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CONSERVATION

FINAL REPORT
MASTER
RANKINE
BOTTOMING CYCLE
SAFETY ANALYSIS

February 1980

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Vector Engineering Inc.
58 Brown Avenue
Springfield, New Jersey 07081

U. S. DEPARTMENT OF ENERGY
IDAHO OPERATIONS OFFICE

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(DOE Contract No. DE-AC05-79ET15445)

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February 4, 1980

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Vector Engineering Inc. (Vector) conducted a safety and hazards analysis of three Rankine Bottoming Cycle Systems in public utility applications: a Thermo Electron system using Fluorinol-85 as the working fluid, a Sundstrand system using toluene as the working fluid, and a Mechanical Technology system using steam and Freon-11 as the working fluids.

Because of limitations on time and budget, Vector (with DOE approval) concentrated its effort primarily on the safety aspects of the working fluids, which were considered to be most critical.

A double-risk assessment was undertaken, in which two independent system failures were assumed to occur simultaneously, and the response of the system to those failures analyzed from a safety standpoint. A double-risk assessment is more stringent than the typical single-risk analysis used in the chemical industry, but less stringent than the type of assessment used in the nuclear industry. A double-risk analysis was considered to be a sufficient safeguard of occupational and public safety for the types of installations studied in this report. Table 12 includes a double-risk assessment for the most important failure modes considered.

The properties of the working fluids considered in this report were flammability, toxicity, and degradation, and the risks to both plant workers and the community at large were analyzed. This included risks associated with potential decomposition products, or oxidation of the working fluids (such as in a fire). In addition, potential avenues were examined by which working fluid (or its decomposition products) could escape from the system. Besides structural failures, corrosion of the metal piping was considered. Corrosion could occur either as a result of the external action of the waste heat source (in this study, the waste heat source for all three systems was diesel generator exhaust gas from public electrical generating stations), or by the internal action of the working fluid or its decomposition products. Decomposition products could also corrode or deposit solids at critical locations, thereby affecting system performance.

Finally, the response of operating personnel (as well as equipment) to system failures was studied. In analyzing the response of personnel, the method by which they determine the severity of a failure is very important. For example, suppose the leaking of working fluid outside the system is detected by odor. While odor may, in some cases, provide an initial warning, it is not calibrated. Furthermore, if at a safe vapor level an odor becomes

commonplace, it will no longer provide an adequate warning if the vapor level rises. As another example, suppose an alarm goes off. Can the situation be easily corrected, or is an evaluation of personnel, or of the community, necessary? In order to determine corrective action, someone must, at the very least, enter the system control room, and perhaps also the structure housing the Rankine Cycle equipment. Under what circumstances is it safe to do so? These considerations influenced the ventilation recommendations included in this report, as well as recommendations regarding personnel procedures.

A general problem with all of the systems is disposal of working fluid. If it degrades, or if the Rankine Bottoming Cycle unit is dismantled, the fluid will have to be disposed of. Toluene can be incinerated, but both Fluorinol-85 and Freon-11 could produce toxic fumes on combustion. To our knowledge, this question has not been addressed in specific terms by any of the system designers.

(NOTE: Throughout this report, superscripts refer to the References listed on pages 64 and 65.)

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DEFINITIONS

The following definitions are particularly important for an understanding of this report:

Threshold Limit Value (TLV) - The American Congress of Government and Industrial Hygienists (ACGIH) defines TLV as follows⁽¹²⁾:

"Conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect... The TLV's must be considered simply as good-practice guidelines and, as such, have been accepted as official U.S. Government standards for industrial air."

The TLV corresponds to a time-weighted average vapor concentration over an 8-hour day.

Lower Explosion Limit (LEL) - This is the minimum vapor concentration in air at which an explosion will occur (below the LEL, the vapor is too lean to cause an explosion).

Upper Explosion Limit (UEL) - This is the maximum vapor concentration in air at which an explosion will occur (above the UEL, the vapor is too rich to cause an explosion).

LD50 - Dose lethal to half the animals in a test group (usually expressed in mg per kg of body weight)

LDLO - Minimum lethal dose (also expressed in mg per kg of body weight)

LC50 - Concentration in air lethal to half the animals in a test group (usually expressed in ppm per time interval of exposure)

LCLO - Minimum lethal concentration in air (also expressed in ppm per time of exposure)

TCLO - Minimum concentration in air at which toxic symptoms first appear (expressed in ppm, or ppm per time interval of exposure)

PART A

THERMO ELECTRON CORP.

