Response to Hydrofluoroethers PFAS

As a representative of fluorine chemical manufacturers, Juhua Group has always been mainly producing fluorine chemical products and basic chemical raw materials, as well as more than 200 products from 17 major categories such as polymer materials, fertilizers and pesticides, and chemical medicine etc. Juhua Group has been making unremitting efforts to comply with national chemical regulations. We support the EU's great attempts to reduce the risk of harmful substances, actively respond and take effective measures to meet the requirements of EU chemical regulations.

Japan Association of Fluorochemical Products (FCJ) believes that the proposed restrictions on fluorinated alkyl compounds (perfluoroalkyl and perfluoroalkyl substances) proposed by five European countries are an excessive measure, as it classifies over 10000 organic fluorine compounds as persistent concern substances equivalent to regulated perfluorooctane sulphonate (PFOS) and perfluorooctanoate (PFOA). With this regard, we support FCJ's opinion which opposes “one-size-fits-all kind” approach, and the specific substances should be differentiated based on their necessity and substitutability, that unrestricted production and application of PFAS should be opposed, and that alternatives should be sought actively. And we intend to provide the following opinions in the public consultation on ECHA.

PFAS response comments on the hydrofluoroethers products involved are mainly provided in this article.

Introduction and Industry Status of hydrofluoroethers

Hydrofluorinated ethers are a class of ether compounds containing C, H, O and F elements. Due to the small C-O-C bond energy, they are prone to decomposition in the troposphere. Most of the degradation products are molecules such as short chain fluoroketones, fluorinated aldehydes and carbon dioxide that can be reused or decomposed by organisms, with a short atmospheric lifespan of approximately 1-5 years[1]. Hydrofluorides are considered environmentally friendly compounds due to their ozone depletion value (ODP) of 0 and low global warming potential (GWP). In

addition to its excellent environmental performance, HFEs also have excellent properties such as no flash point, low toxicity, no corrosion, low surface tension, good chemical stability, and good material compatibility. Therefore, HFEs are widely used as substitutes for third-generation ozone depleting substances (ODS) in various industries. HFEs were initially widely used in fields such as refrigerants, foaming agents, cleaning agents, anesthetics and pharmaceutical intermediates. With the development of technology and the arrival of the information technology era, the application fields of hydrofluoroethers are also constantly expanding. As an electrolyte additive, hydrofluoroethers are applied in the lithium battery industry, and as a heat dissipation medium, they are also used in lithium battery energy storage, semiconductors, 5G communication and data centers.

Characteristics of hydrofluoroethers

In regards with the proposed PFAS restrictions, in combination with the characteristics of hydrofluoroethers themselves and the development needs of the economy and society, we believe that hydrofluoroethers should not be included in the scope of the restrictions.

01 Hydrofluoroethers have low toxicity or non-toxicity

For hydrofluoroethers, relevant toxicological tests on some of these hydrofluoroethers are conducted in our unit with the test results: ①LD_{50}>2000 mg/kg, and no acute oral toxicity is found in the sample for the test; ② No skin irritation reaction; ③ No eye irritation reaction. The above data indicates that the acute toxicity hazard category of hydrofluoroethers belongs to category 5, and they are non acute toxicity substances. The results fully demonstrate that the toxicity of hydrofluoroethers is extremely low or non-toxic.

02 Hydrofluoroethers Have Good Degradability

As there are hydrogen atoms in hydrofluoroethers, they are oxidized by OH radicals

in the atmosphere, which reduces their lifespan in the atmosphere compared to fully halogenated compounds, thereby reducing their global warming potential (GWPs). The gas phase degradation of hydrofluoroethers in the atmosphere mainly involves its reacting with hydroxyl radicals[2], further getting the easily degradable small molecule substances. F. CAVALLI et al.[3] measured the reaction rate constants between hydroxyl ion and hydrofluoroethers compounds in the atmosphere. The reaction rate constants for hydrofluoroethers CF_3OCH_3 and CF_3OCHF_2 were $1.0*10^{-14}$ and $4.2*10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. In addition, the reaction rate constants of some common hydrofluoroethers are shown in Table 1-1.

Table 1-1 Rate constants for the reaction between the OH radial and a series of compounds invested in this study at 295 ± 3 K and 740 ± 5 Torr

Compounds	k^a (cm^3 $molecules^{-1}$ s^{-1})
Ratio $CH_3CH_2CH_3/CH_3CH_3$	4.2 ± 0.8^b
	4.6 ± 1.5^b
CH_3CCl_3	$(9.4 \pm 1.9) \times 10^{-15}$
	$(10.0 \pm 2.0) \times 10^{-15}$
$CHClF_2$	$(3.0 \pm 0.7) \times 10^{-15}$
	$(4.7 \pm 0.9) \times 10^{-15}$
$CHF_2OCF_2OCHF_2$	$(2.4 \pm 0.7) \times 10^{-15}$
$CHF_2OCF_2CF_2OCHF_2$	$(4.7 \pm 1.6) \times 10^{-15}$
$CHF_2OCF_2CF_2OCF_2OCHF_2$	$(4.6 \pm 1.6) \times 10^{-15}$
$CH_3OC_4F_9$	$(7.2 \pm 1.6) \times 10^{-15}$
	$\sim 12 \times 10^{-15}$

During the actual production, the environmental data of the produced hydrofluoroethers are determined in our unit. The results showed that the GWP of hydrofluoroethers substances was only around 100, indicating that the environmental effects of HFE on global warming is extremely low.

