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SELECTION OF FLUIDS FOR TRITIUM PUMPING SYSTEMS

by

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ABSTRACT

The degradation characteristics of three types of vacuum pump fluids, polyphenyl ethers, perfluoropolyethers and hydrocarbon oils were reviewed. Fluid selection proved to be a critical factor in the long-term performance of tritium pumping systems and subsequent tritium recovery operations. Thermal degradation and tritium radiolysis of pump fluids produce contaminants which can damage equipment and interfere with tritium recovery operations. General characteristics of these fluids are as follows:

- Polyphenyl ether has outstanding radiation resistance, is very stable under normal diffusion pump conditions, but breaks down in the presence of oxygen at anticipated operating temperatures.
- Perfluoropolyether fluids are very stable and do not react chemically with most gases. Thermal and mechanical degradation products are inert, but the radiolysis products are very corrosive.

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- Most of the degradation products of hydrogen oils are volatile and the principal radiolysis product is methane. Our studies show that polyphenyl ethers and hydrocarbon oils are the preferred fluids for use in tritium pumping systems. No corrosive materials are formed and most of the degradation products can be removed with suitable filter systems.

INTRODUCTION

The selection of lubricants for mechanical vacuum pumps and fluids for diffusion pumps is a critical factor in the long-term performance of tritium pumping systems. Thermal degradation and tritium radiolysis produce contaminants that can damage equipment and interfere with tritium recovery operations. This damage potential must be assessed beforehand because there is no satisfactory method for analyzing the effluent gas for trace organic or other deleterious material.

(Slide 2)

First, we'll talk about the properties of tritium and about current pump fluids and their degradation products. Then, we'll look at the effects of fluid selection on the long-term performance of a typical tritium pumping system. And, we'll finish with a summary of our studies.

(Slide 3)

Tritium is the radioactive form of hydrogen. It has the same physical properties as normal hydrogen including its solubility in pump fluids. It has a 12.3-year half-life and decays by beta emission. The average decay energy is 5.69 keV.[1] The beta particles emitted by dissolved tritium are almost completely absorbed by the pump fluid and cause it to degrade.

Organic fluids currently used in tritium pumping systems are:

(Slide 4)

- Five-ring polyphenyl ether in diffusion pumps
- Hydrocarbon oils or perfluoropolyethers in turbomolecular pumps and in mechanical fore pumps.

Polyphenyl Ether (Slide 5)

Five-ring polyphenyl ether is a widely used diffusion pump fluid. It is very stable, has a low vapor pressure, resists migration and is said to have outstanding radiation resistance. No corrosive materials are formed.

Polyphenyl ether can degrade thermally to form volatile products if the cooling system fails and the fluid becomes overheated. If the fluid is exposed to air while it is overheated, it can also form carbonaceous deposits in the pump. All of the volatile degradation products would have molecular weights less than 400 amu and would be expected to have molecular diameters less than 10 A.[2]

Tritium radiolysis products are C, CH_4, CO, and CO_2. The "G" value, a measure of the rate of production of radiolysis products, for CH_4 is not well established but is probably <0.02. Current studies at Mound Laboratory indicate that the actual value is very low. The Mound work will be published when it is completed.

Perfluoropolyether (Slide 6)

Perfluoropolyether fluids are commonly used in pumping systems that handle very corrosive gases. They are very stable, do not react chemically with most gases and are good lubricants. When they are degraded thermally or mechanically, they form volatile

compounds with molecular weights less than 550 amu. They don't polymerize, don't form deposits even when bombarded by electron beams, and they are thermally stable up to about 300°C.[3,4] Degradation when exposed to the rubbing action of bearings has been reported,[5] but Steenrod states that this is not observable under normal operating conditions in vacuum pumps. Mechanical pumps normally operate in the 40 to 60°C range and thermal degradation is not significant. Bearing or other mechanical failures that produce very high local temperatures could cause some thermal degradation.

