UNDERSTANDING THE STABILITY AND ENVIRONMENTAL CHARACTERISTICS OF A SUSTAINABLE HALON ALTERNATIVE

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ABSTRACT

FK-5-1-12 [$CF_3CF_2C(O)CF(CF_3)_2$] is a fluorinated ketone recently introduced as a halon alternative. As the industry begins to use this new compound as a clean agent, a review of its atmospheric chemistry is needed. Results are discussed with respect to atmospheric loss rates via various mechanisms and the effect on the atmospheric lifetime of this compound. Research has shown that a fluorinated ketone will decompose in the lower atmosphere leading to an atmospheric lifetime on the order of days rather than years. Though this new compound degrades rapidly in the environment, use as a clean agent requires that the material possess the chemical stability to remain unchanged throughout the working life of a fire protection system. Data from accelerated aging and other studies demonstrate this material to be stable under typical conditions of use. This combination of properties indicates that FK-5-1-12 is a sustainable alternative to halons, perfluorocarbons and hydrofluorocarbons in clean agent applications.

INTRODUCTION

Research into halon alternatives has repeatedly demonstrated that sustainable substitutes require a complex combination of properties. As difficult as the search for non-ozone depleting alternatives to halon has been, concerns over potential climate change have presented the fire protection industry with even greater challenges. The search for low global warming potential compounds has progressed slowly. Sustainable replacements for halon need to be both efficient at extinguishing and low in toxicity. However, the chemical properties providing these attributes are frequently at odds with the goal of creating a material with a low global warming potential. It has often appeared that the goals of creating compounds that are atmospherically short-lived, safe and effective to use were nearly mutually exclusive.

Most in-kind replacements for halon have been halogenated alkanes. This first generation of alternatives has typically provided the extinguishing capability and stability required of clean agents. However, the stability provided via a high degree of fluorination also typically creates a material that can be long-lived in the atmosphere. A class of compounds recently developed for fire protection has been shown to combine both the performance and environmental attributes sought by the industry. Fluoroketones have surprisingly short atmospheric lifetimes and yet have exhibited the stability necessary for use as an extinguishing agent.

FK-5-1-12 [$CF_3CF_2C(O)CF(CF_3)_2$] has recently been introduced as an alternative to halon 1301 and some of the first generation replacements. This new compound has been shown to have the physical and toxicological properties required to function as a clean agent for the protection of special hazards, including occupied spaces [1,2].

With the recognition of the deleterious effects of halons on stratospheric ozone, it has become necessary to evaluate the impact of alternative extinguishing agents on the environment. Prior to the Montreal Protocol, the annual emission rate for halons was 15% of the installed base [3]. The prohibition of discharge tests and industry efforts have reduced the current halon emissions rates to approximately 5%. The fire protection industry predicts that continued efforts could reduce the rate of extinguishing agent emissions. However, the ultimate disposition for the agent in most cases is release to the atmosphere. As a result, a full evaluation of the environmental fate and effects of releasing an extinguishing agent to the atmosphere is required prior to its large-scale adoption as a halon alternative.

ATMOSPHERE LIFETIME OF FK-5-1-12

Once emitted to the environment, there are a number ways for organic compounds to be removed from the atmosphere. Studies conducted on FK-5-1-12 have determined the atmospheric loss rates via these removal mechanisms and the effect on the atmospheric lifetime of this compound. Oxidation by hydroxyl radical and wet deposition/rain out are ineffective at removing this compound from the atmosphere. The principal atmospheric sink for FK-5-1-12 is clearly photolysis.

<u>Oxidation</u>: For many organic compounds released to the environment, a significant atmospheric sink is oxidation via reaction with the hydroxyl radical (OH▶). The hydroxyl radical is the most important reactive species in the lower atmosphere, reacting with many trace gases. Compounds containing carbon-hydrogen bonds react by abstraction of a proton with subsequent decomposition of the alkyl radical produced. The hydroxyl radical can also undergo an addition reaction with olefins and aromatic compounds resulting in formation of a hydroxyalkyl radical which will further decompose. Atmospheric degradation of organic compounds via reaction with hydroxyl radical leads to lifetimes on the order of days to years, depending upon the kinetics of that reaction.

