## **FSSA ECHA Science**

25 September 2023

## **Executive Summary**

FSSA supports rational, science-based efforts to eliminate sources of harm to humans and the environment. Eliminating all PFAS materials due to an unnecessarily broad classification of compounds creates a high risk to society. Because of this, we advocate for a scientific approach that distinguishes Persistent, Bioaccumulative and Toxic PFAS (PBTs) compounds from those that are not known to be PBT or are less so, based upon the best available science. Current science supports that clean extinguishing agents used in fire and explosion protection applications are generally safe when used in accordance with current codes and standards. Any proposed regulation of the sale or use of PFAS should exclude Clean Agents.

Treating all PFAS compounds as a single regulatory group is an approach that is inappropriate and unnecessary. PFAS is a large, diverse group of chemical compounds. All PFAS are not the same - their properties vary widely. Chemical and structural differences among different types of PFAS result in vast differences in physical-chemical properties. Their striking differences, both chemically and physically, must be considered in any effort to understand and address potential health and/or environmental risks.

Implementing broad regulations that ban all PFAS compounds without first considering the scientific evidence and carefully assessing what impact such a ban could have on society, could result in unintended consequences. Furthermore, banning all PFAS compounds is likely to hamper the ability of businesses and consumers to access essential products and obtain replacement parts that are needed to keep mission-critical operations functioning.

Clean extinguishing agents are components recognized and approved for use in listed and/or approved fire suppression systems. They are neat agents or blends of neat agents and are not designed with water as a functional component. Clean extinguishing agents have no affinity to water, nor do they partition to groundwater. They are not PFOA nor PFOS. They are non-ozone depleting and their use has been highly regulated for decades.

A risk assessment for halocarbon clean extinguishing agents (herein referred to as clean extinguishing agents) meeting the definition of per and polyfluoroalkyl substances (PFAS) allows these fire suppression alternatives to be used safely and responsibly in a manner to the satisfaction of the Authority Having Jurisdiction (AHJ) and to comply with regulatory restrictions in force. In addition, other important stakeholders are typically included in the risk assessment process. All involved contribute to an informed protection decision so a proper approval can be promulgated and an effective protection system implemented.

Those stakeholders normally are:

- a. Registered professional engineers experienced in fire protection and life safety system design and risk assessment.
- b. The owner or owner's representative.
- c. Insurance Authority.
- d. Representatives of the authority having jurisdiction.
- e. Representatives of emergency response entities.
- f. Building design professionals (architectural, structural, civil, mechanical, plumbing, and electrical design professionals).

Systems using clean extinguishing agents are designed for fast detection and extinguishment, leaving no residue or contamination. Using sustainable, clean agent protection reduces costs from potential fire damage or remediation due to non-clean agent system discharges while minimizing installation, ongoing inspection, testing and maintenance costs.

There are multiple clean extinguishing agents currently in commercial use today. They protect data and telecommunications centers, power facilities, aircraft, museums, archives, and military installations and equipment -- all hazards with high damageability should they be left unprotected or exposed to foam or water. Systems using clean extinguishing agents have been installed in hundreds 100s of thousands of applications globally since the early 1990s and are subject to current and future regulatory mandates to assure their responsible use.

For the sake of example, we will focus in detail on one clean extinguishing agent that meets the definition of PFAS, FK-5-1-12, recognized for its versatility in a broad spectrum of critical applications.

## Environmental and Regulatory Considerations

FK-5-1-12 is listed by the USEPA under the Significant New Alternatives Policy (SNAP) program as acceptable for total flooding end use for both normally occupied and unoccupied spaces as well as streaming applications. Excerpted from the final rule promulgated in 2002<sup>i</sup>:

"EPA has reviewed the potential environmental impacts of this substitute and has concluded that, by comparison to halon 1301 and other acceptable substitutes, C6perfluoroketone [FK-5-1-12] significantly reduces overall risk to the environment. With no ozone-depletion potential, a global warming potential value of less than 100, and an atmospheric lifetime of less than three days, C6-perfluoroketone provides an improvement over use of halon 1301, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) in fire protection. We find that C6- perfluoro ketone is acceptable because it reduces overall risk to public health and the environment in the end use listed."

