# ADVANCEMENT IN SUSTAINABLE FIRE SUPPRESSION DEVELOPMENT $C_6$ F-KETONE: A NOVEL NEW HALON REPLACEMENT ALTERNATIVE TO HFCS AND PFCS

Paul E. Rivers
3M Specialty Materials Division

## INTRODUCTION

In the past year, **3M** has made significant gains in the development of a new product to be used **as** a halon replacement alternative to conventional first generation solutions, particularly HFCs. Actually, it is not just a new product that has been developed. Rather a whole new patent-pending technology platform **has** been developed for a number **of** industrial and commercial applications. There has been initial success in fire protection applications of this new product, a 6-carbon fluorinated ketone commercially known **as** 3M™ Novec™ Fire Protection Fluid **1230,** with a chemical formula of $CF_3CF_2C(O)\,CF(CF_3)_2$ or dodecafluoro-2-methylpentan-3-one. This has resulted in a new sustainable fire protection product being the furthest along of **all** the fluorinated ketone applications toward commercialization.

## A SUSTAINABLE BALANCE – INCREASINGLY DIFFICULT FOR EXISTING TECHNOLOGIES

Choosing a halon alternative requires the fire protection engineer to consider the sustainability of the product. He must have confidence that the solution chosen can be one that is long-term. His company or client needs assurance their commitment **to** a particular solution can be done without wondering whether or not the solution will come under increasing pressure to limit its use in some way or completely eliminate it as an option. This more or less happened with PFCs in fire protection applications, it is happening for fire protection products containing HCFCs, and there is now increasing pressure to limit the use of high GWP HFC-based products to fire protection applications where there exists no other alternative that is technically feasible from a performance or safety standpoint. **A** product today must have the right balance in its intended end use of four key considerations: extinguishing performance, acceptable toxicity profile, advantageous environmental characteristics, and commercial viability. Drawbacks in any of these reduce the desirability of the extinguishing alternative under consideration.

Increasing pressure continues to be placed upon users and producers of HFCs in **all** categories of end use, not just halon replacement, due to the long atmospheric lifetime and high global warming potential of these compounds. **As** one would expect, there is industry resistance to this pressure in an effort to maintain the status **quo.**

Regardless, the fact is that other countries, including the **US,** have implemented or are implementing voluntary codes **of** practice (VCOP) that **puts** an "essential use" litmus test on the HFC product, promotes best practices with respect to the use of HFCs in fire protection, and promotes minimizing the use of HFCs. In the US VCOP, for example, proposed provisions are made to encourage prevention of <u>any</u> emissions of HFCs, using statements like "prohibit the venting **or** release into the environment of agent" and including a "verifiable data tracking and reporting system on the emissions of HFCs and PFCs across the US fire protection industry." Note that similar statements were made in the **1980s as** a precursor to the phase-out of halons.

## PROPERTIES EVALUATION OF $C_6$ F-KETONE

$C_6$ F-ketone is a liquid at room temperature. With a boiling point of **48** "C, $C_6$ F-ketone is useful **as** a streaming agent in applications such **as** handheld portable extinguishers, large capacity wheeled trolleys, and directional local application fixed systems. Since it has a relatively low heat of vaporization, $C_6$ F-ketone exhibits utility in certain localized flooding applications in fixed systems **for** small volumes. Hence, the reason the commercial designation of this material is that of a "fluid" **is** because it can act **as** a liquid and as a gas, **i.e.,** both are fluids. The fluid is pourable, low in viscosity, and easy to handle. It can be pumped well with hand or electric pumps. An advantage of being a fluid is that it can be shipped in drums or totes rather than pressurized cylinders. This means that it can be air freighted in bulk quantities if needed for refilling a system (see the properties in Table 1).