Fully fluorinated ketones are unreactive with hydroxyl radical. These compounds are in a highly oxidized state and hence are not further oxidized by reaction with hydroxyl radical in the atmosphere. An upper limit on the rate constant for reaction of FK-5-1-12 with OH has been established at $< 5 \times 10^{-16}$ $cm^3 molecule^{-1} s^{-1}$ [4]. If this were the only atmospheric sink for this compound, such a limited reactivity would lead to an atmospheric lifetime greater than 100 years.

Wet Deposition: A number of trace species are removed from the atmosphere via wet deposition or rain out by dissolution into cloud and fog drops or precipitation. For materials with sufficiently high water solubility this can result in removal from the atmosphere in days to weeks. Wet deposition is highly effective at removing many inorganic materials from the atmosphere. However, most organic compounds are too volatile and possess such low solubility in water that wet deposition plays an insignificant role in their atmospheric removal. Even compounds with extremely high water solubility, such as acetone are removed from the atmosphere primarily by other loss mechanisms. The Henry's law constant (H_A) represents the distribution of a compound between the gaseous and aqueous phases of the atmosphere.

$$\text{A(aqueous phase)} \leftrightarrow \text{A(gas phase)}$$

$$[A(aq)] = H_A \blacktriangleright p_A \tag{1}$$

where $[A(aq)]$ is the concentration of compound A in the aqueous phase, p_A is the vapor pressure of A and H_A is the Henry's law constant for A representing the proportionality constant.

A substantial fraction of a compound partitions into the aqueous phase only if H_A is $>$ 5000 M atm^{-1}. For compounds with H_A less than 400 M/atm^{-1}, only 1% of its mass is dissolved in the aqueous phase [5]. The Henry's law constant for FK-5-1-12 is 8 x 10^{-6} M atm^{-1} based upon its solubility in water (0.0032 mol m^{-3}) and its vapor pressure (0.4 atm). Such a low H_A indicates that an extremely small fraction of the FK-5-1-12 released to the atmosphere will be dissolved into a condensed water phase. However, mass transport into the aqueous phase can be enhanced if dissolution into water is followed by dissociation or reaction of the compound.

Fluorinated ketones such as hexafluoroacetone are known to hydrolyze quite vigorously. Although FK-5-1-12 does not exhibit this highly exothermic reaction with water, it has been found to undergo hydrolysis. This transformation in water could enhance the removal of FK-5-1-12 via wet deposition. However, a detailed assessment of the atmospheric distribution of FK-5-1-12 has found that uptake into water and hydrolysis plays an insignificant role in its atmospheric removal [6]. This assessment evaluated both equilibrium and non-equilibrium conditions for transport of the ketone between air and the liquid water phase in the atmosphere. Assuming equilibrium is reached, the removal of FK-5-1-12 via hydrolysis and/or rainout alone would lead to an atmospheric lifetime greater than 1600 years. Non-equilibrium conditions, which are more likely to occur, would lead to a longer lifetime since even lower concentrations of FK-5-1-12 will diffuse into atmospheric water droplets. As found with other compounds exhibiting extremely low water solubility, FK-5-1-12 is not effectively removed from the atmosphere via wet deposition or rainout.