RANKINE BOTTOMING CYCLE DESIGN

A.1. INTRODUCTION

Vector Engineering contracted with DOE to perform safety and hazards analyses for Organic Rankine Bottoming Cycle (ORC) systems applied to utility diesel exhausts. For this type of application, Thermo Electron does not have an operational system in the U.S.

Mitsui Engineering & Ship Building Co. (Japan), a licensee of Thermo Electron, has installed an ORC in an industrial application, using the same working fluid (Fluorinol-85), but a waste heat source that is not from diesel engines. In addition, Thermo Electron has developed a small ORC unit which is currently operating on a truck diesel engine, and uses Fluorinol-50 as the working fluid.

Although not operational, Thermo Electron has designed a 440 kW ORC for utility diesel applications (see Figure 1). At the present time, equipment is being assembled to pilot this design at the Waltham, Mass., headquarters of Thermo Electron.

This safety analysis is based on that design, in the form of documents received from Thermo Electron (listed in Table 1). In addition, Vector visited Waltham, Mass., on August 9, 1979, to discuss the design with Thermo Electron personnel. Information received verbally from them, but not documented, is so noted in this report.

A.2 PROPERTIES OF FLUORINOL-85

The working fluid in the Thermo Electron ORC design is Fluorinol-85, which is a mixture of 85 mole % trifluoroethanol and 15 mole % water. Trifluoroethanol has been produced by Halocarbon Products Corp. since 1960, and is used primarily as a nylon solvent⁽¹⁾. Table 2 lists some pertinent physical properties, and Table 3 compares the combustion properties of Fluorinol-85 with ethanol and with other working fluids.

It is important to note that because of its relatively low heat of combustion, Fluorinol-85 "will not sustain its own flame, that is, it has no fire point"⁽¹⁾. This means that in order to maintain Fluorinol-85 combustion, a continuous source of ignition is needed.

Toxicity data for trifluoroethanol are given in Table 4. The primary manufacturer (Halocarbon Products Corp.) also reports the following for trifluoroethanol⁽¹⁾:

"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 5 ppm be avoided."

Therefore, we recommend that ventilation requirements be based on allowing a maximum vapor concentration of 5 ppm in the work area, and the Fluorinol-85 monitors (see Safety Instrumentation) should be alarmed at 2.5 ppm and 5 ppm, rather than 5 and 10 ppm as presently conceived. Note that trifluoroethanol vapors are more than 3 times heavier than air and will tend to accumulate at floor level.

Since trifluoroethanol can also be absorbed directly through the skin, gloves and a supply of shower water are essential whenever Fluorinol-85 is handled (see Personnel Procedures).

A summary of trifluoroethanol toxicity is also given in Reference 32.

A.3. FLUORINOL-85 DEGRADATION

Halocarbon Products Corp. (the manufacturer of trifluoroethanol) reports the following⁽¹⁾:

"The trifluoromethyl group itself is inert towards the severest conditions of hydrolysis, oxidation, or reduction... The fluorine substitution also reduces the reactivity of the CH_2OH group in oxidation and replacement reactions. The oxygen-hydrogen bond is weaker in the fluorinated alcohol than in ethanol and consequently trifluoroethanol is more acidic than ethanol. In fact, the rates of reaction of the alcohol group in trifluoroethanol resemble those of aromatic alcohols (phenols) more than they do those of other aliphatic alcohols."

The above-mentioned acidity of trifluoroethanol may be responsible for the results of various tests performed with trifluoroethanol/water mixtures at temperatures up to 600°F , for up to 2,000 hours, in the presence of various metals⁽²⁾. Maximum decomposition was about 0.25%, with the metal turning black and the liquid ranging from colorless to light yellow (see Table 13). No analyses were given for the metal surface, or the liquids, and no data were reported for 304 stainless steel, of which the Thermo Electron system is constructed. The maximum bulk temperature of Fluorinol-85 in the Thermo Electron design is 550°F .

Gas phase dissociation (in the absence of oxygen or any other compound) can be estimated by examining the bond energies in the trifluoroethanol molecule. The C-H, C-O, and C-C bonds are weakest, while the C-F bond is strongest. Table 5 lists the theoretical percent dissociation for various temperatures, based on a minimum bond energy of 86 kcal/g-mole. At the maximum gas phase temperature in the Thermo Electron system (550°F), the maximum theoretical dissociation is about 0.06%. This is less than the observed maximum liquid-phase dissociation of 0.3% mentioned above. Decomposition products could include hydrofluoric acid which would attack the stainless piping. However, rates of decomposition are unknown.

If the Thermo Electron system becomes operational, corrosion rates should be carefully monitored.

