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Alternative to liquid perfluorocarbon C6F14 for mono-phase detector cooling applications at CERN

Annex 2: Questions about 3M Novec™649

Abstract

This document contains the questions to be addressed to Novec™ 649 developers at 3M Company.

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HISTORY OF CHANGES

REV. NO.	DATE	PAGES	DESCRIPTIONS OF THE CHANGES
1.0	2015-03-24	8	First version, to be sent to Mr. B.Kaiser of 3M Switzerland
1.1	2015-04-22	8	Preliminary responses by 3M experts are added

TABLE OF CONTENTS

Acronyms

C6K – Novec™649, perfluoroketone FK-5-1-12

PFPrA – perfluoropropionic acid, one of the final products of C6K hydrolysis

1. Introduction

After reviewing the published information on C6K [1] and other 3M Novec™ fluids - including of course all 3M publications, patents and articles (by J. Owens, Ph. Tuma et al.) - a number of points, related to our intended application of C6K for cooling of particle detectors at CERN [2], still remained unclear to us. We would wish to address our questions directly to the developers of those fluids and, if possible, establish direct links with them for further consultations.

Getting the answers from the first-hand source (possibly, with references to published or unpublished reports) could spare us the need to perform independent laboratory tests, or render such tests more focused. For the topics that might require investigation (like, for example, the radiation resistance of C6K), we would like to know whether the corresponding tasks could be delegated to 3M labs, and on which conditions.

The Ref. [3], describing the explicit R&D tasks to validate C6K for our application, is complementary to the present document.

2. The questions to Novec fluids developers

A2.1 Radiation resistance of the fluid[1]. Is anything known about it? Had the fluid been tested (or used) under ionizing or neutron radiation? If so, what are main radiolysis products and their yields per unit ionizing dose or neutron fluence? Of our main concern are HF, CF2O, as well as solid or soluble compounds with higher boiling points than the initial fluid. Would 3M be willing to perform in-house radiation resistance tests or analyze the samples irradiated at CERN, given that the expected activation level is about nil?

A: 3M has completed no work in this area but would be willing to perform analysis of samples irradiated by CERN.

A2.2 What the initial impurities in Novec 649 (typically ~0.2% [4]) consist of? Do they contain compounds with hydrogen, like acids, hydrocarbons or non-saturated fluorocarbons? This is important for assessing the radiation resistance of the as-provided fluid. See also A2.11.

A (to A.2.11): The typical impurities are known and can be shared under NDA.

A: Detailed H-NMR and F-NMR analysis indicates that the impurities are other fluorinated materials including other perfluorinated ketones and perfluorinated dimers. Hydrogenated components are typically at much lower levels and include diols and alkyl-perfluoropropionates. Perfluoropropionic acid, which is often undetectable by the above methods, is typically 5ppm or less.

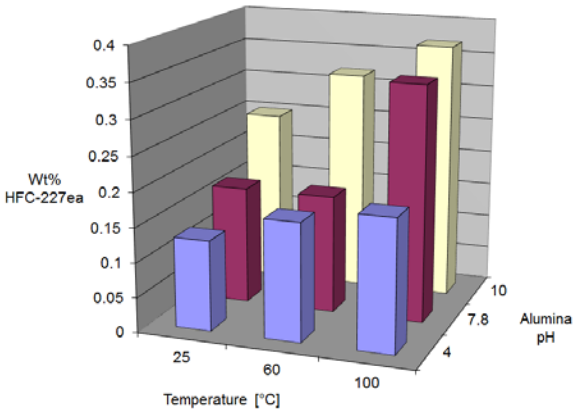
A2.3 What are the recommended and tested drying methods (desiccants) for C6K? Can you give an example of an existing C6K application with commercial moisture filters, or recommend commercial moisture filters that we could start with?

[1] By “the fluids” below we assume Novec fluids, primarily **Novec 649** (C6K), but the 744 (C7K), 7100 and 7200 are of interest, as well.

A: Though silica gel has been (used) to dry the headspace in 2-phase immersion cooling systems, reactivity has been observed in lab experiments, particularly at elevated temperatures when the silica gel is heavily loaded with moisture. Preliminary experiments suggest significant reactivity with 4A molecular sieves. Data suggest that metal sulfates may be preferable to both.

A2.4 Same, for acid removal methods/filters.

A: 72-hour exposure testing with activated alumina show reactivity (quantified by HFC-227 formation rate) that increased with pH of the alumina and temperature as shown below:
A (to A2.5) : Some very cursory work has been done in this area to find alternatives to alumina, molecular sieves and activated carbon, each of which exhibited some kind of reactivity at elevated temperature.