FK-5-1-12 complies with all relevant, global regulatory requirements. Table 1 below is a list of the agencies for which FK-5-1-12 has gained chemical registry approvals:

## **Chemical Registry Approvals**

Chemical: dodecafluoro-2-methylpentan-3-one (FK-5-1-12) CAS#:756-13-8

Country/Region	Status
USA (TSCA)	Listed
Canada (CDSL)	Listed
EU (ELINCS)	EC# 436-710-6
Australia (AICS)	Listed
Japan (METI)	METI# (2)-4024
Korea (KECI)	KECI# 2002-3-2022
China (IECSC)	Listed
Philippines (PICCS)	Listed

 Table 1: Global Chemical Registry Approvals for FK-5-1-12

#### **PFOA and PFOS**

FK-5-1-12 is a neat (pure, single component) agent. Industry end users recognize the dangers of PFOA and PFOS as the environmentally and biologically dangerous molecules subject to current regulatory scrutiny. FK-5-1-12, like all other clean extinguishing agents, has no affinity with PFOA or PFOS, functional components in AFFF (Aqueous Film Forming Foam). Unlike AFFF, which may partition to the groundwater in end use, FK-5-1-12 will quickly become a gas when discharged from a properly designed fire protection system, and it partitions to the atmosphere breaking down within about one week. Thus, FK-5-1-12 is not considered persistent in the environment.

Clean extinguishing agents like FK-5-1-12 have been extensively evaluated for their suitability in the intended applications and their safety in the intended uses. Important information regarding responsible use of clean extinguishing agents can be found at:

## **US Government:**

#### Strategic Environmental Research and Development Program (SERDP) Environmental Security Technology Certification Program (ESTCP) Phone (571) 372-6565

4800 Mark Center Drive, Suite 16F16, Alexandria, VA 22350-3605 https://www.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs

## Industry Fire Fighting Foam Coalition

The environmental voice for users and manufacturers of AFFF 1001 19th Street, Suite 1200 Arlington, VA 22209 <u>cortinaec@comcast.net</u> (571) 384-7915 Phone | (571) 384-7959 Fax https://www.fffc.org/

## **Atmospheric Chemistry of FK-5-1-12**

A study conducted by MIT<sup>ii</sup> examined the atmospheric loss mechanisms for C2F5C(O)CF(CF3)2 commercially known at the time as 3M<sup>™</sup> Novec<sup>™</sup> 1230 Fire Protection Fluid commonly referred to as FK-5-1-12. The authors of this study determined that this compound does not react with hydroxyl radical (OH), but that substantial decay occurs when exposed to UV radiation. The authors measured the UV cross-section for FK-5-1-12 finding a maximum wavelength of absorbance at 306 nm. Since this compound shows significant absorbance at wavelengths above 300 nm, photolysis in the lower atmosphere will be a significant sink for this compound. The authors conclude that "In fact, the absorption spectrum is similar to that of acetaldehyde<sup>iii</sup>, a species whose lifetime against solar photolysis is about 5 days<sup>iv</sup>.

The absorption cross sections of L-15566 (the experimental product designation at the time for FK-5-1-12) are somewhat larger; hence, we expect the atmospheric lifetime of L-15566 against solar radiation to be of the order of 3 to 5 days".

Subsequent 3M laboratory measurements of the photodissociation rate of FK-5-1-12 found it to be equivalent to that of acetaldehyde, within experimental error<sup>v</sup>. Hence, an atmospheric lifetime of 5 days is appropriate for FK-5-1-12. The potential for FK-5-1-12 to impact the radiative balance in the atmosphere (i.e., climate change) is limited by its very short atmospheric lifetime and low global warming potential (GWP). The quantitative IR cross-section of FK-5-1-12 was measured in accordance with section 4.6 of the US EPA FTIR Protocol<sup>vi</sup>. The IR measurements were made with a 0.5 cm<sup>-1</sup> spectral resolution at 293K on a MIDAC (Model I2001) FTIR spectrometer which employs a mercury-cadmium-telluride infrared detector maintained at 77 K. The experimental setup used a nominal 4 m pathlength which was calibrated using certified ethylene gas standards.

