Reducing Emissions of PFC Heat Transfer Fluids

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Abstract

PFCs were used during the 1950s in some defense applications in the United States. The PFCs became widely used in the semiconductor industry during the 1980s, mainly in etch, plasma vapor deposition, ion implant and test processes. In an effort to reduce the PFC emissions, a voluntary coalition of companies joined together and made a Memorandum of Understanding (MOU) with the US EPA. In 1999, the World Semiconductor Council (WSC) made a commitment to decrease the PFC gaseous emissions by 10% below the 1995 baseline by 2010. Then, in 2001, the MOU was renewed with the US EPA, spurring widespread international participation by several countries including Japan, Korea, China and Taiwan.

The efforts to decrease emissions from PFC gases was largely successful, due to process optimization, abatement and investigation of alternative chemistries. In this talk, two approaches to reducing emissions from PFC liquids are addressed. The first approach is to implement system optimization of onsite processes to identify leakage and minimize evaporative losses. The second approach is to adopt alternative chemistries. Segregated hydroflouroethers (HFEs) have a global warming potential of 0.5-5% of those from PFC liquids. In addition, they are non-flammable, non-corrosive, have zero ozone depletion, and are not regulated in the US for toxicity. The use of HFEs requires little to no equipment modification from systems currently set up for PFCs liquids.

Introduction

The Semiconductor Industry has pledged to reduce its emissions of various PFC gases

1980s	1995	1999	2001
Introduction of PFCs to commercial semiconductor manufacturing	Voluntary MOU with US EPA to reduce PFC gas emissions	WSC commits to reducing PFC gas emissions by 10% below industry's 1995 baseline level by 2010	Renewal of MOU, spurring international participation from Japan, China, Korea, Taiwan, etc.

PFC Gas Emissions

Commonly used PFC gases in semiconductor industry:

Gases	Application		Atmospheric Lifetime (years)*	GWP (100 year)*
	CVD Chamber Cleaning	Plasma Etching		
CO_2	N/A	N/A	variable	1
C_2F_6	X	X	10000	9200
CF_4		X	50000	6500
SF_6		X	3200	23900
NF_3	X	X	740**	10800**
CHF_3		X	264	1170
C_3F_8	X		2600	7000
c-C_4F_8	X	X	3200	8700

*IPCC, 1995

**IPCC, 2001

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http://www.epa.gov/highgwp/semiconductor-pfc/overview.html

PFC Gases Emissions

Emission reduction efforts for gases have been successful

– Process optimization; abatement, capture and recycle programs; adoption of alternative plasma chemistries.

– Emissions are quantified via WSC Tier 2 methods

PFC Liquids in Industry

PFC liquids are also widely used in the Semiconductor Industry as heat transfer media

- Etchers, ion implanters, deposition, test, etc.
- Needed for wide operating temperature range, dielectric properties, safety, inertness

PFC Liquids Emissions

A typical high volume fab may consume 500 gallons of PFC Heat Transfer fluid per year.

- Consumption is roughly equal to emission
- This equates to 0.0079 million metric tons of carbon equivalent (MMTCE) per fab per year
- Liquid emissions are a growing percentage of the total emissions (gaseous + liquid)

PFC Liquids Emissions

Table 1 - PFC Heat Transfer Fluid Emissions Compared to Total Greenhouse Emissions from a Typical 200mm Fab.

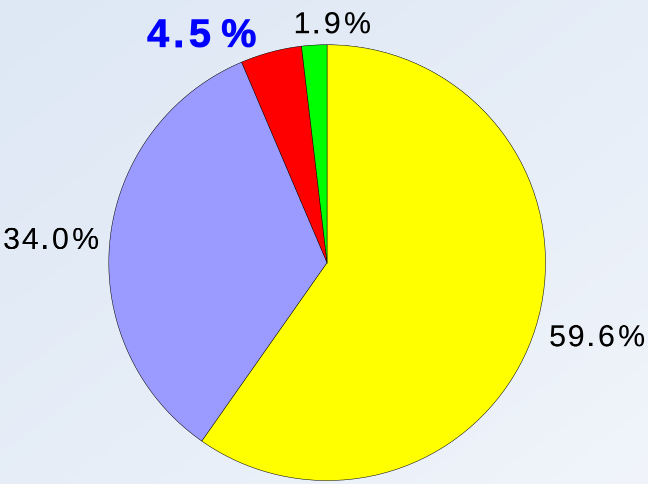
	Total MMTCE MOU Gases	PFC liquid % of Total
1999 Tier 2a	0.03904	16.8
1999 Tier 2b	0.03401	18.8
1999 Tier 2c	0.03468	18.5
2002 Tier 2a	0.00642	55.2
2002 Tier 2b	0.01105	41.7
2002 Tier 2c	0.00756	51.1