TABLE 1. $C_6$ F-KETONE PROPERTIES DESCRIPTION.

| Properties | Units |
|---|---|
| Chemical formula | $CF_3CF_2C(O)CF(CF_3)_2$ |
| Molecular weight | **316.04** |
| Boiling point @ 1 atm | **48.0 °C (118.4°F)** |
| Freezing point (pour point) | **-108** °C **(-162.4** "F) |
| Density, saturated liquid @ **25 °C** | **1.60 g/ml (99.9** lbm/ft$^3$) |
| Density, gas **1 ATM @ 25** °C | **0.0184 g/ml (1.15** lbm/ft$^3$) |
| Specific volume, **1** ATM @ **25** °C | **0.0543** m$^3$ **/kg (0.870** A' **/lb)** |
| Heat of vaporization @b.p. | **41.4** BTU/lb **(96.4** kJ/kg) |
| Liquid viscosity @ **25/0** "C | 0.41/0.56 centistokes |
| Solubility of water in $C_6F_{12}O$ @ **25** °C | <0.001 % by wt. |
| Vapor pressure @ 25.0 °C | **0.40** bar **(5.87** psia) |
| Dielectric strength | ~40-60 kV |

Products intended for use as halon replacements normally adhere to a certain level of quality. While the quality criteria may vary, a reasonable benchmark could be the NFPA 2001 specifications [1] (Table 2).

TABLE 2. HALOGENATED AGENT QUALITY REQUIREMENTS.

| Agent Purity | 99.0 mole %, Minimum |
|---|---|
| Acidity | 3.0 ppm, maximum (by weight HCL equivalent) |
| Water content | 0.001%, by weight, maximum |
| Nonvolatile residues | **0.05 g/100** ml, maximum |

In terms of purity, the manufacturing process presently used will result in a product that will significantly exceed 99.0 mole % minimum. It is expected that, once all quality specifications for manufacture of $C_6$ F-ketone are set, they will be very close to or meet the remaining specifications included in NFPA 2001. Table 3 shows a comparison of $C_6$ F-ketone with Halon 1211 and 1301 and a sample of commercially available clean agents.

TABLE 3. PROPERTIES COMPARISON.

| Properties | $C_6$ F-ketone | Halon 1211 | Halon 1301 | FC-5-1-14 | HFC 227ea | HFC 236fa | IFC 1311 | HCFC Blend B |
|---|---|---|---|---|---|---|---|---|
| Molecular weight | **316.04** | **265.38** | **148.93** | **338.0** | **170.03** | **152.04** | **195.91** | **150.7** |
| Boiling point ("C) | **48.0** | **-3.4** | **-57.8** | **56** | **-16.4** | **-1.4** | **-22.5** | **27.0** |
| Cup-burner propane fuel (% v/v)* | **3.5'** | **3.6'** | **4.3'** | **4.0'** | **6.3'** | **6.3'**<br>heptane | **3.6'**<br>heptane | **6.7'** |
| Mass to 1211 ratio | **1.86** | 1.00 | **1.08** | **2.27** | **1.80** | **1.61** | **1.09** | **1.55** |
| **Use** in occupied areas | Yes | No | Yes | Yes | Yes | Yes | No | No (flooding) |

* Propane unless noted otherwise

† **3M** Company data

‡ British Standards

§ Manufacturer's data

## COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Sufficient compatibility testing has been completed to show that $C_6$ F-ketone is very "PFC-like" in terms of its lack of reactivity with standard materials of construction. $C_6$ F-ketone has no effect on various metal types or vice versa (Table 4). Testing shows $C_6$ F-ketone to be very compatible with standard carbon steel, aluminum, or stainless containers and with copper components or standard brass valves.

TABLE 4. EFFECTS OF BOILING $C_6$ F-KETONE ON METALS.

| Product Boiling Point | $C_6$ F-ketone (48 "C) |
|---|---|
| Metals (10 days minimum exposure) | |
| Aluminum Alloy 6262 T6511 | A |
| Brass Alloy UNS C36000 | A |
| AISI Type 304L Stainless Steel | A |
| AISI Type 316L Stainless Steel | A |
| Copper UNS C12200 | **A** |
| ASTM A 516, Grade **70** carbon steel | A |

**A** = No discoloration or destruction of fluid or metal at temperatures indicated.

Table 5 shows representative samples of elastomers and their state when immersed in $C_6$ F-ketone and conditioned at ambient room temperature, and at an elevated temperature and then tested in accordance with **ASTM** standards. For elastomers and O-rings, almost any non-fluorinated material will be compatible, but material with minimal or no plasticizers will work most effectively. Note that these tests have been performed with the test samples totally immersed in the $C_6$ F-ketone. Typically, gaskets and O-rings are not normally in constant direct contact with an agent. So, this is a very conservative test to indicate the compatibility of elastomers with $C_6$ F-ketone. Extended exposure time (12 weeks and 26 weeks) for elastomers in $C_6$ F-ketone is in progress. Additionally, testing to determine the compatibility of $C_6$ F-ketone with various plastics is planned.

