Dichlorotetrafluoroethane	190	1	0.58	10000	8590	76-14-2
CFC-115 (C2F5Cl) Monochloropentafluoroethane	1020	0.6	0.5	7370	7670	76-15-3
Group II						
Halon 1211 (CF2ClBr) Bromochlorodifluoromethane	16	3	7.9	1890	1750	353-59-3
Halon 1301 (CF3Br) Bromotrifluoromethane	65	10	15.9	7140	6290	75-63-8
Halon 2402 (C2F4Br2) Dibromotetrafluoroethane	20	6	13.0	1640	1470	124-73-2
Group III						
CFC-13 (CF3Cl) Chlorotrifluoromethane	640	1	1	14420	13900	75-72-9
CFC-111 (C2FCl5) Pentachlorofluoroethane		1	1			354-56-3
CFC-112 (C2F2Cl4) Tetrachlorodifluoroethane		1	1			76-12-0
CFC-211 (C3FCl7) Heptachlorofluoropropane		1	1			422-78-6
CFC-212 (C3F2Cl6) Hexachlorodifluoropropane		1	1			3182-26-1
CFC-213 (C3F3Cl5) Pentachlorotrifluoropropane		1	1			2354-06-5
CFC-214 (C3F4Cl4) Tetrachlorotetrafluoropropane		1	1			29255-31-0
CFC-215 (C3F5Cl3) Trichloropentafluoropropane		1	1			4259-43-2
CFC-216 (C3F6Cl2) Dichlorohexafluoropropane		1	1			661-97-2
CFC-217 (C3F7Cl) Chloroheptafluoropropane		1	1			422-86-6

Group IV						
CCl4 Carbon tetrachloride	26	1.1	0.82	1400	1730	56-23-5
Group V						
Methyl Chloroform (C2H3Cl3) 1,1,1-trichloroethane	5	0.1	0.16	146	160	71-55-6
Group VI						
Methyl Bromide (CH3Br)	0.8	0.7	0.66	5	2	74-83-9
Group VII						
CHFBr2		1	1			
HBFC-12B1(CHF2Br)		0.74				
CH2FBr		0.73	0.73			
C2HFBr4		0.3-0.8	0.3-0.8			
C2HF2Br3		0.5-1.8	0.5-1.8			
C2HF3Br2		0.4–1.6	0.4–1.6			
C2HF4Br		0.7–1.2	0.7–1.2			
C2H2FBr3		0.1–1.1	0.1–1.1			
C2H2F2Br2		0.2–1.5	0.2–1.5			
C2H2F3Br		0.7–1.6	0.7–1.6			
C2H3FBr2		0.1–1.7	0.1–1.7			
C2H3F2Br		0.2–1.1	0.2–1.1			
C2H4FBr		0.07–0.1	0.07–0.1			
C3HFBr6		0.3–1.5	0.3–1.5			
C3HF2Br5		0.2–1.9	0.2–1.9			
C3HF3Br4		0.3–1.8	0.3–1.8			
C3HF4Br3		0.5–2.2	0.5–2.2			
C3HF5Br2		0.9–2.0	0.9–2.0			
C3HF6Br		0.7–3.3	0.7–3.3			
C3H2FBr5		0.1–1.9				
C3H2F2Br4		0.2–2.1	0.2–2.1			
C3H2F3Br3		0.2–5.6	0.2–5.6			
C3H2F4Br2		0.3–7.5	0.3–7.5			

C3H2F5Br		0.9–1.4	0.9–1.4			
C3H3FBr4		0.08–1.9	0.08–1.9			
C3H3F2Br3		0.1–3.1	0.1–3.1			
C3H3F3Br2		0.1–2.5	0.1–2.5			
C3H3F4Br		0.3–4.4	0.3–4.4			
C3H4FBr3		0.03–0.3	0.03–0.3			
C3H4F2Br2		0.1–1.0	0.1–1.0			
C3H4F3Br		0.07–0.8	0.07–0.8			
C3H5FBr2		0.04–0.4	0.04–0.4			
C3H5F2Br		0.07–0.8	0.07–0.8			
C3H6FBr		0.02–0.7	0.02–0.7			
Group VIII						
CH2BrCl Chlorobromomethane	0.37	0.12	0.12			