L. Beu, J. Peterson and P. Brown, "Analysis of IPCC Emissions Estimating Methodology," Partnership for PFC Emissions Reduction, Semicon Southwest, Austin, Texas, 16 October 2000.

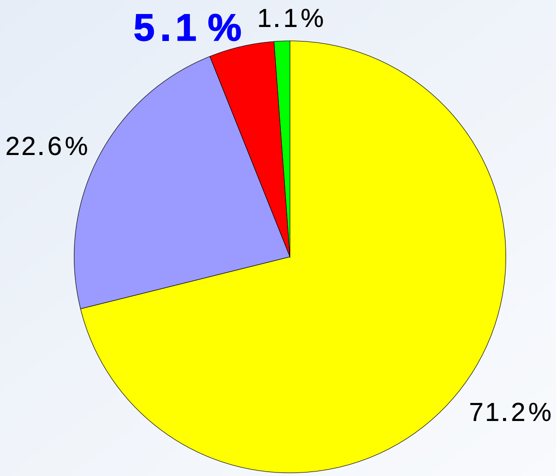
Case Example: Advanced Micro Devices, Inc. (AMD) Corporate Greenhouse Gas Emission Distribution

- **Heat transfer fluid fugitive emissions**
- Energy emissions (On-site fuel combustion and emissions due to purchased electricity)
- N_2O process emissions
- PFC process emissions

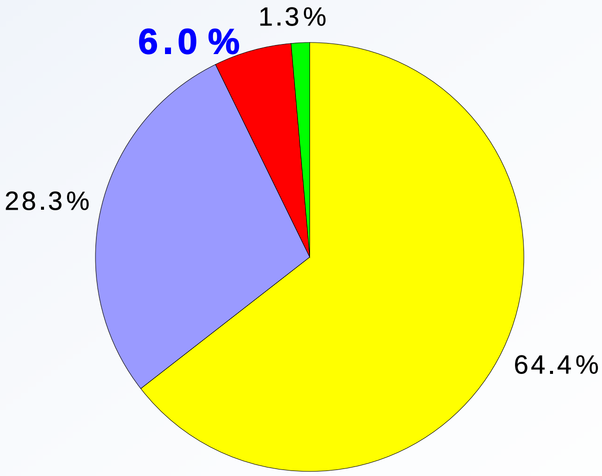
2001



2002



2003



Manufacturing Profile:
3 Fabs
1 R&D Center
4 Final Assembly Sites

Manufacturing Profile:
H1-02: 3 Fabs
H2-02: 2 Fabs (1 fab closed)
1 R&D Center
4 Final Assembly Sites

Manufacturing Profile:
H1-03: 2 Fabs
H2-03: 5 Fabs (3 Fabs added)
1 R&D Center
H1-03: 4 F.A. Sites
H2-03: 5 F.A. Sites (1 added)

Slide provided by Dan Seif of AMD 1-17-05

Lowering PFC Liquid Emissions

Process Optimization/Source Reduction:

- Review on site systems for common fluid leakage.
  - Connections, valves, pumps, plumbing, vents, etc.