TABLE 5. COMPATIBILITY OF "O" RINGS WITH $C_6$ F-KETONE.

| | | | Property | | |
|---|---|---|---|---|---|
| Elastomer Type | Exposure Temp. °C | Time, wk. | Change in Shore A Hardness | %Change in Weight | % Change in Volume |
| Neoprene | 25 | 1 | -1.8 | -0.6 | -1.2 |
| | 100 | 1 | -2.2 | +2.3 | +0.8 |
| Butyl rubber | 25 | 1 | *-2.1* | +0.2 | +0.1 |
| | 100 | 1 | -4.0 | 14.3 | +4.2 |
| Fluoro elastomer | 25 | 1 | -6.2 | +0.7 | +0.6 |
| | 100 | 1 | -12.6 | +9.5 | +10.6 |
| EPDM | 25 | 1 | -4.7 | +0.6 | +0.3 |
| | 100 | 1 | -5.7 | +3.3 | +2.4 |
| Silicone | 25 | 1 | | +3.1 | +2.8 |
| | 100 | 1 | -5.4 | +6.0 | +5.1 |
| Nitrile | 25 | 1 | -0.7 | -0.3 | -0.5 |
| | 100 | 1 | +2.5 | +4.6 | +0.7 |

## TOXICITY CONSIDERATIONS FOR $C_6$ F-KETONE

$C_6$ F-ketone fluid is a fluorinated ketone. It is a material that is safe when used as intended for the expected end use. Acute toxicity testing completed shows that $C_6$ F-ketone fluid is low in toxicity. The effective toxicity exposure limit is greater then 100,000 ppm (>10% v/v) for the 4-hour acute inhalation exposure, The acute cardiac sensitization No Observed Adverse Effect Level (NOAEL) has been tested and is at 100,000 ppm (10% v/v) with the Lowest Observed Adverse Effect level (LOAEL) greater than 100,000 ppm (>10% v/v) (see the toxicity properties comparison in Table 6).

TABLE 6. TOXICITY PROPERTIES COMPARISON.

| Properties, (% v/v) | $C_6$ F-ketone | Halon 1211 | Halon 1301 | FC-5-1-14 | HFC-227ea | HFC-236fa | IFC-1311 | HCFC-Blend B |
|---|---|---|---|---|---|---|---|---|
| Physical State @ 25 °C | Liquid | Gas | Gas | Liquid | Gas | Gas | Gas | Liquid |
| LC-SO 4-hour acute Inhalation (UNO) | >10 | 20 (15 min) | >80 | >30 (@ sat) | >80 | >80 | ~ 16.0 | 3.2 |
| NOAEL/LOAEL Cardiac sensitization | 10/>10 | 1.0/2.0 | 5.0/7.5 | 17/>17 | 9.0/10.5 | 10.0/15.0 | 0.2/0.4 | 1.0/2.0 |

## ATMOSPHERIC CHEMISTRY OF $C_6$ F-KETONE

A unique property of C, F-ketone is its apparent lack of persistence when discharged into the atmosphere. A study conducted by MIT [2] examined the atmospheric loss mechanisms for $C_6$ F-ketone. The authors of this study determined that this compound does not react with hydroxyl radical (OH); however, substantial decay occurs when exposed to UV radiation. The authors measured the UV cross-section for $C_6$ F-ketone 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, “In fact, the absorption spectrum is similar to that of acetaldehyde [3], a species whose lifetime against solar photolysis is about 5 days [4]. The absorption cross sections of $C_6$ F-ketone are somewhat larger; hence, we expect the atmospheric lifetime of $C_6$ F-ketone against solar radiation to be of the order of 3 to 5 days.” Recent laboratory measurements of the photodissociation rate of C, F-ketone found it to be equivalent to that for acetaldehyde, within experimental error [5]. Hence, an atmospheric lifetime of 5 days is appropriate for C, F-ketone (Table 7).