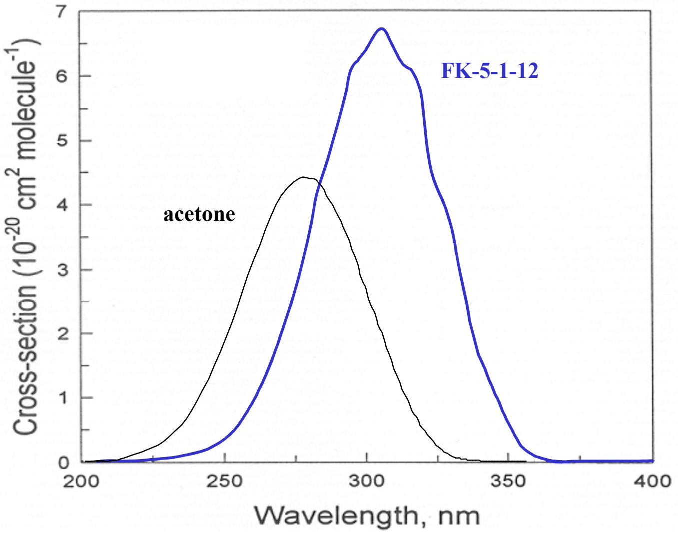
Photolysis: Many compounds in the atmosphere decompose upon absorption of certain wavelengths of sunlight. This photolysis process varies with altitude due to the change in the wavelengths of light that penetrate the atmosphere. Only longer wavelength (lower energy) light penetrates into the lower atmosphere due to the absorbance of the shorter wavelengths of light (higher energy) by the natural atmosphere. As a result, compounds that require shorter wavelengths of light for decomposition will travel to much higher altitudes for photolysis to occur. The halons were subject to photolysis at short enough wavelengths (200-220 nm) that they were transported well into the stratosphere (10-50 km) prior to decomposition, resulting in atmospheric lifetimes on the order of decades. Compounds that absorb energy at much longer wavelengths, approaching the near ultraviolet (UV) at 300 nm or higher, will have much shorter atmospheric lifetimes.

Common ketones, such as acetone, have peak UV absorption around 280 nm. However, the fluorinated analogues of these ketones exhibit a bathochromic shift in absorbance (i.e., absorbance at higher wavelengths). Many fluoroketones demonstrate strong UV absorption with a maximum absorbance just above 300 nm as shown in Table 1. FK-5-1-12 exhibits significant absorbance in the near UV with a maximum absorbance at 305 nm (see Figure 1 below).

Table 1. UV Absorption of Fluorinated Ketones

Compound	Peak UV Absorption (nm)
$CF_3C(O)CF_3$	302
$CF_3CF_2C(O)CF(CF_3)_2$	305
$(CF_3)_2CFC(O)CF(CF_3)_2$	302
$CF_3CF_2CF_2C(O)CF(CF_3)_2$	307

Figure 1. UV Absorption of acetone and FK-5-1-12



This strong absorption in the near UV results in a very short atmospheric lifetime for FK-5-1-12. The rate of photolysis under atmospheric conditions and the mechanism of decomposition of this compound have been investigated [4]. The rate of photolysis of

FK-5-1-12 was measured relative to that of CH_3CHO which has a known atmospheric lifetime by photolysis of 3 to 4 days. The photolysis rate of the ketone leads to an atmospheric lifetime of 4.5 to 15 days or “approximately 1-2 weeks” [4]. The authors of this study have concluded that their work is consistent with a previous study conducted by 3M which found the atmospheric lifetime of FK-5-1-12 to be on the order of 5 days or about one week [8].

Absorption of a photon from UV radiation results in cleavage of one of the carbon-carbon bonds alpha to the carbonyl group in FK-5-1-12 (i.e., CF_3CF_2▶ C(O)▶ $CF(CF_3)_2$). Scission at either of these positions results in formation of a perfluoroalkyl and perfluoroacyl radical (either CF_3CF_2(▶) and $(CF_3)_2CFC(O)$(▶) or $CF_3CF_2C(O)$(▶) and $(CF_3)_2CF$(▶)). Previous studies had indicated that under laboratory conditions the photolysis of fluorinated ketones led to formation of perfluoroalkanes [9]. These degradation products are due to the recombination of perfluoroalkyl radicals that are generated in sufficiently high concentration in a reaction cell. However, under atmospheric conditions such perfluoroalkyl radical recombination is never observed. The fate of haloalkyl radicals in the atmosphere has been studied extensively [7]. The decomposition of the perfluoroalkyl radicals produced by FK-5-1-12 is analogous to those formed from decomposition of other fluorochemicals. The concentration of FK-5-1-12 in the atmosphere will have been substantially diluted by the time significant photolysis takes place (on the order of days rather than seconds or minutes). In addition, with the inherently large concentrations of oxygen present, the perfluoroalkyl and perfluoroacyl radicals rapidly react with O_2 to form peroxy radicals (typically on the time scale of μ-seconds) [7]. In the atmosphere, the concentration of perfluoroalkyl radicals is insignificant compared to O_2 ensuring decomposition via formation of the peroxy radicals as opposed to radical recombination.