Recycling/Proper Waste Methods of Used Fluids

- Utilize third party/independent recycling services
- Utilize manufacturer's waste treatment recommendations
  - For free NOVEC™ recycling: 1-800-we-care-1

Lowering PFC Liquid Emissions

PFC liquids have GWPs comparable to PFC gases

- Little literature data available for liquids
- Standard practice to use data for C_6F_{14}
  - Atmospheric lifetime=3200 years, GWP=9000

Investigate the use of alternative liquids

- Most alternative liquids have limitations
  - Chlorinated - Ozone depleting, toxic or regulated
  - Silicones - flammable, residue
  - Aromatics - flammable or corrosive
  - DI/Glycol – Narrow operating temperature range, high maintenance, high waste

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Utility of Segregated Hydrofluoroether (HFE) Heat Transfer Liquids

Not all HFEs are the same:

Hydrofluoroether properties can vary widely
- Some are unstable
- Others have toxic or anesthetic effects
- Others have GWPs like PFCs

Segregated Hydrofluoroethers posses a balance of properties
- $C_3F_7OCH_3$, $C_4F_9OCH_3$, $C_4F_9OC_2H_5$, $C_6F_{12}OCH_3$ and $C_3F_7CF(OC_2H_5)CF(CF_3)_2$

Environmental properties
- All HFEs are non ozone-depleting
- HFE GWPs can vary widely
- Segregated HFEs have GWPs that are only 0.6 to 4.4% those of common PFC liquids;
- they do not contribute to photochemical smog and are non-flammable
- They are low in toxicity

