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HAZARDS OF ORGANIC WORKING FLUIDS

SAMUEL SILBERSTEIN

AUGUST 1977

BIOMEDICAL AND ENVIRONMENTAL ASSESSMENT DIVISION
NATIONAL CENTER FOR ANALYSIS OF ENERGY SYSTEMS

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FOREWORD

This review of the hazards of organic working fluids proposed for use in organic Rankine and bi-phase bottoming cycles defines the risks of these fluids apart from the technology. To put these risks into perspective, one must take account of the probabilities of their being released when used in the proposed technologies. Clearly if the risk of release were very small, the hazards would be similarly diminished. The situation here is analogous to the hazards of radiation in the nuclear fuel cycle. The risks are dose-dependent and the degree of risk is directly effected by the amount of radioactivity one permits to be released.

L. D. Hamilton

ABSTRACT

We present several brief reviews on working fluids proposed for use in organic Rankine and bi-phase bottoming cycles. These were prepared for the U.S. Energy Research and Development Administration, Assistant Administrator for Environment and Safety/Division of Technology Overview during its preparation of an Environmental Development Plan for the ERDA Division of Conservation Research and Technology. There are several general problems with many organic working fluids: flammability, toxicity, and a tendency to leak through seals. Besides, two of the proposed working fluids are to be used at temperatures above the manufacturer's maximum recommended temperature, and one is to be used in a way different from its customary usage.

It may, in some cases, be more profitable to first seek alternative working fluids before committing large amounts of time and money to research projects on unsafe working fluids.

Introduction

This report collects brief reviews on working fluids proposed for use in organic Rankine and bi-phase bottoming cycles, prepared for the U.S. Energy Research and Development Administration Assistant Administrator for Environment and Safety/Division of Technology Overview during its preparation of an Environmental Development Plan for the ERDA Division of Conservation Research and Technology. The proposed working fluids, their projected operating conditions and the manufacturers' recommended operating conditions are presented in Table 1.

We present below some of the general problems of these working fluids and present some recommendations.

At least two of the fluids are to be used at temperatures above those recommended by the manufacturer. Freon 11 is customarily used as a refrigerant. We recommend that any proposed deviation from manufacturers' recommendations or from customary usage should be justified in detail.

Some of the working fluids are highly flammable and possibly explosive. "It is characteristic of most organic heat transfer fluids to have a tendency to leak through joints and fittings at high temperatures unless these fittings are very tight"⁸ exacerbating the risk of fire. Therefore the use of inorganic fluids should be explored.

Some of the fluids are toxic. Leakage may result in worker and possibly general population exposure. Since leakage is a common feature of organic fluids, it should in no way be considered an extraordinary event or an accident. While a fluid like Freon 11 is not ordinarily toxic, it may be quite toxic under elevated operating temperatures. Fluorinol 85 is toxic, but the extent of toxicity is undetermined.

Thus it must be determined whether each fluid is safe under the actual conditions of operation. When it is known that a fluid is unsafe, it may be more profitable to try to find a safe substitute than to embark upon a lengthy and expensive research project to determine the exact extent of the fluid's toxicity.

Table 1

Working Fluids Proposed for Organic Rankine and Bi-phase Bottoming Cycles

exh gas temp (°C) ¹⁷ inlet outlet		working fluid	fluid operating ¹⁷ temp (°C) ⁺ press (atm)		max recommended temp (°C) press (atm)	
<u>Middle Grade Heat Utilization</u>						
90	540					
ORBC Sundstrand 425-540	165+	toluene		34		
Thermo-Electron 362		Fluorinol 85			329 ¹⁸	
Mechanical Technology, Inc. (MTI)		Freon 11			300 ¹⁰	
<u>Advanced Heat Utilization Cycles</u>						
<u>Biphase bottoming cycle</u>						
230-540						
tube fin heat exchanger 382*	116	Dowtherm A	349*	168		
contact heat exchanger 382*		Therminol 66	349*		343 ⁹	8,9 unpressurized

+necessarily less than exhaust gas inlet temperature.