Using the measured IR cross-section and the method of Pinnock et al<sup>vii</sup> the instantaneous radiative forcing for FK-5-1-12 is calculated to be 0.50 Wm<sup>-2</sup> ppbv<sup>-1</sup>. This radiative forcing value and a 5-day atmospheric lifetime results in a GWP value of 1 using the WMO 1998 method<sup>viii</sup> and a 100-year integration time horizon. Clearly, compounds with such short atmospheric lifetimes are of no concern with respect to potential climate change.

FK-5-1-12 is expected to rapidly degrade in the atmosphere to fluorinated alkyl radicals (CF3CF2-, CF3CF-CF3) similar to those produced by other fluorochemicals. Studies of the atmospheric chemistry of these radicals and their degradation products have concluded that they have no impact on stratospheric ozone<sup>ix</sup>. This, combined with its very short atmospheric lifetime, leads to the conclusion that FK-5-1-12, like other fluorinated compounds, has an ozone depletion potential of zero. The degradation products resulting from the atmospheric decomposition of FK-5-1-12 (CO2, HF, CF3COOH) are similar to those produced by other fluorochemicals and are not expected to pose any significant environmental hazard.

See Table 2 below of environmental properties of FK-5-1-12 compared with other gaseous clean agents in use:

Properties	FK-5-1-12	Halon 1211	Halon 1301	HFC-125	HFC-227ea
Ozone Depletion Potential (ODP) <sup>1</sup>	0.0	4.0	12.0	0.0	0.0
Global Warming Potential (CO <sub>2</sub> = 1) IPCC <sup>2</sup>	0.114	1930	7200	3740	3600
Atmospheric Lifetime (years) IPCC <sup>2</sup>	0.019	16	72	30	36
US EPA SNAP listed	Yes	N/A	N/A	Yes	Yes

<sup>1</sup> World Meteorological Organization 1998, Model Derived

<sup>2</sup> Intergovernmental Panel or Climate Change (IPCC) 2021, 6AR Method, 100 Year integrated time horizon Table 2: Environmental Properties Comparison of Clean Extinguishing Agents

#### Toxicity Assessment

FK-5-1-12 has been independently tested for required toxicological endpoints at Huntington Research (UK and USA) and NOTOX (NL). The results included in Table 3 are:

Properties	FK-5-1-12		
4-hour Acute Inhalation	Practically Non-Toxic (LC50 >10,000 ppm)		
Cardiac Sensitization	Not a Sensitizer (NOAEL = 100,000ppm)		
Acute Dermal Toxicity	Low Toxicity (LD50 > 2000 mg/kg		
Ames Assay	Negative		
Primary Skin Irritation	Non-Irritating		
Primary Eye Irritation	Minimally Irritating		
Acute Oral Toxicity	Low Toxicity (LD50 > 2000 mg/kg		
Skin Sensitization	Not a Skin Sensitizer		
Chromosomal Aberration	Negative		

 Table 3: Toxicity Test Results of FK-5-1-12

The no observable adverse effect level (NOAEL) of FK-5-1-12 for any end point of acute toxicity has been determined to be 10 volume percent (100,000ppmv) in air. With a NOAEL of 10%, there is consensus that FK-5-1-12 is safe for its intended end use and provides a large margin of safety relative to the typical design concentrations of fire protection systems. Typical design concentrations in the range of 4.5 to 6.0 volume percent result in safety margins of 67% to 122%, giving FK-5-1-12 the widest margin of safety amongst commercially viable clean extinguishing agents. See Table 4.