The radiolysis products of perfluoropolyether are reported to be the same as those of Teflon®. They are HF, CO, CO_2 and, when oxygen is present, COF_2, an extremely reactive compound. In addition, F atoms are present in the fluid at all times during radiolysis. These F atoms are available continuously for attack on bearings and other parts of the pumps. The "G" values for the formation of HF and COF_2 are 0.06 and 3.5, respectively. Our conclusions are based on published data for polytetrafluoroethylene.[6]

Hydrocarbon Oil (Slide 7)

Hydrocarbon oils are the customary fluids used in mechanical pumps. In normal environments, they are very stable and are excellent lubricants. Extrained organic materials in the effluents from pumps lubricated with hydrocarbon fluids are readily controlled with common filters.

The principal radiolysis product of hydrocarbon oil is CH_4 and the "G" value for its formation is 0.02. No corrosive materials are formed. All the degradation products except the most volatile are easily controlled with appropriate filters.

We recognize that hydrocarbon oil is a source of protium and that exchange would take place. The exchange rate is small and annual oil changes would control the buildup of tritium in the oil if that were perceived to be a problem.

(Slide 8)

Typically, a tritium pumping system is a closed loop like the mass spectrometer system shown in this slide. A tritium mixture is sampled, analyzed, and returned to the process. The loop is closed and is maintained at subatmospheric pressure to prevent loss of tritium to the atmosphere. Diffusion pumps or turbomolecular pumps backed by mechanical pumps evacuate the mass spectrometer and the sample system. The effluent is usually filtered to remove entrained organic material and is transferred to an accumulator tank. At intervals, the gas is returned to the process through a purification system.

(Slide 9)

Potential problems in these systems include:

- Pluggage, fluid degradation and backstreaming in diffusion pumps
- Bearing failure, corrosion and lubrication problems in turbomolecular pumps

- Bearing failure, and sticking vanes and valves in mechanical pumps
- Damage to the purification system by radiolysis products, e.g., destruction of palladium filters by HF or COF_2

These reactions take place because tritium dissolves in the pump fluids (Slide 10). It is about equally soluble in all three types of fluid. The amount of degradation is proportional to the amount of tritium dissolved in the fluid and the "G" value for the reaction. The total volume of degradation products is proportional to the total volume of fluid. The next slide (Slide 11) shows the volumes of the various fluids in our typical system and the anticipated tritium pressures over them. It is apparent that the majority of the degradation products will be produced in the mechanical fore pumps.

Now let's take a look at how the type of fluid affects our typical system. The next slide (Slide 12) shows the worst-case result of charging turbomechanical and mechanical pumps with perfluoropolyether. Corrosive products are formed in the turbomolecular and mechanical pumps. The quantities are small but they are available continuously to react with bearings and other pump components, and to migrate into the recovery system.

The next slide (Slide 13) shows the same system charged with hydrocarbon oil. No corrosive products are formed. Only methane and other organic materials are present in the pumps and the effluent gas.

Summary and Conclusions (Slide 14)

This table is a direct comparison of the total amounts of degradation products produced under worst-case conditions with each of the fluid charges evaluated in the previous slides. With a perfluoropolyether charge, F atoms are generated continuously, and HF and, if oxygen is present, COF_2 are produced. With hydrocarbon oil no corrosive products are formed and most of the degradation products can be removed with suitable filters. The production of degradation products is very small. This comparison leads us directly to the conclusion that (Slide 15) polyphenyl ethers and hydrocarbon oils are the preferred fluids for use in tritium pumping systems.

REFERENCES

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SLIDE 1

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SLIDE 2

TRITIUM

PUMP FLUIDS

DEGRADATION PRODUCTS

TYPICAL PUMPING SYSTEM

EFFECT OF FLUID SELECTION

CONCLUSIONS

SLIDE 3

TRITIUM

RADIOACTIVE HYDROGEN

HALF-LIFE	12.3 YEARS
AVERAGE DECAY ENERGY	5.69 keV

SLIDE 4

CURRENT PUMP FLUIDS

PUMP TYPE	FLUID
DIFFUSION	POLYPHENYL ETHER
TURBOMOLECULAR	HYDROCARBON OIL PERFLUOROPOLYETHER
MECHANICAL	HYDROCARBON OIL PERFLUOROPOLYETHER