A.4 EXHAUST GAS ACID CONDENSATION

The stainless piping in the waste heat exchanger, which is finned on the outside, can also corrode as a result of external attack by the flue gas. The low-sulfur No. 2 fuel used in oil-fired diesels can contain up to 0.33 weight % sulfur, which will oxidize in the combustion zone. In combination with water vapor, these oxides can form sulfuric acid. The sulfuric acid dew point, or condensing temperature, for such fuels has been measured as 236° to 248° F in diesel engine exhausts⁽³⁾. Data obtained from Public Service Electric & Gas (N.J.)⁽⁴⁾ in utility applications indicate an acid dew point for a No. 6 fuel oil with 0.3% sulfur to be between 250° and 260° F.

In the Thermo Electron design (see Figure 1), the flue gas leaving the vaporizer zone has a bulk temperature of 231° F. Both the inside wall of the stack and the outside wall of the vaporizer tubes can be cooler than 231° F, as a result of heat conduction through the wall. In addition, as a demonstration unit, frequent start-ups and shut-downs are to be anticipated, which means that the vaporizer surfaces may often start out near ambient temperature.

For these reasons, there is a considerable likelihood of acid condensation on the stainless steel vaporizer tubes closest to the flue gas exit. If this occurs, corrosion could be severe (304 stainless will corrode as fast as low carbon steel in sulfuric acid service⁽⁵⁾), raising the possibility of a leak developing in the vaporizer tubes, allowing Fluorinol-85 to escape into the flue gas and out the stack (see Community Safety).

However, in an experimental study using a No. 6 fuel oil with 0.8% sulfur, the following results were obtained⁽³⁴⁾:

"The presence of sulfuric acid vapor had been verified by numerous acid dewpoint measurements. The acid dewpoint was determined to be 117° C (242° F)... Soot analysis verified the presence of sulfuric acid, yet visual and physical observations failed to detect any corrosive reaction to any of the materials used... It is theorized that two fouling mechanisms are active in the 66 to 288° C temperature range: acid condensation and hydrocarbon condensation. Initially, a thin layer of acid is condensed on the cold, bare metal surfaces. After the surfaces become wetted, soot particles attach to the surface and a fouling layer is built up. As the layer increased, the high thermal resistance of the soot causes the surface temperature exposed to the exhaust gas to increase above the acid dewpoint,

preventing additional acid condensation... Operating below the acid dewpoint contributed to fouling, but the layers of soot, in turn, worked to inhibit further acid condensation, with immeasurable corrosion levels. This beneficial effect of fouling on inhibiting corrosion must be viewed with caution until the effects of fouling and cleaning on heat exchanger performance are evaluated..."

The potential for acid condensation corrosion cannot be determined at the Waltham, Mass., pilot facility of Thermo Electron, because they are not using flue gas as the waste heat source. Instead, a recirculating hot oil system will be used to vaporize the Fluorinol.

A.5. COMMUNITY SAFETY

If a leak develops in the vaporizer tubes, Fluorinol-85, and/or its decomposition products, will escape into the environment.

The recommended industrial TLV for Fluorinol-85 is 5 ppm (see properties of Fluorinol-85). This assumes an 8 hour exposure of a healthy worker. However, the community at large breathes its atmosphere 24 hours a day and includes infants, the elderly, and the sick. Although no official ambient regulation exists for Fluorinol-85, an acceptable level of 0.1 ppm was chosen for the purposes of this analysis (this is probably below the odor threshold, which for ethanol is 10 ppm⁽⁸⁾). Using that as the maximum allowable ground-level concentration, dispersion calculations were used to determine the maximum allowable stack discharge rate (see Appendix I). In order for these calculations to be valid, the discharge stack should have a vertical opening (rather than the side opening of the present design). The result of the calculations is that the allowable Fluorinol-85 discharge rate is 0.72 gal/hr, which amounts to the loss of the entire Fluorinol-85 inventory of 350 gallons in about 20 days. A decline of even 1 or 2% in inventory should prompt an immediate investigation of the cause of the leak, and equally prompt repair. Particularly since this will be a demonstration facility, periodic shut-down and examination of the vapor generator heat transfer surface is recommended.

Although a declining inventory could be measured at the condenser sump, the sump level will vary with operating conditions. These variations will make detection of a 1 or 2% loss very difficult. It is, therefore, recommended that a Fluorinol detector be placed in the exhaust stack (see Safety Instrumentation recommendations).