*maximum

I. Toluene and benzene

The Sundstrand organic Rankine bottoming cycle (ORBC) is designed for toluene as working fluid for 425°C or above. Is it advisable to use a highly flammable liquid at these elevated temperatures? If air contains 12,000 ppm of toluene, it can be ignited. What safeguards will prevent this concentration from being approached?

While reagent grade toluene is relatively pure, industrial grade toluene can contain as much as 25% benzene,^{1,2} resulting in a vapor that could be 50% benzene.² Toluene is toxic; benzene even worse.

Heat catalyzes the following reactions:

Are these reactions significant in the Sundstrand ORBC producing highly explosive H₂? If so, what are the safety measures?

There are two dangers associated with exposure to working fluids: chronic low-level exposure to workers and the general population due to leakage, and acute high level exposure in the vicinity of the unit due to catastrophic release of fluid.

Table 2

Inhalation of Toluene and Benzene (Humans Unless Otherwise Stated).^{2,3}

<u>Low Dose.</u>	0.5-0.9 ppm benzene 0.4 ppm toluene	acute	enhanced brain electropotential
	50-100 ppm toluene	chronic	drowsiness and mild headache no aftereffects
	200 ppm toluene — benzene	chronic	insomnia headache dizziness fatigue nausea
	— benzene	chronic	stable and unstable chromosome aberration
	25 ppm benzene	chronic	anemia thrombocytopenia thrombocytopathy leukopenia low hemoglobin conc increased cell size eosinophil count elevation
	100 ppm benzene	chronic	leukopenia
	— benzene	chronic	leukemia
	200 ppm toluene	chronic	unstable chromosome aberrations; not statistically significant.
	450-500 ppm benzene rats	chronic	increase in cytochrome P450 and aminopyrine demethylase activity.
	133 or 13.3 ppm toluene rats, rabbits	chronic	decrease in cholinesterase leukocytosis reticulocytosis at higher conc immunological inhibition at both levels
<u>High Dose.</u>	20,000 ppm benzene	acute (5 min)	death
	4000 ppm toluene rats	4 hours	death
<u>Suggestive study.</u> Rats injected.			
	1 mg/kg/day toluene	chronic	bone marrow chromosome damage
	0.8 gm/kg/day toluene	chronic	stimulation of neutropoiesis chromosome breaks metaphase aberrations

Human Exposure to Toluene and Benzene. (Refer to Table 2)

Exposure to about 0.4 - 0.5 ppm^{2,3} (0.27 ppm for toluene in Ref. 1) of either toluene or benzene produces an enhanced brain electropotential of unknown significance. The OSHA Occupation Standard for toluene is 100 ppm time weighted average (TWA) for 8 hours/day and a 40 hour workweek with a ceiling of 200 ppm.⁴ The central nervous system effects of toluene are seen at concentrations even below this standard. Low-level chronic exposure to benzene results in similar central nervous system symptoms.^{5,6} In addition, there is also damage to the hematopoietic system. These effects occur at a previous ceiling limit of 25 ppm of the Occupational Safety and Health Administration (OSHA). The OSHA ceiling limit has recently been lowered to 1 ppm from 10 ppm time weighted average for an 8 hour workday; the new ceiling limit is 5 ppm for 15 minutes.¹⁶ These revisions were made because benzene is associated with increased risk of leukemia.^{3,4,7,16} Does toluene cause chromosome aberrations in the bone marrow? The experiment that seems to suggest that it does was done by injecting rats with toluene, while the more likely route of introduction of toluene for humans is inhalation. Does toluene also affect the hematopoietic system? Benzene seems to effect liver function (by raising cytochrome 450 and aminopyrene demethylase activity). Does toluene lessen the ability of liver to detoxify blood?

At high acute concentrations, benzene and toluene cause narcosis because of their affinity for nerve-cell lipids. This can cause death either directly or by rendering an exposed worker incapable of leaving the site of leakage of working fluid after which he may die if the fluid ignites.