TABLE 7. ENVIRONMENTAL COMPARISON.

| Agent | ODP | ALT, yrs | GWP (100 yr. ITH) |
|---|---|---|---|
| Halon 1211 | 4 | 11.0 | 1300 |
| C, F-ketone | 0 | 0.014 | 1 |
| FC-5-1-14 | 0 | 3200.0 | 9000 |
| HFC-227ea | 0 | 36.5 | 3800 |
| HFC-236fa | 0 | 226.0 | 9400 |
| FIC-1311 | 0.0001 | 0.005 | <1 |
| HCFC Blend B | 0.014 | 1.4 | 120’ |

* Based on HCFC-123 only. HCFC Blend B also contains CF4, a PFC with a GWP of 5700.

The potential for $C_6$ F-ketone 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). Using a measured IR cross-section and the method of Pinnock et al. [6] the instantaneous radiative forcing for $C_6$ F-ketone is calculated to be 0.50 $Wm^{-2}ppbv^{-1}$. This radiative forcing and a 5-day atmospheric lifetime results in a GWP value of 1 using the WMO 1999 method and a 100-year integration time horizon. Clearly, compounds with such short atmospheric lifetimes are of no concern with respect to potential climate change.

Actual laboratory tests simulating sunlight have been performed at 3M in an effort to validate the opinions of experts and that in the literature **as** it relates to $C_6$ F-ketone. Those tests concluded that for three days simulated sunlight, 69% of the parent compound was decomposed, lending credence to the conclusions discussed above.

$C_6$ F-ketone is expected to rapidly degrade to fluorinated alkyl radicals similar to those produced by other fluorochemicals. Studies of the atmospheric chemistry of these radical species and their degradation products have concluded that they have **no** impact on stratospheric ozone [7]. This, combined with its very short atmospheric lifetime, leads to the conclusion that $C_6$ F-ketone, like other fluorinated compounds, has an ozone depletion potential of zero.

## SYSTEM AND FIRE EXTINGUISHING PERFORMANCE CONSIDERATIONS

The unique properties of a high boiling, low vapor pressure fluid such **as** $C_6$ F-ketone are characterized in the following charts. Because of the low vapor pressure of $C_6$ F-ketone, when superpressurized to a pressure of, say, 25 bar **(360** psi), the cylinder pressure delta over a very wide range of temperatures is quite small (Figure 1).

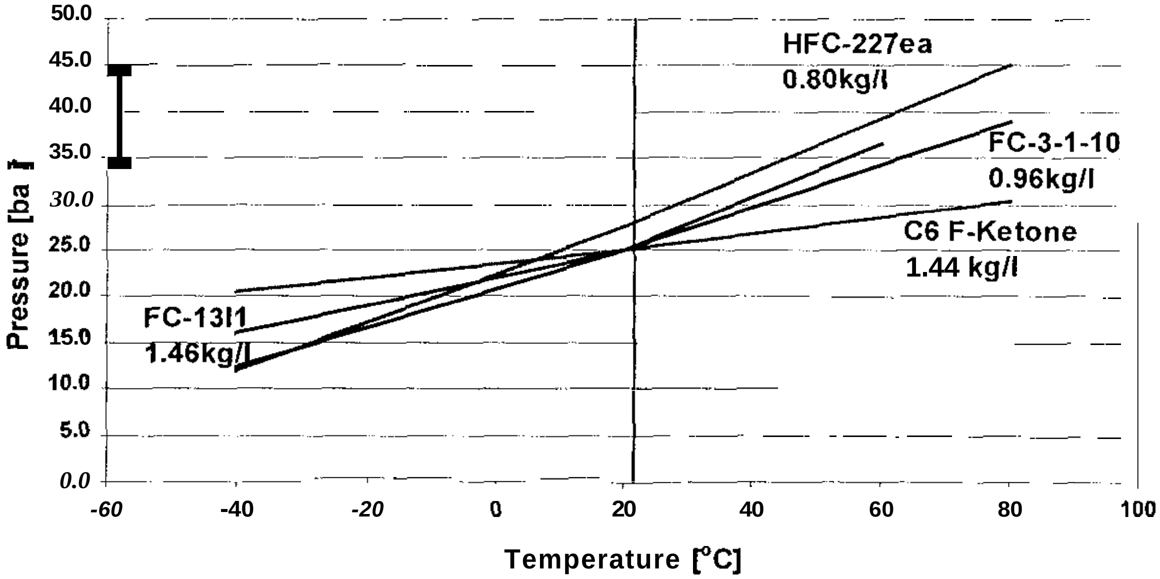

Figure 1. Superpressurization comparison of $C_6$ F-ketone with low boiling gaseous agents