A2.5 Is anything known about compatibility of C6K with ion-exchange resins? If they are compatible, which resins can be recommended for drying and/or acid removal?

A: Some very cursory work has been done in this area to find alternatives to alumina, molecular sieves and activated carbon, each of which exhibited some kind of reactivity at elevated temperature.

In their dry state, Ion-exchange resins of the types described below exhibited reasonable compatibility at 50C for 48 hours.

1. Strong Base Anion (SBA) - quaternary amine functional group. Potentially useful for removing deprotonated impurities.
2. Weak Base Anion (WBA) - tertiary amine functional group. Potentially useful for removing acidic impurities.
3. Non Ionic - no ionic functional groups. Potentially useful for removing non ionic, oils etc.

A2.6 Is there a practical experience of using activated carbon to purify Novec fluids? What kind/grade of activated carbon is most suitable for C6K?

A: Yes. Ordinary activated carbon will contain carbonate groups that will react with the C6K. Acid washed carbon of the type used to clean drinking water is therefore used but only after drying. It is often pre-saturated with C6K to avoid the exotherm that occurs upon first submersion in the fluid. It has proven very effective at removing hydrocarbon impurities.

NOTE: The reactivity observed with carbonate-containing carbon was originally thought to be an incompatibility with the carbon itself. However re-treating the carbon with C6K inerted it. It was then we realized that the fluid was in fact reacting with carbonate groups that were absent from acid washed carbon. It is thought that similar functional groups could be the causes of observed incompatibilities with other reagent such as molecular sieves however this has not been studied.

A2.7 Compatibility of C6K with zeolytes, activated alumina, molecular membranes? Of our concern is the possible reactivity of C6K with activated alumina, mentioned in the Ref. [5].

A: No work has been done with molecular membranes. Others as noted above.

A2.8 Can gas chromatography be used to analyze C6K, given the potential reactivity with the alumina-based columns? What kinds of stationary phases are compatible with C6K?

A: Yes, it can. We analyze C6-ketone and all of the potential related components using a 105 m RTX-200. The stationary phases is a trifluoropropylmethyl polysiloxane. The catalog number is 15075.

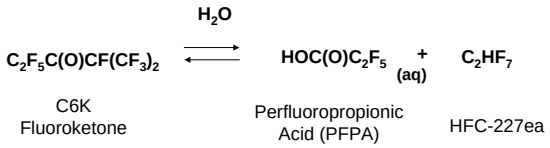
A2.9 Can FTIR spectrometry be used for on-line monitoring of C6K impurities like HF, PFPrA, COF2 and if so, what are your recommendations about using this technique for C6K (specific instrument, type of cells, range etc).

A: Most of the likely impurities should be detectable in the IR but it will be a question of the detection limits for the specific situation in which the measurements are made.

A2.10 Hydrolysis of perfluoroketones C6K (C7K).

- will the water dissolved in C6K be completely hydrolyzed, thereby prompting further water intake and posing no limit on the increase of acidity? Does it make sense to speak of the "water content" in the as-provided fluid[2]?

A: The mechanism of hydrolysis is a little different than that suggested by your query. The hydrolysis is not typically a reaction between the ketone and water dissolved in it. Little if any reaction is observed in C6K in equilibrium with moist air. Rather, a separate water phase is required for the hydrolysis to advance. The liquid water is needed to solvate the primary hydrolysis product and allow the reaction to progress. The primary hydrolysis product is perfluoropropionic acid (PFPA) and the reaction will progress until the aqueous phase reaches a pH of about 3.



- what is the dynamics of water intake from the liquid water phase in direct contact with C6K, as function of temperature (between +45°C and freezing point);

A: Water tends to behave like a light gas and will obey Henry's law. Its concentration in the fluid is therefore proportional to the water partial pressure in the headspace (effective or real) saturating at 20ppmw at 25C. The uptake of water from the headspace to the liquid is a diffusion process and will be quite slow in a quiescent system. Mixing will hasten the uptake.

- Will C6K interact with solid water phase (ice, frost)?

A: This has not been studied but it seems reasonable that ice can solvate PFPA in the same way water does though probably more slowly since the water is cold and in a solid state.

- How the air (oxygen) dissolved in C6K affects the hydrolysis (if at all)?

A2.11 What is the main chemical process of the C6K synthesis? From that we get an idea on the nature of the initial impurities, unless they are known (see A2.2 above).

A: The typical impurities are known and can be shared under NDA.

A2.12 What is the expected lifetime of the C6K coolant in a hermetic circulation system?

A: In the absence of reactive species, the life should be indefinite. C6K is routinely stored for many years in fire protection systems.

