

Application for Exemption from REACH

PFAS for Refrigerants

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The development of refrigerants dated back to the 1830s and has lasted for about two hundred years, from the first generation of NH_3 , CO_2 and other less safe natural substances to the second generation of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), and then to the third generation of hydrofluorocarbons (HFCs), which are still used in large quantities, and finally to the fourth generation of refrigerants, hydrofluoroolefins (HFOs), which are being developed and popularized.

Refrigerants are chemical substances known as fluorocarbons, which include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs). Due to ozone depletion, global warming and climate protection, The Montreal Protocol, The Kyoto Protocol and The Kigali Amendment have entered into force to systematically control the production and use of such chemical compounds and mixtures. Therefore, this REACH PFAS control does not need to once again cover the use of these chemicals in the gaseous state.

More than that, a refrigerant will not be completely replaced until decades of development and use. REACH PFAS make proposals, and committees or councils pass resolutions which shall come into force after a short time. During such a short time, the existing refrigerants can't be partially or completely replaced by others.

Those compounds can form trifluoroacetic acid (TFA) through atmospheric degradation. For example, HFC-134a can form CF_3CFO , which further forms TFA. HFO-1234yf can form CF_3CFO , which further forms TFA. Please refer to Figures 10 and 11

in the attached article which was published by S. Madronich et al. in June 2023. In summary, after use, those fluorinated gaseous substances will enter the atmosphere, pass through intermediates and eventually degrade and form TFA. TFA is formed as an acid in the atmosphere, and when it reaches the surface (soil or water), it forms salts with alkali metals (e.g., sodium, potassium, calcium, etc.). The TFA salts lack reactivity and are relatively persistent in the environment, with an estimated half-life in the range of centuries to millennia. Its persistence does not matter much since it does not react with biomolecules. TFA and its salts can be easily excreted by animals, thus biological accumulation can be avoided in the food chain. TFA salts have a weak toxicity for flora and fauna, thus minimal risks will be posed. Please refer to Chapter 3.8 in the attachment for details.

Regarding the PFAS control measures proposed by the EU, we sincerely share the above views and suggestions based on the actual production in this industry. We are applying for exemption of refrigerants from REACH PFAS control. Details of relevant refrigerants are shown in the table below.

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Classification	Refrigerant	Preferred IUPAC Name	CAS No.	Chemical Formula
HFCs	HFC-134a	1,1,1,2-tetrafluoroethane	811-97-2	CF ₃ CH ₂ F
	HFC-125	1,1,1,2,2-pentafluoroethane	354-33-6	CF ₃ CHF ₂
	HFC-143a	1,1,1-trifluoroethane	420-	CF ₃ CH ₃

			46-2	
HFOs	HFO-1234yf	2,3,3,3- tetrafluoropropene	754- 12-1	$\text{CF}_3\text{CF}=\text{CH}_2$
	HFO-1234ze	1,3,3,3- tetrafluoropropene	29118 -25-0	$\text{CF}_3\text{CH}=\text{CHF}$
	HCFO- 1233zd	1-chloro-3,3,3- trifluoropropene	460- 71-9	$\text{CF}_3\text{CH}=\text{CClH}$

References:

S. Madronich and etc., "Changes in tropospheric air quality related to the protection of stratospheric ozone in a changing climate". *Photochemical & Photobiological Sciences*, Published online: 13 June, 2023.