In addition, although the structural formulas of most hydrofluoroethers themselves are within the restrictionss of PFAS, these substances are prone to degradation and their degradation products do not fall within the restrictionss of PFAS. Taking HFE-458 (named 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether systematically) as an example, its degradation products are the substances of such as difluoroacetic acid, which are not within the scope of PFAS restrictions. Therefore, it seems too absolute to list the entire hydrofluoroethers in the restrictions scope of PFAS.

03 Hydrofluoroethers Have Rrreplaceability

(1) From the perspective of chemical safety, hydrofluoroethers have no flash point with incombustibility. However, after the defluorination, C-F bond becomes C-H bond with a flash point. Against the backdrop of “Peak Carbon Dioxide Emissions” and “Carbon Neutrality”, the researchers are actively developing renewable and clean energy. Lithium ion batteries are widely used in fields of such as portable products, electric vehicles, and green grid energy storage due to their advantages of fast charging and discharging and high energy density, etc.[4-5]. However, due to the inevitable use of volatile or flammable components in lithium-ion batteries, which can easily lead to safety accidents such as fires, adding hydrofluoroether co-solvents to lithium-ion batteries can effectively reduce the safety risks of such as battery fires and explosions.

(2) The rapid rise of immersion liquid cooling technology in data centers worldwide has promoted the research and application of cooling liquids. Data centers are strategic resources and new infrastructure that support modern economic and social development. Liquid cooling improves cooling efficiency through liquid circulation heat exchange, which can significantly reduce the total energy consumption and carbon dioxide emissions of data centers, meeting the low-carbon development requirements of China's data centers[6-7]. Fluorocarbons are a kind of organic compounds obtained by exchanging some or all of the hydrogen contained in hydrocarbons into fluorine. They generally have good comprehensive heat transfer performance，which can achieve non flash and non combustible properties. They are widely used as heat dissipation media in data centers, 5G base stations and other fields. However, its GWP value can reach thousands, while HFE has a lower GWP value, which is a good candidate to replace perfluorocarbon heat transfer fluids. Doubek M et al.[8] tested the PC-SAFT parameters of HFE fluid and modeled the mixtures of various hydrofluoroethers, predicting their equilibrium curves, solubility, and absorption curves, which intended to support the advancement of hydrofluoroethers based substances used in cooling systems to be more

environmentally friendly fluids.

(3) Unlike long fluorocarbon chain PFAS, many substances from PFAS are non-bioaccumulative and almost harmless to the organisms. If these substances are used reasonably, they can bring the benefits to humans being and the environment. For example, the drugs and blood substitutes can save lives, among which hydrofluoroether pharmaceutical products represented by sevoflurane are widely used as inhalable anesthetics[9].

Selection of anesthetics for the patients with myocardial infarction is very challenging. Sevoflurane is a volatile anesthetic commonly used in recent years. Several studies supported the intraoperative hemodynamic stability of sevoflurane and suggested it to be used in patients with heart disease[10]. Fahd Abdullah Alsobayil et al. [11] studied the use of sevoflurane in adult healthy donkeys. The results showed that during the maintenance of sevoflurane anesthesia, HR, MBP, RT, red blood cell, hematocrit, total white blood cells, neutrophils and lymphocytes of the donkey were significantly reduced, while the levels of OHS and glucose were significantly increased. Concentrations of oxygen, carbon dioxide and lactate in venous blood significantly increased, while pH value significantly decreased. After the recovery, calcium levels immediately decreased significantly. Incidence of sternal lying and standing is 15.8 ± 2%, which are 6 minutes and 28.2 ± 2.2 minutes respectively after turning off the evaporator. Overall, the recovery result is good and relatively quick. Therefore, sevoflurane has been proven to be able to provide safe and effective anesthesia, function of induction and rapid recovery on donkeys.

Desflurane is one of the third-generation inhalation anesthetics. It is a halogenated inhalable anesthetic with the lowest solubility in blood and tissue, which can promote rapid balance and elimination after after anesthesia is stopped[12]. Especially in the overweight patients and during longer treatment periods, the low lipid solubility of desflurane provides significant pharmacological benefits, and ten years of clinical experience provide evidence for the safe and effective use of desflurane as a general anesthetic.