Class II ODS

Chemical Name	Lifetime, in years	ODP1 (Montreal Protocol)	ODP2 (WMO 2011)	GWP1 (AR4)	GWP2 (AR5)	CAS Number
HCFC-21 (CHFCl2) Dichlorofluoromethane	1.7	0.04		151	148	75-43-4
HCFC-22 (CHF2Cl) Monochlorodifluoromethane	11.9	0.055	0.04	1810	1760	75-43-6
HCFC-31 (CH2FCl) Monochlorofluoromethane		0.02				593-70-4
HCFC-121 (C2HFCl4) Tetrachlorofluoroethane		0.01-0.04				354-14-3
HCFC-122 (C2HF2Cl3) Trichlorodifluoroethane		0.02-0.08			59	354-21-2
HCFC-123 (C2HF3Cl2) Dichlorotrifluoroethane	1.3	0.02	0.01	77	79	306-83-2
HCFC-124 (C2HF4Cl) Monochlorotetrafluoroethane	5.9	0.022				2837-89-0
HCFC-131 (C2H2FCl3) Trichlorofluoroethane		0.007–0.05				359-28-4
HCFC-132b (C2H2F2Cl2) Dichlorodifluoroethane		0.008–0.05				1649-08-7
HCFC-133a (C2H2F3Cl) Monochlorotrifluoroethane		0.02–0.06				75-88-7
HCFC-141b (C2H3FCl2) Dichlorofluoroethane	9.2	0.11	0.12	725	782	1717-00-6
HCFC-142b (C2H3F2Cl) Monochlorodifluoroethane	17.2	0.065	0.06	2310	1980	75-68-3
HCFC-221 (C3HFCl6) Hexachlorofluoropropane		0.015–0.07				422-26-4
HCFC-222 (C3HF2Cl5) Pentachlorodifluoropropane		0.01–0.09				422-49-1

HCFC-223 (C3HF3Cl4) Tetrachlorotrifluoropropane		0.01–0.08				422-52-6
HCFC-224 (C3HF4Cl3) Trichlorotetrafluoropropane		0.01–0.09				422-54-8
HCFC-225ca (C3HF5Cl2) Dichloropentafluoropropane	1.9	0.025	0.02	122	127	422-56-0
HCFC-225cb (C3HF5Cl2) Dichloropentafluoropropane	5.9	0.033	0.03	595	525	507-55-1
HCFC-226 (C3HF6Cl) Monochlorohexafluoropropane		0.02–0.1				431-87-8
HCFC-231 (C3H2FCl5) Pentachlorofluoropropane		0.05–0.09				421-94-3
HCFC-232 (C3H2F2Cl4) Tetrachlorodifluoropropane		0.008–0.1				460-89-9
HCFC-233 (C3H2F3Cl3) Trichlorotrifluoropropane		0.007–0.23				7125-84-0
HCFC-234 (C3H2F4Cl2) Dichlorotetrafluoropropane		0.01–0.28				425-94-5
HCFC-235 (C3H2F5Cl) Monochloropentafluoropropane		0.03–0.52				460-92-4
HCFC-241 (C3H3FCl4) Tetrachlorofluoropropane		0.004–0.09				666-27-3
HCFC-242 (C3H3F2Cl3) Trichlorodifluoropropane		0.005–0.13				460-63-9
HCFC-243 (C3H3F3Cl2) Dichlorotrifluoropropane		0.007–0.12				460-69-5
HCFC-244 (C3H3F4Cl) Monochlorotetrafluoropropane		0.009–0.14				
HCFC-251 (C3H4FCl3) Monochlorotetrafluoropropane		0.001–0.01				421-41-0
HCFC-252 (C3H4F2Cl2) Dichlorodifluoropropane		0.005–0.04				819-00-1
HCFC-253 (C3H4F3Cl) Monochlorotrifluoropropane		0.003–0.03				460-35-5
HCFC-261 (C3H5FCl2) Dichlorofluoropropane		0.002–0.02				420-97-3
HCFC-262 (C3H5F2Cl) Monochlorodifluoropropane		0.002–0.02				421-02-03
HCFC-271 (C3H6FCl) Monochlorofluoropropane		0.001–0.03				430-55-7