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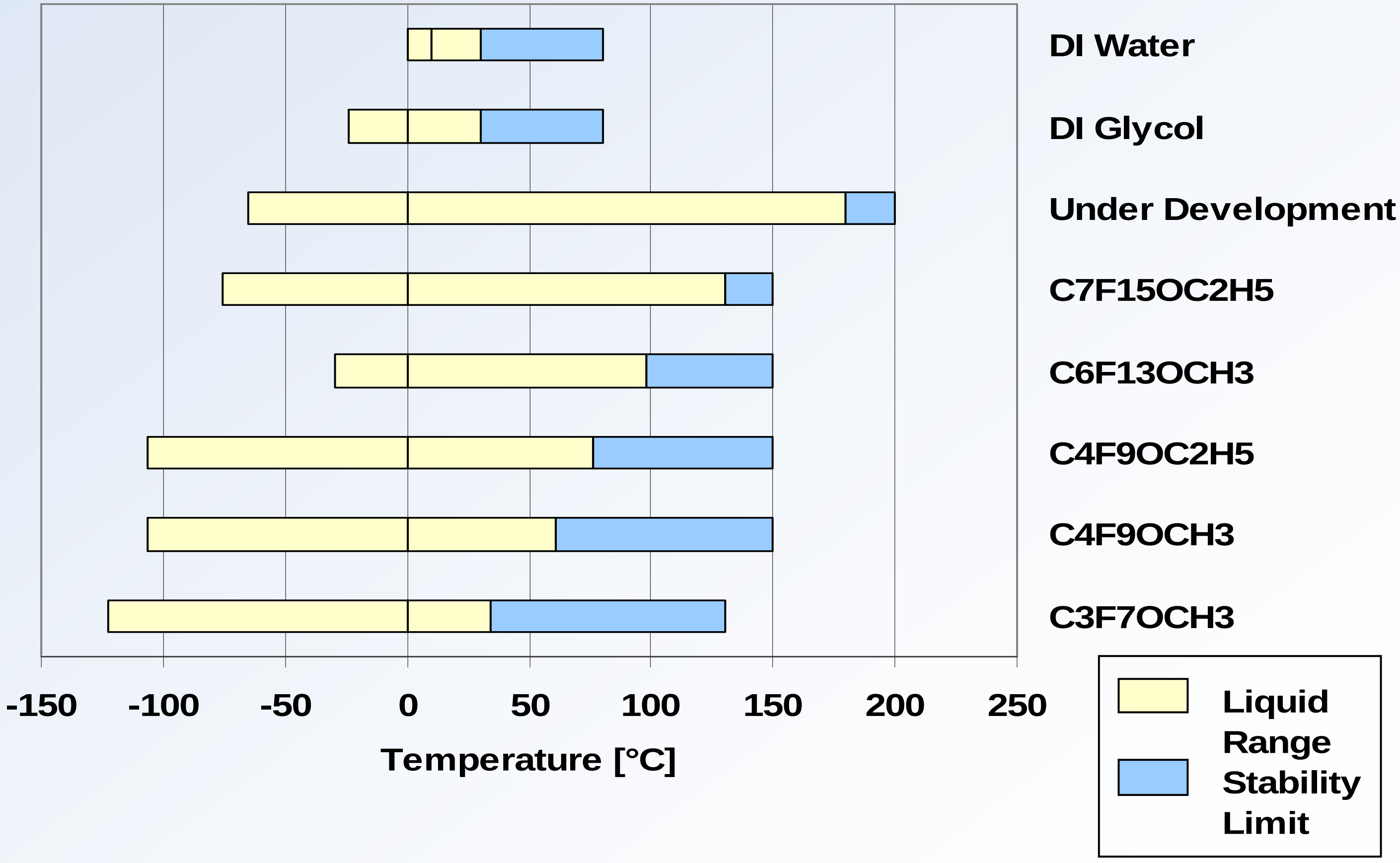
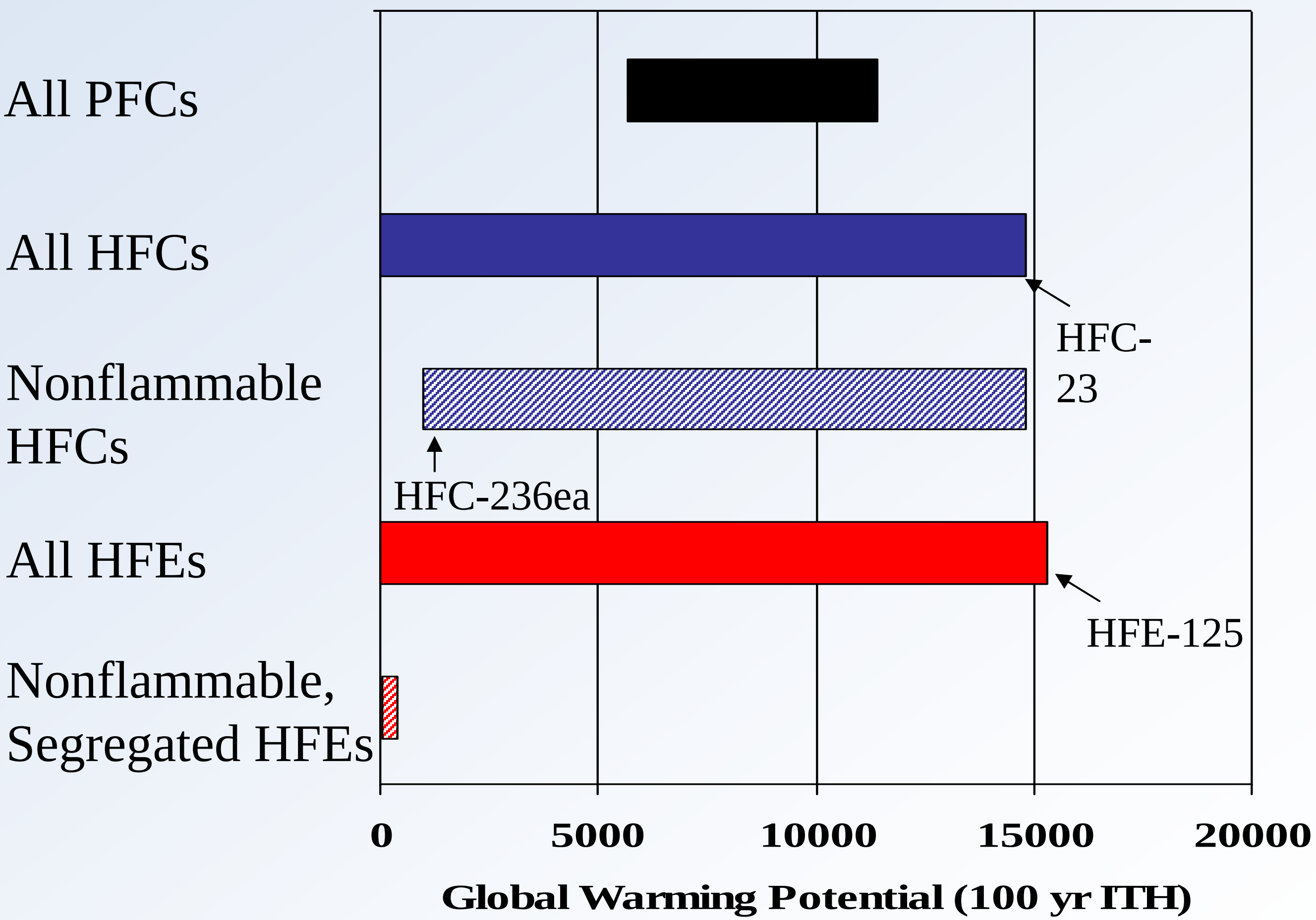
Utility of Segregated Hydrofluoroether (HFE) Heat Transfer Liquids