Therefore, such substances are related to people's livelihood security, which play a crucial role in personal security, health, safety or social functions, so they should not be included in the scope of PFAS restrictions. They should appy for permanent exemptions.

(4) As a substitute for third-generation ODS (ozone depleting substances), hydrofluoroethers have the environmentally friendly characteristics of zero ODP and low GWP. In the fields of refrigerants, cleaning agents, anesthetics, drug intermediates etc., many of these applications and uses are considered "basic uses" with irreplaceable functions[13].

Main objections to PFAS restrictions macroscopically

In addition, regarding the proposed PFAS restrictions, we have the following objections regarding their scope, risk assessment, and effects on economy and society:

a. PFAS restrictions are too broad and not specific

"Substance" is defined by REACH as "chemical elements and their compounds" [REACH Article 3 (1)]. This is also clearly reflected in the guidelines of European Chemicals Agency (ECHA) for the preparation of Annex XV dossiers (page No. 108), which stipulate that the restriction recommendation must provide “detailed information about the substance's characteristics (including name, CAS, EC number, registration number, molecular formula, structural formula, purity, and impurities)”. The proposed restriction measures did not fully identify and list the specific chemical substances recommended for restriction. On the contrary, it prohibits the manufacture, use, or placing on the market of any substance that contains at least one perfluoromethyl ($_{CF3}$-) or methylene (-$_{CF2}$-) carbon atom without accompanying H/Cl/Br/I. It did not provide the names or identification numbers of the specific substances covered by this broad definition as required.

The scope of the proposed PFAS restrictions is based on the OECD definition of PFAS. This definition is based solely on the chemical structure without considering

the hazardous properties or risks recognized by the proposed restrictions of perfluoroaromatic hydrocarbons, which are substances with very different physical, chemical and biological characteristics and behaviors[13]. This broad definition does not consider the specific and unique properties of different PFAS individuals, making it unsuitable for the purposes of regulatory risk management. Organization for Economic Cooperation and Development (OECD) itself acknowledges that this definition "cannot lead to the conclusion that all perfluoroalkyl substances have the same characteristics, uses, exposures and risks". It can only serve as a starting point and reference point, therefore it "may be considered too broad" (OECD, 2021, *"Compilation of Terminology for Perfluoroalkyl and Polyfluoroalkyl Substances: Recommendations and Practical Guidelines*").

b. PFAS restrictions have not undergone legal and scientific risk assessments

The scope of the proposed restrictions is very broad, which is based on OECD PFAS definition, EU has not conducted a legally and scientifically reasonable risk assessment. The proposed restriction categorizes all perfluorinated pollutants into one group for risk assessment without identifying and considering the specific and unique characteristics of each perfluorinated pollutant or perfluorinated pollutants subgroup, and thus it can not evaluate and describe the hazards and risks associated with these characteristics so as to demonstrate that they pose unacceptable risks to human health or the environment.

Before taking the preventive measures, a scientific risk assessment must be conducted, which includes four steps: hazard identification, hazard characteristics, exposure assessment and risk characteristics. And the four steps were not followed in PFAS restriction recommendations. The so-called hazards of PFAS have not been confirmed yet, and there is also little actual contact with PFAS. These factors are proposed based on unproven assumptions. In absence of reliable information on hazards and contact, there is no basis to determine the characteristics of the risks, and therefore it is not possible to conduct the necessary scientific risk assessment for the

application of prevention principles.

c. PFAS restrictions did not take into account the effects on the entire economy and society

The proposed PFAS restrictions includes tens of thousands of organic fluorine compounds, which are widely used in various industries, from as big as aircraft and automotive manufacturing to as small as plastic products of such as films, which have penetrated into everyone's daily life. However, the proposed PFAS restrictions did not provide a substantive evaluation of "available alternative solutions", including: 1) if alternatives have been identified, they must be compared with the risks and benefits of the substances recommended for restricted use; 2) If no alternative has been found, the risks of continuing to use the substances recommended for restricted use should be compared to the socio-economic consequences of no longer using these substances without available alternatives.

Preventive measures must be reasonable with non discriminatory, and consistent with similar measures based on examining potential benefits and costs. But the proposed PFAS restrictions by EU did not achieve this. Therefore, 1) it mainly restricts the entire category of PFAS for all applications based on “persistent issues”; 2) It did not fully evaluate the risks and applicability of the so-called available alternatives, and 3) it did not fully evaluate the socio-economic effects of this broad restriction on the so-called “significant benefits”..

Given the above situation, we thnik it is too absolute to list the entire hydrofluoroethers as PFAS. We suggest that EU countries limit the scope of restrictions to necessary, essential, reasonable, scientific and specific levels, rather than simply denying or limiting a series of fluorinated compounds with the same chemical structural units; On the other hand, if the scope of restrictions remains unchanged, it is recommended that EU should consider extending the transition period of restrictions, so that we have sufficient and necessary time to develop suitable alternatives.

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