If it is determined that toluene can safely be used in this application, a grade uncontaminated with benzene should be used. "In 1971, a conference of the International Labour Office (ILO) adopted a Convention and Recommendation concerning protection against hazards of poisoning arising from benzene which

specified an environmental concentration in the workplace not to exceed a ceiling value of 25 ppm (80 mg/cu m) for benzene or products containing benzene at more than 1% by volume. Restrictions on the use of benzene specified that whenever harmless or less harmful substitute products were available, substitution was mandatory."^{7,19}

The aquatic toxicity ratings are:

Both benzene and toluene are acutely toxic to aquatic vertebrates. Poisoning can occur at 5 - 10 ppm and death at 20 ppm.^{2,3}

Half of the absorbed benzene is ultimately eliminated unchanged by the lungs, with only 0.1-0.2% excreted unchanged by the kidneys. The remainder is oxidized to phenols and diphenols and excreted as such or conjugated with $\text{SO}_4^{=}$ ions in the liver and excreted as esters of glucuronic and sulfuric acid in 48 hours.

Only 20% of the absorbed toluene is exhaled by the lungs. The remaining 80% is oxidized to benzoic acid, complexed with glycine to hippuric acid and excreted. (Sixty-eight percent of the absorbed toluene is excreted as such within 18 hours in one study.)

This metabolic pathway may account in part for the greater toxicity of benzene over toluene. Toluene may slow down the metabolism of benzene, thus making a fixed amount of benzene more toxic.⁷

II. Therminol 66

Therminol 66, manufactured by Monsanto Industrial Chemicals Co., St. Louis, Missouri, is proposed as the working fluid for testing the direct contact heat exchanger of the bi-phase bottoming cycle turbine system. The Therminols are a class of heat transfer fluids of varying operating temperature ranges; for example, Therminol 66 is designed to be operated between -9°C and 343°C .⁹ Therminols are hydrogenated ter-phenyls whose double bond content is proprietary information.

Therminols are quite flammable. The following information is given by the manufacturer: "Heat transfer fluids are intended only for indirect heating purposes."⁸ "In heat transfer installations, the fluid is used in a closed, non-pressurized system free from leaks..."⁹ "It is characteristic of most organic heat transfer fluids (including Therminol) to have a tendency to leak through joints and fittings at high temperatures unless these fittings are very tight.... Control of piping leaks is especially important, since fluid-soaked insulation poses a more serious hazard than the leaking fluid itself.... Organic heat transfer fluids such as Therminol exhibit a slow oxidation with the air trapped inside the voids of the insulating material when the system temperatures reach about 260°C This temperature build-up can result in ignition of the fluid when the space between the piping and the saturated insulation is exposed to air."⁸ "To minimize fluid oxidation, systems utilizing Therminol 66 fluid should be blanketed with an inert atmosphere."⁹

In the bi-phase cycle system, Therminol 66 is to be used not in a closed, tightly sealed system blanketed with inert gas, but in direct contact with exhaust gases. According to Resource Planning Associates, Inc. (RPA),¹⁷ these gases, having a maximum temperature of 382°C will heat up the working fluid to a maximum temperature of 349°C .

There are some disturbing features of this intended use of Therminol 66:

1. It is to be used at a temperature beyond its useful operating range.

This problem could easily be solved by substituting another fluid from the Therminol series since there are Therminols that can be used up to 427°C , but there are more serious problems.

2. Therminol 66 will be used in an open system, exposed to hot gases.

Several questions are raised: Is enough O_2 present in these gases to ignite or oxidize the working fluid? Can NO or NO_2 substitute for O_2 ? Will the working fluid be exposed to burning particulate matter that can ignite it?

3. It is not clear from the description in the RPA working paper¹⁷ whether the working fluid spends any of its time in a pressurized system. As we have seen, the Therminols are designed for use in non-pressurized systems. (Further: Therminol 66 fluid is designed for use in non-pressurized indirect heating systems."⁹).