The indication previously was that the fire protection end use for this class of compounds expected to have the best initial effectiveness is **as** a streaming agent, in manual handheld application or perhaps flight line suppression. This has been shown and continues to be the case. System optimization to accommodate the use of $C_6$ F-ketone is underway with manufacturers presently. However, it has been shown that this liquid fire protection fluid can have effectiveness in a localized flooding application in small rooms [8, 9].

Independent cup-burner values using $C_6$ F-ketone for various fuels have been run and are being validated at this time. Indications are that for n-heptane, IPA, acetone and toluene, the cup-burner values will be in the **3.5-5.5%** range. Quantification of additional cup-burner values for other fuels is planned. **As** seen in small scale testing performed to date, Class **A** fuels have been shown to be effectively extinguished using $C_6$ F-ketone at 3.5% v/v. More tests are planned.

Thermal decomposition products testing with $C_6$ F-ketone have shown comparable results with other commercially available halon alternatives. The three key factors affecting TDP generation are the fire size-to-room volume ratio, the agent concentration, and discharge time. **An** increase of agent concentration to 20% of the extinguishing concentration results in a reduction in TDP of up to 40%. **A** 67% decrease in discharge time results in a **50%** reduction in TDP generation. This shows the emphasis for system design should be on early fire detection and rapid discharge [8].

Mather and Tapscott [10] have shown that high boiling, low vapor pressure liquids such as $C_6$ F-ketone that have a low heat of vaporization, can readily vaporize and may have utility in certain small-scale flooding applications, even to very low temperatures. Figure 2 shows a curve for a 48 °C boiling fluid like $C_6$ F-ketone. The expected range in use concentrations for C, F-ketone are shown on the chart. Vapor pressure and density curves for $C_6$ F-ketone are as shown below in Figures 3 and 4.

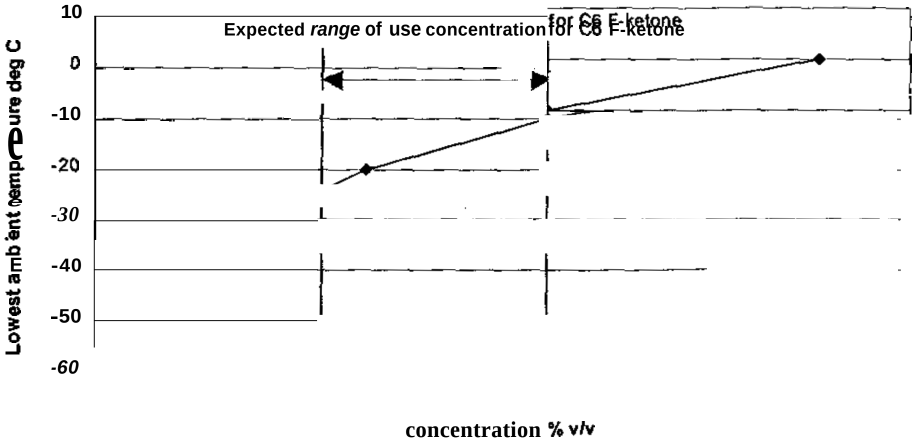

Figure 2. Concentrations C, F-ketone, a liquid agent boiling at 48 °C, is expected to achieve at a given ambient temperature (based on [10]).