Useful Temperature Ranges:



Environmental Properties of Segregated HFEs

Segregated HFEs have low GWP



Novec™ 7300 – The Newest Fluid

Properties	HFE-7300
Molecular Weight, g/mol	350
Flash Point	None
Pour Point, °C	-38
Boiling Point, °C	97
Critical Temperature, °C	243.3
Critical Pressure, MPa	1.877
Critical Density, kg/m3 (estimated)	570
Heat of Vaporization @ B.P., kJ/kg	101.7
Surface Tension, dynes/cm	15
Solubility of Water in Fluid, ppm by weight	67
Solubility of Air in Fluid, percent by volume @ 1 atm	43
Typical Dielectric Strength (0.1 in. gap), kV (RMS)	0.267
Dielectric Constant, 100 Hz – 10 MHz	6.14
Volume resistivity, ohm-cm	3.3x1011
Ozone depletion potential1–ODP	0.00
Global warming potential2–GWP	200
Atmospheric lifetime–ALT (years)	3.8
Solubility of fluid in water (ppb)	586

Comparison of HT200/135 Liquid Emissions For a Typical Fab

	Galden Fluid	Equivalent Novec HFE-7300
Annual HT-135 usage [lbs]	**3,000**	**-**
Annual HT-200 usage [lbs]	**4,000**	**-**
Annual HFE-7300 equivalent to both [lbs]		**6292***
GWP of HT-135	8600	-
GWP of HT-200	9400	-
GWP of HFE-7300	-	200
Total MTCE of fluid per year	7860	156
Total MT CO_2 equiv/year	28818	572
lbs CO_2 equiv/year	63,400,000	1,258,360