As with other haloalkyl radicals formed in the atmosphere, the peroxy radicals formed by decomposition of FK-5-1-12 will continue a series of alpha-scissions and oxidations ultimately leading to the formation of $CF_3C(O)F$ and COF_2. The carbonyl compounds are incorporated into water and hydrolyzed to $CF_3C(O)OH$, CO_2 and HF. These degradation products are the same as those produced by many of the commercially important fluorochemicals[7]. Taniguchi et al have concluded that “At the concentrations expected in the environment, none of these degradation products is considered harmful.”

OZONE DEPLETION POTENTIAL OF FK-5-1-12

As indicated above, FK-5-1-12 rapidly degrades to fluorinated alkyl radicals similar to those produced by other fluorochemicals. Studies of the atmospheric chemistry of these radical species (such as CF_3CF_2(▶) and $(CF_3)_2CF$(▶)) and their degradation products (such as CF_3(▶)) have concluded that they have no impact on stratospheric ozone [7]. This leads to the conclusion that FK-5-1-12, like other compounds containing only the halogen fluorine, has an ozone depletion potential of zero.

GLOBAL WARMING POTENTIAL OF FK-5-1-12

The Global Warming Potential (GWP) is an index that provides a relative measure of the possible climate impact due to a compound which acts as a greenhouse gas in the atmosphere. The GWP of a compound, as defined by the Intergovernmental Panel on Climate Change (IPCC), is calculated as the integrated radiative forcing due to the release of 1 kilogram of that compound relative to the warming due to 1 kilogram of CO_2 over a specified period of time (the integration time horizon (ITH)):

$$GWP_x = \frac{\int_0^{ITH} F_x C_{xo} \exp(-t/\tau_x)\, dt}{\int_0^{ITH} F_{CO_2} C_{CO_2}(t)\, dt} \tag{2}$$

where F is the radiative forcing per unit mass of a compound (the change in the flux of radiation through the atmosphere due to the infrared (IR) absorbance of that compound), C is the atmospheric concentration of a compound, τ is the atmospheric lifetime of a compound, t is time and x is the compound of interest [10].

The commonly accepted ITH is 100 years representing a compromise between short-term effects (20 years) and longer-term effects (500 years or longer). The concentration of an organic compound, x, in the atmosphere is assumed to follow pseudo first order kinetics (i.e., exponential decay). The concentration of CO_2 over that same time interval incorporates a more complex model for the exchange and removal of CO_2 from the atmosphere (the Bern carbon cycle model).

The potential for FK-5-1-12 to have an impact on the radiative balance in the atmosphere (i.e., climate change) is limited by its very short atmospheric lifetime and low global warming potential. The quantitative IR cross-section of FK-5-1-12 was measured in accordance with section 4.6 of the U.S. EPA FTIR Protocol [11] and appears in Figure 2. The IR measurements were made with a 0.5 cm^{-1} 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. [12] the instantaneous radiative forcing for FK-5-1-12 is calculated to be 0.50 $Wm^{-2}ppbv^{-1}$. This radiative forcing value and a 5 day atmospheric lifetime results in a GWP value of 1 using the IPCC 2001 method [10] and a 100 year integration time horizon. The method of Pinnock et al. assumes that the compound emitted to the atmosphere will be well mixed throughout the troposphere. A material as short lived as FK-5-1-12 obviously does not meet this condition. As a result, this calculation over estimates the GWP. Taniguchi et al. have concluded that "With an atmospheric lifetime of 1-2 weeks, $CF_3CF_2C(O)CF(CF_3)_2$ will have a global warming potential that, for all practical purposes, is negligible."