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[2] The 3M Product Information [5a] quotes 20 ppm for water solubility in C6K. NB: the corresponding MSDS quotes "Nil" for C6K solubility in water.

A2.13 Are there any specific recommendations on the type of circulation pumps (mag drive, diaphragm, rotary, centrifugal etc) and pump head materials for C6K?
A: Thermodynamically, the fluid behaves like a perfluorocarbon so the same pumps used for perfluorohexane should be applicable.

A2.14 Can you propose the method(s) of initial purification of the as-provided fluid (C6K) to reduce the impurities to <0.1%?
A: Production C6K is typically distilled and column treated. These procedures could likely be tightened (higher reflux ratio for example) to increase fluid purity.

A2.15 Can 3M Company provide a sample of research-grade purified C6K for our irradiation studies? See also A2.1.
A: We should review the purity expectations but this is quite possible.

A2.16 Compatibility of C6K with materials. The only explicit information we have on this subject comes from [6], as follows:

Materials Compatibility

Compatibility of "O" Rings with Novec 649

Exposure Time: 1 Week@ 25°C, 100°C

Elastomer Type	Exposure Temperature	Change in Shore A Hardness	% Change in Weight	% Change in Volume
Neoprene	25°C	-1.8	-.06	-1.2
	100°C	-2.2	+2.3	+0.8
Butyl rubber	25°C	-2.7	+0.2	+0.1
	100°C	-4.0	+4.3	+4.2
Fluoroelastomer	25°C	-6.2	+0.7	+0.6
	100°C	-12.6	+9.5	+10.6
EPDM	25°C	-4.7	+0.6	+0.3
	100°C	-5.7	+3.3	+2.4
Silicone	25°C	N/A	+3.1	+2.8
	100°C	-5.4	+6.0	+5.1
Nitrile	25°C	-0.7	-0.3	-0.5
	100°C	+2.5	+4.6	+0.7

Effect of Novec 649 on Various Metals

Metals	Effect
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 temperature indicated, 10 days minimum exposure, 48°C.

3M has extensive data on compatibility with various materials. For more information, contact your local 3M technical service representative.

We would greatly appreciate obtaining the available data on C6K compatibility with a wider set of metals, polymers and elastomers, including

- Polymers: Hard PE, PTFE used as seals in pumps, Nylon, polycarbonate, ABS
- Metals: Titanium alloy grade 5, Alumunum alloys
- Elastomers: ultra-pure plasticizer-free silicone rubbers (eg Tygon 2075, 2001) or PU rubbers (eg Tygotan C-555-A).

A: The fluid's solvency is very similar to C6F14. Therefore, its propensity to infiltrate (and potentially swell) an elastomer, for example, is very similar. Likewise, its ability to extract and solvate mobile phases such as plasticizers is similar. This generally means that wetted materials themselves will exhibit similar compatibility with the C6K and C6F14.

HOWEVER, C6K is able to interact with some of these extracted species can be very different. One might expect, for example, some reaction of the fluid with polyols or other nucleophilic

additives. Wetted materials should therefore be studied by Soxhlet extraction to isolate and identify extracted species to see if they might be reactive.

A2.17 Compatibility of Novec fluids with Fluoroinert fluids (e.g. Novec 649 with C6F14). We expect them to be fully miscible and non-reactive with each other. Is that correct? This information is needed to design the procedure of filling the cooling circuits previously used with C6F14, where traces of the old coolant could remain.

A: To the best of our knowledge, this is correct. We anticipate no reaction between C6K and isomers of C6F14.

References for the Annex 2

1. P.Gorbounov, Project: 3M Novec 649 as a replacement of C6F14 in liquid cooling systems (the literature review), https://twiki.cern.ch/twiki/pub/LHCb/C6K/Novec_Memo.pdf
2. P.Gorbounov, E.Thomas, M.Battistin, Work Package: Alternative to liquid perfluorocarbon C6F14 for mono-phase detector cooling applications at CERN (attached to this document)
3. P.Gorbounov, Annex 1 to Ref. [2]: Commentaries to C6K validation tasks (attached to this document)
4. 3M Certificate of Analysis (Dec-09-2013, Stock Number 98-01212-3240-4), for the 17 kg batch of Novec 649 purchased by CERN from 3M Switzerland.
5. P.E. Tuma, Fluoroketone C2F5C(O)CF(CF3)2 as a Heat Transfer Fluid for Passive and Pumped 2-Phase Applications, 24th SEMI-THERM Symposium, 2008 http://ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=04509386
6. B. Kaiser (3M Switzerland, bkaiser@mmm.com) Private communication.