SLIDE 5

POLYPHENYL ETHER

VERY STABLE

LOW VAPOR PRESSURE

RESISTS MIGRATION

DEGRADES THERMALLY

OUTSTANDING RADIATION RESISTANCE

RADIOLYSIS PRODUCTS ARE NOT CORROSIVE

RADIOLYTIC DEGRADATION PRODUCTS ARE:

C, CH_4, CO, AND CO_2

'G' VALUE FOR CH_4 <0.02

SLIDE 6

PERFLUOROPOLYETHER

VERY STABLE

CHEMICALLY INERT

GOOD LUBRICANT

THERMAL DEGRADATION PRODUCTS ARE VOLATILE

RADIOLYSIS PRODUCTS ARE CORROSIVE

RADIOLYTIC DEGRADATION PRODUCTS ARE:

HF, CO, CO_2 AND COF_2*

'G' VALUE FOR HF =0.06

'G' VALUE FOR COF_2 =3.5

F ATOMS PRESENT DURING RADIOLYSIS

---

* ONLY FORMED WHEN O_2 IS PRESENT

SLIDE 7

HYDROCARBON OIL

EXCELLENT LUBRICANT

NORMALLY STABLE

RADIOLYSIS PRODUCTS ARE NOT CORROSIVE

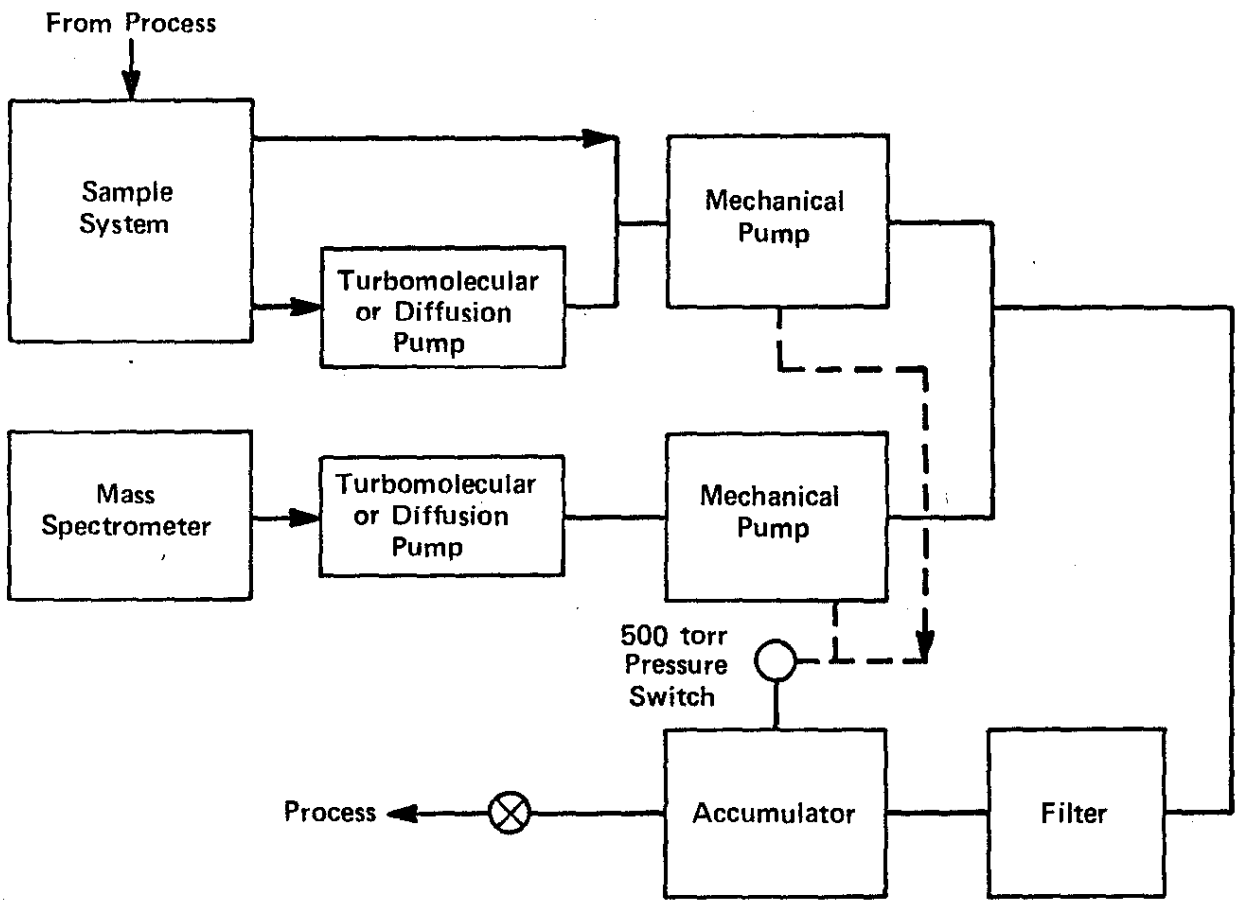
PRINCIPAL RADIOLYSIS PRODUCT IS CH_4

'G' VALUE FOR CH_4 =0.02

SOURCE OF PROTIUM

SLIDE 8

TYPICAL INSTRUMENT LOOP



SLIDE 9

POTENTIAL PROBLEMS

PUMPING SYSTEM	PROBLEM
DIFFUSION	PLUGGAGE
	FLUID DEGRADATION
	BACKSTREAMING
	MIGRATION
TURBOMOLECULAR	CORROSION
	LUBRICATION FAILURE
MECHANICAL	CORROSION
	LUBRICATION FAILURE
	FLUID DEGRADATION

RECOVERY SYSTEM

PALLADIUM DIFFUSER	CHEMICAL DAMAGE

SLIDE 10

TRITIUM SOLUBILITY

SOLUBILITY AT 20°C	BUNSEN'S COEFFICIENT *
POLYPHENYL ETHER	0.08
PERFLUOROPOLYETHER	0.08