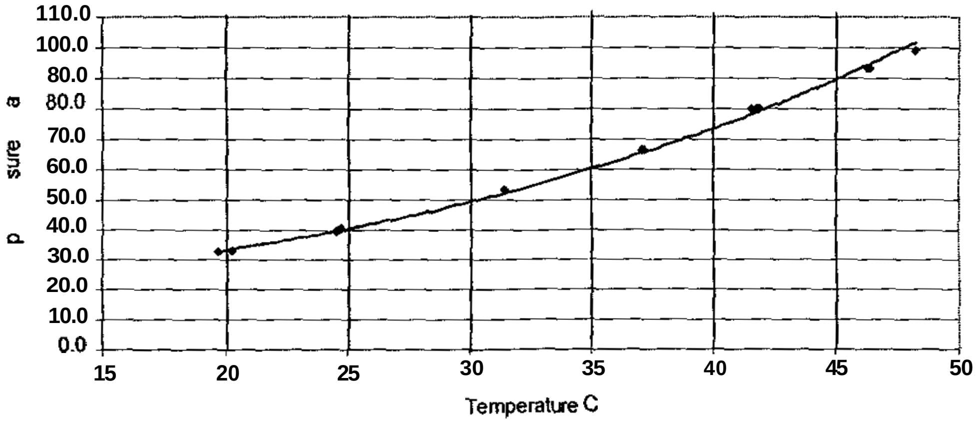

Figure 3. Vapor pressure vs temperature—$C_6$ F-ketone.

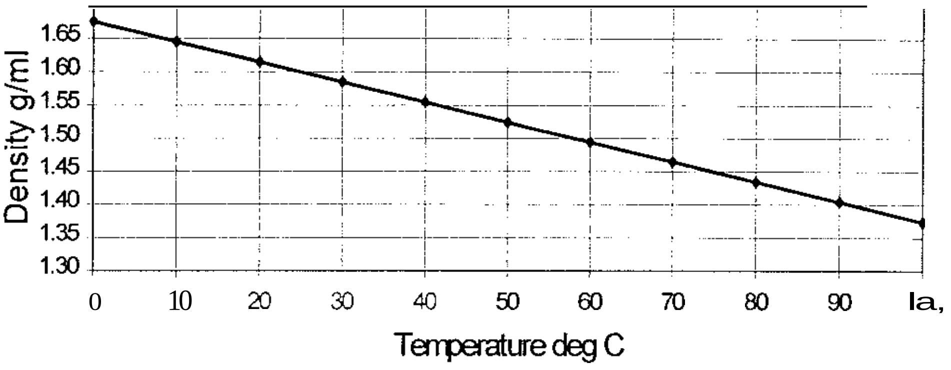

Figure 4. Liquid density vs temperature: $C_6$ F-ketone.

## REGULATORY APPROVALS

Presently, $C_6$ F-ketone is listed on the TSCA registry in the United States and is in process for chemical registration in the European Union. Completion of EU registration is expected in 2001. Other country registrations around the world are expected in due course. The USEPA Significant New Alternatives Program (SNAP) review of $C_6$ F-ketone has been completed for fire protection streaming applications, and $C_6$ F-ketone is acceptable, with the recent TSCA listing, for commercial sale in the **US.** Formal published SNAP recognition for $C_6$ F-ketone is forthcoming.

## COMMERCIAL PROGRESS

Full commercialization of $C_6$ F-ketone is on track and expected the end of the third quarter of 2001. Test quantities of $C_6$ F-ketone are available now, with commercial manufactured quantities available by the end of summer, 2001. A key advantage in terms of handling is that $C_6$ F-ketone is a low vapor pressure fluid. As such, $C_6$ F-ketone will be commercially packaged in non-pressurized containers in the following container sizes (Table 8).

TABLE 8. CONTAINER SIZES FOR $C_6$ F-KETONE.

| Container | Quantity, kg |
|---|---|
| 1-gallon amber glass jug | 5 |
| 30-gallon drum | 160 |
| 220-gallon tote | 1200 |
| ISO **bulk** container | **18,000** |

At least two manufacturers have initiated a project for $C_6$ F-ketone at Underwriters Laboratories (USA) and have commenced with the one-year leak test, the longest duration test required as part of the listing process to attain a UL listing. Full **UL** listings are on track for completion in early 2002, although fire testing should be complete well before that. UL component recognition for $C_6$ F-ketone is in progress at this time.

## CONCLUSIONS

$C_6$ F-ketone has been shown to be excellent candidate alternative to ozone-depleting compounds that has the right combination of performance, safety, environmental properties, and commercial acceptance. It is a new molecule that is part of a newly developed patent pending technology platform expected to be a sustainable long-term halocarbon candidate to replace halons.

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