Note: CO2 equiv. = Carbon equiv.×44/12

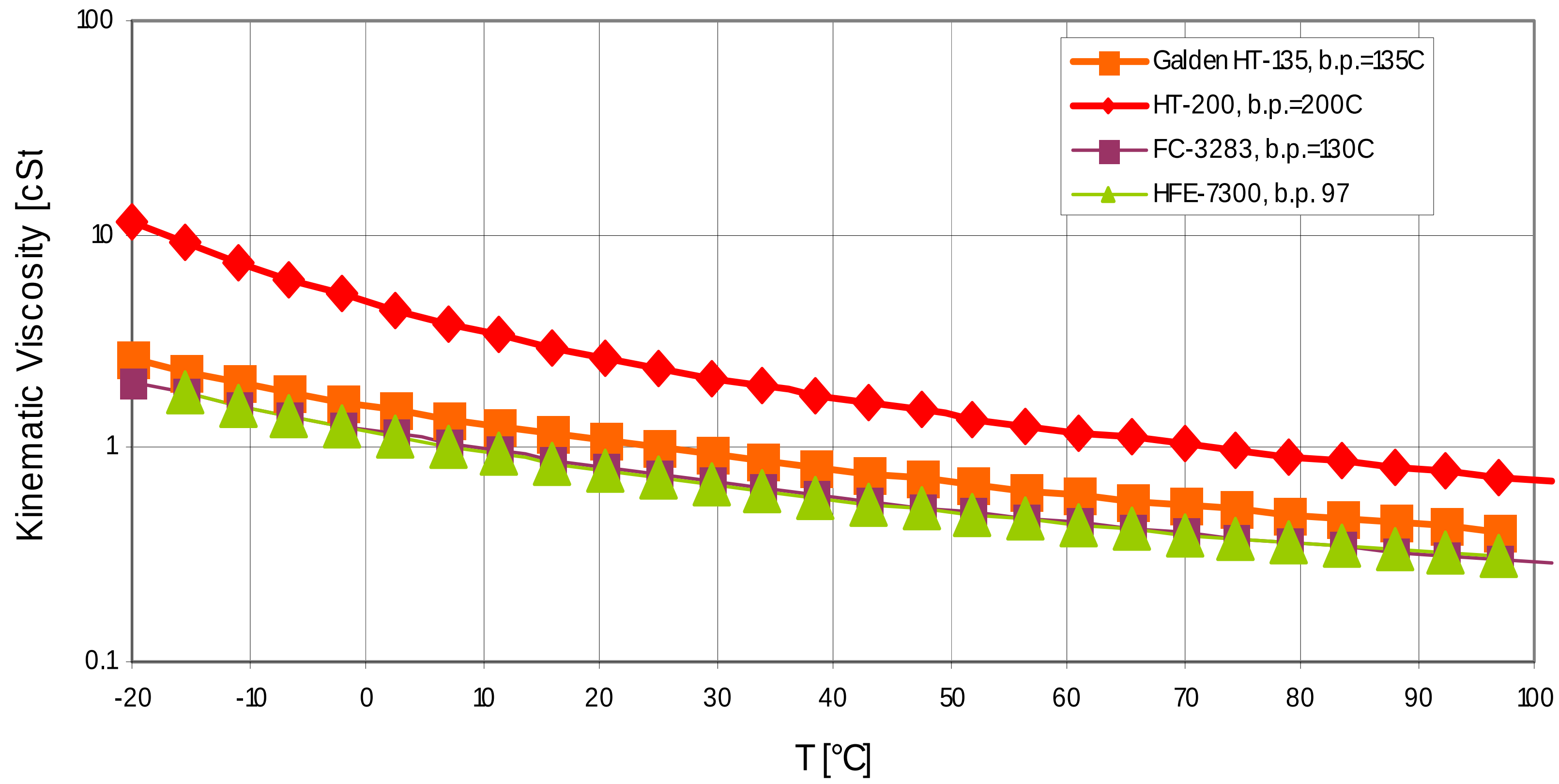
* Lower usage due to lower liquid density

62,141,640

Reduction

Performance versus Boiling Point

The performance of heat transfer fluid is largely dictated by the fluid's viscosity.
Viscosity at a given temperature will generally increase with boiling point.
This is shown in the Figures below.