4. If Therminols contain any double bonds or aromatic rings, they can probably react with some of the components of the exhaust gases (CO , NH_2 , NO , NO_2 , SO_2 , SO_3 , and water), especially in the prevailing acidic conditions of the exhaust gas. Reactions may produce toxic substances and will render the Therminols unfit for their intended use.

5. Therminols are ring compounds that may contain an aromatic ring. Compounds of this nature may be carcinogenic.

It appears that Therminol 66 was a poor choice for the application described above. A more suitable fluid, preferably an inorganic one, should be found.

III. Freon 11

Mechanical Technology, Inc. (MTI) proposes to use Freon 11 as the working fluid for its ORBC. RPA states that the system is in early stages of planning so that no component specifications are available. The exhaust gas temperature is not specified; it is somewhere between 90°C and 540°C. (It is not clear how the selection of a working fluid could be made without detailed knowledge of operating conditions like temperature and pressure.)

Freon 11 is a fluorocarbon refrigerant and can undergo three types of reactions that are typical of these compounds and are of special concern for the proposed application:

1. Pyrolysis.¹⁰

The following two reactions take place:

occurs first but only to a limited extent. Disproportionation:

Further disproportionation of Freon 12 yields Freon 13 (CClF_3) and eventually CCl_4 . CCl_4 decomposes to carbonaceous solids and chlorine gas.

DuPont, the manufacturer, recommends that a refrigerant not be used above that temperature at which the rate of decomposition (pyrolysis) exceeds 1%/year. For Freon 11 this temperature is ~300°C. The stability of fluorocarbon refrigerants follows the order:

2. Reaction with lubricating oil.¹⁰

Fluorocarbon refrigerants react with oils to form unsaturated oils, which can polymerize to form varnish, sludge and coke deposits that foul the system. Aluminum

seems to catalyze this reaction. The stability towards oil follows the order:

Freon 11<12<114<115<22.

3. Reaction with metals.

Fluorocarbon refrigerants react with metals to form metal chlorides, fluorides and carbon.¹¹ When left in a sealed tube for two years at 150°C, less than 1% of the Freon 11 decomposes, even in the presence of aluminum, inconel alloy or iron. SS 316 alloy increases the extent of decomposition to 5.3%, and copper to 60%. Air increases the decomposition of the refrigerant. At 260°C and 41 atmospheres of pressure for 25 hours, SS 316 alloy decomposes Freon 11 7.1% and inconel alloy 10%. At 370°C and the same pressure, both alloys decompose Freon 11 19% in 25 hours.¹² Parmelee's data¹² seem contradictory, especially for copper, aluminum and oil. Tests with the actual heat exchanger tubing should be conducted under operating conditions.

The stability of fluorocarbon refrigerants towards metals follows the order:¹²

Freon 11<113<13B1<12, 114<22<115<C318.

MTI should justify its choice of Freon 11 as the working fluid when it has the lowest overall stability towards reactions that can occur in the proposed application (assuming that a fluorocarbon refrigerant should be used at all).

Carcinogenicity

Freon 11 contains the impurities Freon 12 (CCl_2F_1) and carbon tetrachloride (CCl_4).¹² If heated high enough, Freon 11 will break down to Freon 112 ($\text{CFCl}_2\text{CFCI}_2$) and additional Freon 12. Freon 12 decomposes to Freon 114 ($\text{CClF}_2\text{CClF}_2$) and Freon 13 (CClF_3), which yields Freon 116 (CF_3CF_3) and Freon 14 (CF_4 , carbon

tetrafluoride). Freon 11, 12, and 13 all ultimately yield CCl_4 . CCl_4 ¹⁰, Freon 112 and Freon 113 (as well as the closely related chloroform (CHCl_3)) are known to be carcinogenic alkylating agents.¹³ The remainder of the above compounds, especially Freon 11, should be tested because of their obvious chemical similarity to these known carcinogens. The amount of contamination of the atmosphere should be tested under normal and extraordinary operating conditions to determine whether there is any detectable exposure to carcinogens. It should be noted that by selecting one of the least stable fluorocarbon refrigerants as the working fluid, the likelihood of obtaining carcinogenic decomposition products is maximized (assuming that the working fluid itself is not carcinogenic).