Agent	FK-5-1-12	Halon 1301	HFC-125	HFC-227ea
Use Concentration(1)	4.5-6%	5%	8.7-12.1%	6.7-8.7%
NOAEL(2)	10%(3)	5%	7.5%	9%
Safety Margin(4)	67-122%	Nil	Nil	3-34%

<sup>1</sup>Adjusted per 2012 NFPA 2001 requirement for minimum values (excluding halon) paragraph 5.4.2.4 and Table A.5.4.2.2(b)

<sup>2</sup> NOAEL for cardiac sensitization

3 NOAEL for acute toxicity, including cardiac sensitization

4 Safety Margin = (NOAEL - Use Concentration)/Use Concentration

#### Table 4: Safety Margin Comparison of Halogenated Clean Extinguishing Agents

#### Products of Thermal Decomposition

The following background discussion and references can be found in a WPI thesis paper by Ditch<sup>x</sup>, with a focus on FK-5-1-12, referred to in the Thesis as the experimental product designation L-15566. References also include voluminous data on other clean extinguishing agents.

Human safety can arguably be the most important consideration when dealing with any fire extinguishing agent, with two toxicological aspects to consider for clean extinguishing agents: a toxicity assessment of the agent itself and that of the thermal decomposition products (TDP) generated when a halocarbon clean agent is discharged under fire conditions<sup>xi</sup>.

The TDPs are those compounds produced due to an agent's exposure to a fire. The TDPs of halocarbon clean agents like FK-5-1-12 have been extensively investigated. When halocarbons thermally decompose upon exposure to a fire. the TDPs of most concern are hydrogen halides (HX) and carbonyl halides (COX2)<sup>xii</sup>.

Concerns over the effects of exposure to acid gases have led to several studies on the effects of the concentrations of these exposure levels<sup>xiii</sup> xiv xv xvi. Studies have shown that acid-gas production by in-kind halocarbons in total flooding applications is between two and 10 times greater than that of halon 1301. It has also been shown that the three key factors resulting in thermal decomposition production are the fire size-to-volume ratio, the agent volumetric concentration, and the discharge time.<sup>xvii</sup>

To illustrate, a composite of Peatross and Ditch work is shown in the following graphic excerpted from the thesis (Figure 3). It shows plotted HF produced as a function of a normalized fire size/room volume ratio. Peatross examined fires ranging from 0.1 kw to greater than 8.0 MW size fires conducted at <del>and</del> numerous laboratories, including, for example, the NRL, USAF, USCG, Hughes Associates, NMERI, agent, and OEM equipment manufacturers.



Figure 3: Comparison of TDP for halon alternatives (Peatross et al<sup>xvii</sup> plus Ditch<sup>xv</sup> data for L-15566. were L-15566 = FK-5-1-12)

The key takeaway here is to understand the thermal decomposition reality, that the fire size to room volume ratio is important. One must design to keep the fire small relative to room volume. The smaller fire size to room volume ratios results in a lower less chance to develop high thermal decomposition concentrations.

Figures 4 and 5 excerpted from Ditch show the resultant TDP when the fire size/room volume is LARGE and when it is SMALL.



Figure 4: Data from Master's Thesis – Ditch, BD, WPI, 2002



Figure 5: Data from Master's Thesis – Ditch, BD, WPI, 2002

Ditch and other researchers referenced in the thesis also confirmed that increases in agent concentration and shortening the extinguishing time dramatically reduces TDP, in some tests by 50% or more.

Bottom line, a properly designed system using clean extinguishing agents, like FK-5-1-12, with advanced detection technology currently in industry use, can minimize TDP by detecting and extinguishing a fire rapidly in a protected space before it gets large, keeping the fire size/room volume ratio small.

## **Conclusion and Final Assessment**

A risk assessment involving all the stakeholders provides confidence that to the best of their ability, the design team has considered and determined this to be the best approach operationally, regulatorily, environmentally, and with consideration of life safety.

Clean extinguishing agents are generally safe in end use protecting both people and assets when properly designed and engineered in advanced fire suppression systems. Designed for fast detection and extinguishment, the clean extinguishing agent systems can readily be engineered to minimize thermal decomposition to very low levels.

The FSSA is concerned that a "total ban" approach to PFAS compounds could impact society's ability to protect mission-critical applications that keep people safe without a more comprehensive safety risk cost analysis. The FSSA strongly urges ECHA to use methodical, data-driven methods with respect to PFAS rulemaking for clean agents in critical fire and life safety applications. Any regulation restricting the manufacture, import, distribution, sale, or use of PFAS should exclude Clean Agents when used in fire and explosion protection applications.