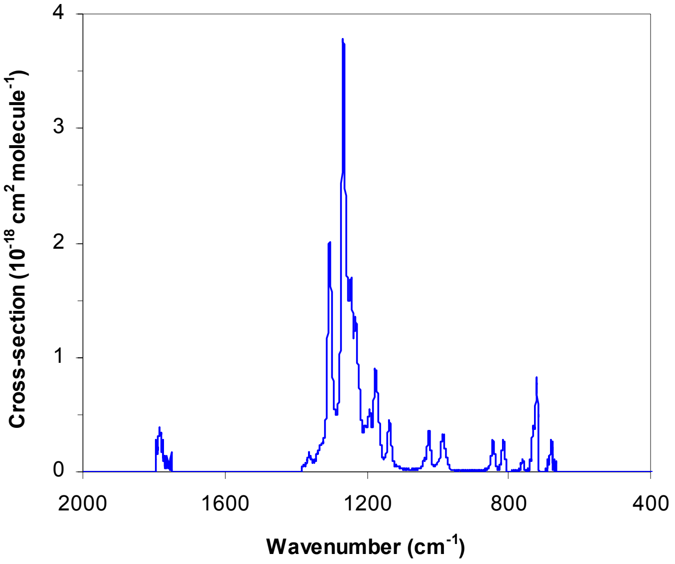
The GWP calculated thus far is the *direct* GWP which accounts for the potential warming effects due to the parent compound released to the atmosphere. In some cases, it is possible to calculate an *indirect* GWP in an attempt to account for the potential warming effects due to the atmospheric degradation products from that compound. While IPCC has indicated that these indirect GWPs are much less certain [10], it is possible to estimate an indirect GWP for FK-5-1-12 since its atmospheric chemistry is fairly well understood.

The decomposition mechanism determined by Taniguchi et al. indicates FK-5-1-12 produces fluorinated degradation products which are atmospherically short lived [7], resulting in negligible GWP. However, this decomposition mechanism indicates that one mole of FK-5-1-12 will produce 4 moles of CO_2. Since the direct GWPs are calculated on a mass basis, the indirect GWPs need to be calculated on this basis as well. Therefore, release of 1 kg of FK-5-1-12 to the atmosphere will produce 0.56 kg of CO_2.

$$1000 \text{ g FK-5-1-12}/(316 \text{ g/mol})(4 \text{ mols } CO_2/\text{mol FK-5-1-12})(44 \text{ g/mol}) = 556 \text{ g } CO_2 \qquad (3)$$

This results in an indirect GWP of 0.56, regardless of the time horizon chosen. Both the direct and indirect GWP for FK-5-1-12 are less than one. Clearly, compounds with such low GWP are not of concern with respect to potential climate change.