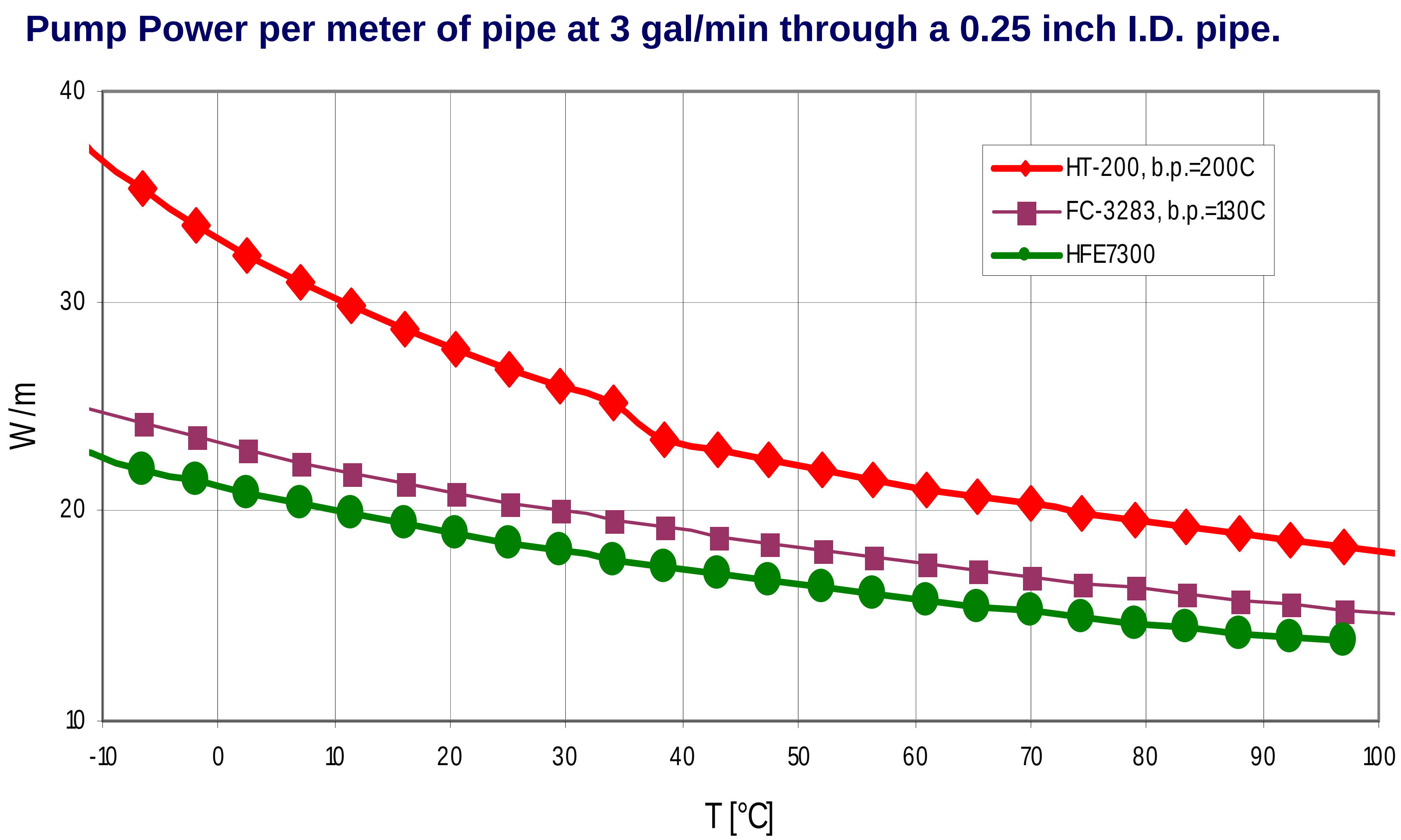
Heat Transfer Properties vs. Boiling Point

•The use of high boiling point fluids will reduce heat transfer performance.

• If a low viscosity, low boiling point fluid is used, more heat is transferred per unit of surface area in the tool and in the chiller. Alternatively, the same amount of heat can be removed using a higher fluid operating temperature.

• All of this means that a low viscosity fluid offers reduced time to setpoint, increased chiller capacity, lower minimum temperature and reduced chiller wear.

Novec™ Fluids Increase Efficiency



Material Compatibility

3M HFEs are compatible with all common metals and "hard" polymers:

Polyethylene	**Polypropylene**	**ABS**
Nylon	**polyvinylchloride (PVC)**	
Rulon™	**Polycarbonate (Lexan™)**	
Ryton™	**Acrylic (Plexiglas™)**	
PTFE (Teflon™)	**polysulfone**	
phenolic	**Thermoplastics**	
polyetheretherketone (PEEK)		

and many others

Material Compatibility

3M HFEs have higher solvency than perfluorinated fluids for plasticizers used to manufacture elastomers. Must choose elastomers which contain little plasticizer

– 3M Engineers will recommend suitable compounds and provide testing services.

Like perfluorinated fluids, HFEs will swell fluorinated elastomers like Fluorel®, Viton® and Kalrez®.

3M Technical Service

40+ years of experience with fluorinated heat transfer fluids in all types of applications.

Regional and on-site seminars on the use of 3M Fluorinated heat transfer fluids.

Heat transfer system design assistance.

Free material compatibility testing for materials of construction.

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