# References

<sup>&</sup>lt;sup>i</sup> Federal Register/Vol. 67, No. 245/Friday, December 20, 2002/Rules and Regulations 77931-77932

<sup>&</sup>lt;sup>ii</sup> Guschin, A.G., Molina, L.T., and Molina, M.J., Atmospheric Chemistry of L-15381, L-15566 and L-14703 and Integrated Band Strengths of L-14374, L-14375, L-14752, L-13453 and L- 14703, Report prepared for 3M Company, July, 1999.

<sup>&</sup>lt;sup>III</sup> Finlayson-Pitts, B.J. and Pitts Jr., J.N., Atmospheric Chemistry: Fundamentals and Experimental Techniques; John Wiley & Sons, New York, 196, 1986.

<sup>&</sup>lt;sup>iv</sup> Seinfeld, J.H. and Prandis, S.N., Atmospheric Chemistry and Physics, John Wiley & Sons, New York, 288, 1998. <sup>v</sup> Plummer, G., "Laboratory measurements and calculations related to the photo-disassociation of L-15566 in the Earth's lower atmosphere," 3M Environmental Laboratory Report Number E01-0549, 2001.

<sup>&</sup>lt;sup>vi</sup> Addendum to Method 320 – Protocol for the Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry for the Analyses of Gaseous Emissions from Stationary Sources (40 CFR Part 63).

<sup>&</sup>lt;sup>vii</sup> Pinnock, S., Hurley, M.D., Shine, K.P., Wallington, T.J., Smyth, T.J., J. Geophys. Res., 100, 23227, 1995.

 <sup>&</sup>lt;sup>viii</sup> WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 1998, Global Ozone Research and Monitoring Project – Report No. 44, World Meteorological Organization, Geneva, Switzerland, 1999.
 <sup>ix</sup> Wallington, T.J., Schneider, W.F., Worsnop, D.R., Nielsen, O.J., Sehested, J., Debruyn, W.J., Shorter, J.A., Environ. Sci. Technol., 28, 320, 1994.

<sup>&</sup>lt;sup>×</sup> Ditch, BD, WPI Thesis, Thermal Decomposition Products Testing With 1,1,1,2,2,4,5,5,5 nonafluoro-4-trifluoromethyl pentan-3-one (C<sub>6</sub> F-ketone) During Fire Extinguishing, December, 2002.

<sup>&</sup>lt;sup>xi</sup> J.Z. Su, A.K. Kim, J.R. Mawhinney, "Review of Total Flooding Gaseous Agents as Halon 1301 substitutes," Journal of Fire Protection Engineering, 8 (2), pp 45-64, 1996

<sup>xii</sup> P.J. DiNenno, E.W. Forssell, M.J. Peatross, M. Maynard, "Evaluation of Alternative Agents for Halon 1301 in Total Flooding Suppression Systems – Thermal Decomposition Product Testing," Halon Options Technical Working Conference, Albuquerque, NM, 1993

<sup>xiii</sup> M. Meldrum, "Toxicology of Substances in Relation to Major Hazards: Hydrogen Fluoride," Health and Safety Executive, ISBN 11 882100 8, 1993

xiv A.H. Mann, "Possible Health Risks From Exposure to Hydrogen Fluoride Generated From the Use of Fluoride-Containing Fire Extinguishing Agents," Robens Institute of Industrial and Environmental Health & Safety, University of Surrey, Guildford, Surrey, United Kingdom, 1996

<sup>xv</sup> D.P. Kelly, "A Review of the Inhalation Toxicity of Hydrogen Fluoride," Halon Options Technical Working Conference, Albuquerque, NM, 1998

<sup>xvi</sup> W.J. Brock, "Hydrogen Fluoride: How Toxic is Toxic? (A Hazard and Risk Analysis)," Halon Options Technical Working Conference, Albuquerque, NM, 1999

<sup>xvii</sup> M.J. Peatross, "A Review of Thermal Decomposition Product Testing of Halocarbon Fire Suppression Agents," Halon Options Technical Working Conference, Albuquerque, NM, 1998