Figure 2
IR Cross-section of FK-5-1-12

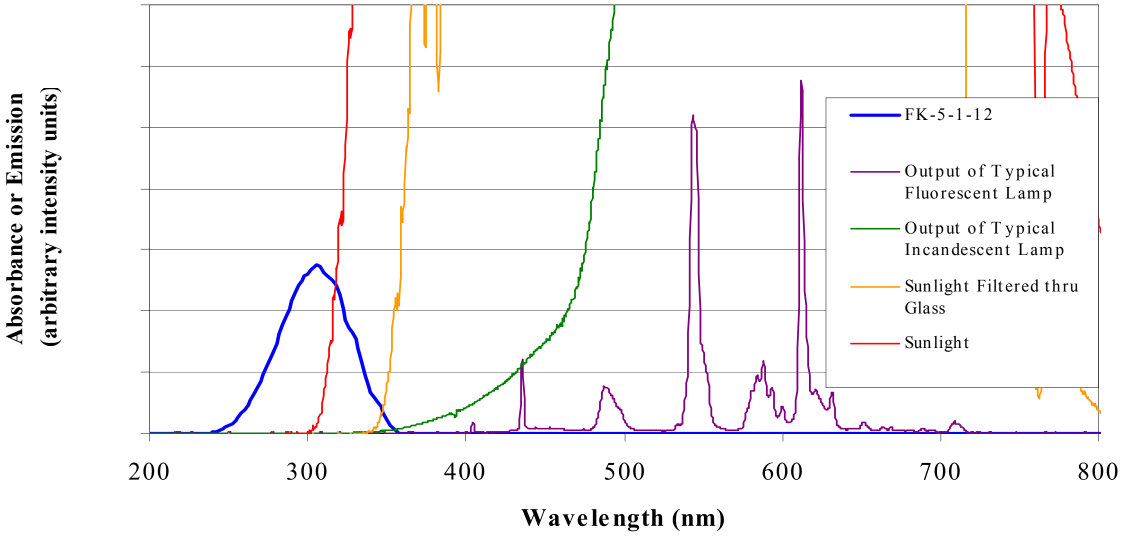


STABILITY OF FK-5-1-12 DURING USE AS A CLEAN EXTINGUISHING AGENT

Though FK-5-1-12 degrades rapidly in the environment, use as a clean agent requires that the material possess the chemical stability to remain unchanged throughout the working life of a fire protection system. Several factors need to be considered for their potential effects on an agent during handling, storage and use in a fire protection system.

Exposure to light: As discussed above, natural sunlight degrades FK-5-1-12. However, this agent is unaffected by other light sources (see Figure 3). Typical room lighting such as fluorescent or incandescent lights do not emit energy at wavelengths absorbed by FK-5-1-12. Conventional window glass filters out the lower wavelength, higher energy light from the sun leaving very little overlap with the UV absorption spectrum of FK-5-1-12. Only natural, unfiltered sunlight will degrade the agent – a condition that will not be experienced during storage of FK-5-1-12 in fire protection systems.

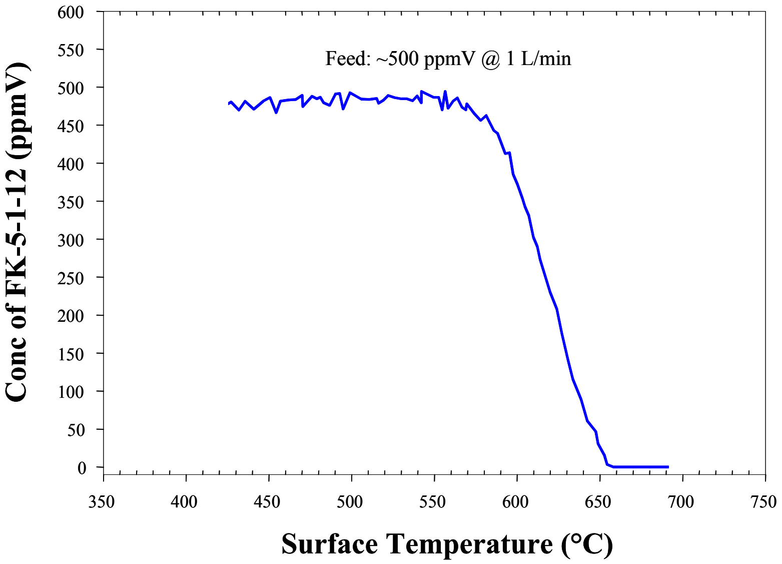
Figure 3. UV Absorption of FK-5-1-12 Compared to Light Sources