HYDROCARBON OIL	0.07

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* GAS VOLUME PER UNIT VOLUME OF FLUID

SLIDE 11

FLUID VOLUMES AND TRITIUM PARTIAL PRESSURES

(TYPICAL)

PUMP TYPE	FLUID VOLUME	FORE PRESSURE
DIFFUSION (2)	150 CM^3	<0.2 TORR
OR		
TURBOMOLECULAR (2)	40	<0.2
MECHANICAL (2)	1200	50 - 500

SLIDE 12

EFFECT OF PERFLUOROPOLYETHER CHARGE

(WORST CASE)

PUMP TYPE	RADIOLYSIS PRODUCT	VOLUME, CM^3 (STP)/YEAR
DIFFUSION (POLYPHENL.) OR	CH_3T	$1X10^{-2}$
TURBOMOLECULAR	HF	$3X10^{-5}$
	COF_2*	$2X10^{-3}$
	F ATOMS	$1X10^{10}$/MIN
MECHANICAL	HF	24
	COF_2*	1400
	F ATOMS	$1X10^{16}$/MIN

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* IF O_2 IS PRESENT

SLIDE 13

EFFECT OF HYDROCARBON OIL CHARGE

(WORST CASE)

PUMP TYPE	RADIOLYSIS PRODUCT	VOLUME, CM^3 (STP)/YEAR
DIFFUSION (POLYPHENL.)	CH_3T	$1X10^{-2}$
OR		
TURBOMOLECULAR	CH_3T	$1X10^{-5}$
MECHANICAL	CH_3T	8

SLIDE 14

SUMMARY

(TYPICAL SYSTEM)

FLUID CHARGE	RADIOLYSIS PRODUCT	TOTAL VOLUME/YEAR CM^3 (STP)
PERFLUOROPOLYETHER	HF	24
	COF_2*	1400
	F ATOMS	$1X10^{16}$/MIN
HYDROCARBON OIL	CH_3T	8

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* IF O_2 IS PRESENT

SLIDE 15

CONCLUSIONS

POLYPHENYL ETHERS AND HYDROCARBON OILS ARE THE PREFERRED FLUIDS FOR TRITIUM PUMPING SYSTEMS