Other potential problems

Since the boiling point of Freon 11 is 24°C , it is a liquid at ambient temperatures a good part of the year and can, therefore, contaminate water through leakage. (The solubility is 44 ppm at 4.4°C and 168 ppm at 38°C .)¹⁴

It is possible that if there is a leak in the system and the hot working fluid comes into contact with air or exhaust gas, poisonous gases like phosgene (COCl_2), fluorophosgene (COF_2), COClF , HF , HCl , as well as F_2 and Cl_2 might be released.

Phosgene has been used as war gas. It is an "insidious poison as it is not irritating immediately, even when fatal concentrations are inhaled. May cause severe pulmonary edema (may be quickly fatal) or pneumonia....Vapors strongly irritating to eyes."¹⁵ The Merck index then warns that specially soaked paper must always be present as an indicator whenever generation of phosgene is possible or suspected.

Fluorophosgene is "a strong irritant to skin, eyes, mucous membranes, respiratory tract."¹⁵

Finally, it should be specified how used working fluid will be disposed of.

"...we can appreciably enhance the destructivity of the stratosphere for ozone by the infiltration of a relatively small amount of F-11 or F-12."¹⁶ (F = Freon.)

The result of ozone destruction can be higher incidences of skin cancers,¹⁶ which will be equally severe whether the fluorocarbon refrigerants enter the atmosphere through "accidental" leakage or through "intentional" disposal.

IV. Fluorinol 85

Fluorinol 85 ($\text{F}_3\text{CCH}_2\text{OH}$, trifluoroethanol) may be capable of breaking down to fluorophosgene at high temperatures. (see section on Freon 11).

The information below was supplied by the manufacturer, Halocarbon Products Corp. ¹⁸

TOXICITY

Preliminary toxicity data for trifluoroethanol are: acute oral LD_{50} : 240 mg./kg.; acute dermal LD_{50} : 1680 mg./kg.; and acute inhalation $\text{L}(\text{ct})_{50}$: 4600 ppm. hrs. According to standards established by the Manufacturing Chemists Association ^(a) the acute oral LD_{50} falls in the category of a toxic substance. Therefore, if ingested, efforts should be made to remove it from the stomach. A series of subhypnotic doses of ethanol is antidotal for trifluoroethanol toxicity in animals ^(b) and probably in humans.

Trifluoroethanol is not classified as toxic via the dermal or inhalation pathways ^(a). Nor is it a primary skin irritant, but contact with the skin should be avoided to prevent dermal absorption. Spills are readily washed off with water. Inhalation of the vapors should be avoided by working in a well ventilated area.

Animal studies have shown that trifluoroethanol causes severe eye damage similar to many chemicals (such as isopropyl alcohol and toluene). Immediate washing of the eye with water should be used following any splashes.

Subchronic inhalation exposure (6 hours per day, 5 days a week for 4 weeks) of male rats to 150 ppm of trifluoroethanol caused testicular depression (hypospermatogenesis and atrophy of the seminiferous tubules) leading to infertility lasting for at least 5 weeks after the exposure. Similar exposure to 10 ppm had no effect and the effect was transient after exposure to 50 ppm. While the significance of these observations for human safety is unknown at the present time, it is recommended that continuous exposure to atmospheric concentrations greater than 10 ppm be avoided.

(a) "Guide to Precautionary Labeling of Hazardous Chemicals", Seventh Edition, 1970, Manufacturing Chemists Association, 1825 Connecticut Ave., N.W., Washington, D.C. 20009.

(b) D. A. Blake, H. F. Cascorbi, R. S. Rozman and F. J. Meyer, Toxicology and Applied Pharmacology 15, 83 (1969).

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