Exposure to heat: FK-5-1-12 exhibits the thermal stability typically observed with highly fluorinated compounds. Figure 4 displays the results of experiments conducted in a tube furnace. FK-5-1-12 does not show any measurable thermal decomposition until surface temperatures exceed 500°C. FK-5-1-12 will clearly be thermally stable under storage conditions in a fire suppression system. Discharge of a system in an actual fire event can of course expose the agent to temperatures exceeding 500°C when it comes into contact with the flame front. The production of thermal decomposition products during fire suppression is dependent upon a number of factors such as the size of the fire, the volume of the protected space and the time to extinguish the fire (which is related to a number of extinguishing system variables such as the agent concentration used and the time to discharge the agent). The principal thermal decomposition product generated from use of fluorine-containing extinguishing agents is hydrogen fluoride (HF). Most studies have found that alternatives to halon generate HF at concentrations 2 to 10 times that generated by halon 1301 [13]. Industry practice over the last decade has demonstrated that fire extinguishing systems using halogenated halon alternatives can be designed to minimize HF formation to prevent adding to the toxic threat of a fire event (i.e., the hazards already created by the combustion products of the fire).

Studies conducted using FK-5-1-12 have determined that the concentrations of HF produced during fire extinguishing are comparable to the HF levels produced by the fluorinated halon alternatives currently used within the industry [14]. Fire extinguishing system manufacturers recognize the importance of early detection of the fire, an optimum system discharge time and the appropriate design concentration for the specific protected space in minimizing thermal decomposition of an agent. A properly designed and operating system will prevent generation of agent thermal decomposition products to levels that would add to the hazard posed by a fire.

Figure 4. Thermal Degradation of FK-5-1-12 in Air



Long-term storage: Halon systems installed in commercial aviation, merchant shipping and military applications were expected to have a working life in excess of 30 years. It was necessary that the halon contained in those systems maintain its chemical composition throughout that period in order to effectively perform as a clean agent at the time of discharge. Similar requirements are necessary for halon alternatives.

Since FK-5-1-12 has only recently become commercially available, there are no samples of the agent which have been aged beyond 4 years. However, accelerated aging studies have been performed on this agent which predict the condition of the material over much longer periods of time. Samples of FK-5-1-12 were heat aged at 100°C for over 1500 hours in the presence of various metals (aluminum, brass, copper, plain steel, and stainless steel). Based on the van't Hoff principle this would simulate more than 30 years of aging at room temperature.

The purity of the FK-5-1-12 both before and after the heat aging is shown in Table 2. The heat aged FK-5-1-12 exhibits little change in chemical composition remaining consistent with the minimum agent purity requirements specified in clean agent fire extinguishing system standards such as NFPA 2001 and ISO 14520. Based upon these results, FK-5-1-12 has been found to be shelf stable and is expected to perform as a clean agent throughout the useful life of a properly designed, maintained and operated fire extinguishing system.

Table 2. Accelerated Aging of FK-5-1-12

Sample Condition	$CF_3CF_2C(O)CF(CF_3)_2$ purity by GC-MS, $^{19}F/^{1}H$-NMR (weight %)
Initial – 0 hours	99.93
1514 hours @ 100°C	
average of 7 samples	99.92
minimum of 7 samples	99.90

CONCLUSIONS

FK-5-1-12 is a fluorinated ketone recently commercialized as a clean extinguishing agent. It has undergone a thorough environmental assessment by both the regulatory agencies which have approved its manufacture and use as well as in the peer reviewed literature. Oxidation by hydroxyl radical and wet deposition have been shown to be ineffective at removing FK-5-1-12 from the atmosphere. This compound has been shown to rapidly photolyze in the atmosphere, leading to an atmospheric lifetime of 5 days to two weeks. The degradation products resulting from the atmospheric decomposition of FK-5-1-12 already exist in the environment and are not expected to be detrimental. The short atmospheric lifetime of FK-5-1-12 results in a direct global warming potential which is negligible. The indirect global warming potential due to the atmospheric degradation products of FK-5-1-12 is also so small that it is of no consequence. Neither FK-5-1-12 nor its degradation products affect stratospheric ozone.

Although FK-5-1-12 degrades rapidly in the environment, the compound is sufficiently stable for use as a clean extinguishing agent. Studies have shown that this material has the chemical and thermal stability to allow its handling and storage with essentially no change in composition. This combination of environmental degradability with stability in use makes FK-5-1-12 a sustainable alternative to halon and first generation alternatives such as hydrofluorocarbons and perfluorocarbons.

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