In addition to trifluoroethanol escaping into the atmosphere, its decomposition products can also escape, and furthermore, it can react with the oxygen present in the flue gas to form (among other compounds) trifluoro methanol, trifluoro acetaldehyde, trifluoro acetic acid, and carbonyl fluoride. Since the stack residence time is only 7 seconds (see Appendix II), during which the stack temperature drops from 683 to 231⁰ F, it is considered unlikely that trifluoroethanol would undergo significant conversion to these oxidation products. Toxicity data for the last two of these, along with hydrofluoric acid and phosgene, are presented in Tables 6A and 6B. Carbonyl fluoride (also known as fluorophosgene) is the fluorine analog of phosgene, with similar chemical properties. An examination of these tables would seem to indicate that carbonyl fluoride is probably no more toxic than phosgene, with a maximum allowable concentration of .05 ppm. In order to reach this concentration, assuming a maximum ground-level concentration of 0.1 ppm trifluoroethanol, 50% of the escaping trifluoroethanol would have to be converted to carbonyl fluoride in the stack. This is considered to be highly unlikely. However, such potential oxidation products emphasize the need to quickly determine if any Fluorinol-85 is leaking from the vaporizer.

A.6. FIRE PROTECTION

As stated under Properties of Fluorinol-85, it cannot independently sustain its own flame, and needs a continuous ignition source to maintain combustion.

Thermo Electron claims that a deluge system is to be installed in the Power Conversion Module (PCM) building. As yet, however, no working drawings or specifications have been received by Vector Engineering. According to Thermo Electron, the deluge system was to operate on detection of 1.2 volume % of trifluoroethanol vapors (i.e. 20% of LEL). In addition, we would recommend that it operate on detection of high temperature or heat (indicating a fire). Since trifluoroethanol and water are completely miscible, water acts as an excellent fire extinguisher. This system should be augmented with multi-purpose dry chemical fire extinguishers (rated 3-A; 20-B:C, or better), and a fire hydrant located within 200 feet of the PCM building.

If a fire starts in the power conversion building, the deluge system should prevent the general involvement of large quantities of Fluorinol-85. However, a fire could also start in the waste heat exhaust stack if Fluorinol leaks from the vaporizer. Although a fire in the stack is considered to be unlikely, the potential consequences could be quite severe (see discussion of oxidation products in Community Safety). Therefore, it is recommended that a CO₂ extinguishing system be installed in the waste heat stack, external to the vaporizer tubes, which would operate on detection of excessive stack temperature. A fire in the stack would require at least a double system failure: (1) a leak, and (2) a continuous source of ignition (since trifluoroethanol does not have a fire point). Furthermore, the oxygen content of the stack gas may not be high enough to support combustion.

Also because of the toxicity of its combustion products, fire fighters must be appraised of the danger, and self-contained breathing apparatus used, if Fluorinol-85 becomes involved in a fire.

Of course, the PCM building must be designated a "NO SMOKING" area, and combustible materials (other than the working fluid) should never be stored or be allowed to accumulate there.

The Thermo Electron design includes a control shed, which is a separate structure from the PCM building. This is appropriate not only from the point of view of personnel safety, but also for protection of safety equipment and instrumentation. If a CO₂ extinguisher is installed on the vaporizer, the cylinders should also be kept in the control shed.

A.7. PCM BUILDING VENTILATION

According to verbal information from Thermo Electron, a vent system is intended to change the air in the PCM building once every minute (fan capacity equals 15,750 cfm). This means that it can handle a daily loss rate of about 0.65% of the Fluorinol-85 inventory, without allowing the air in the building to reach the 5 ppm level (see Appendix III for calculations). As at the Waltham, Mass., pilot facility of Thermo Electron, the PCM fan is supposed to draw air from three levels in the PCM building: floor, mid-level, and ceiling. This is considered to be adequate from a ventilation standpoint (the minimum required fan capacity is only 2,600 cfm).

A.8. NON-CONDENSIBLE VENT

Non-condensibles (primarily from air in-leakage, and from dissolved gases in the original Fluorinol charge) will accumulate in the condenser and cause a gradual rise in the condenser pressure. At a high pressure set-point (as yet to be specified), the condenser will be vented across a refrigeration coil operating at 0° F. Liquefied Fluorinol from the vent vapors will be returned to the condenser, while Thermo Electron proposes to draw the remaining gases through a vacuum pump and exhaust them via a 55 gallon drum of activated carbon. Thermo Electron reports a carbon capacity of 0.5 lb. of Fluorinol/lb. of activated carbon.

A determination has yet to be made of the life of the carbon drum or its method of disposal.

A.9. OTHER VENTS

In the present design, there are 3 rupture disks: on the condenser, Fluorinol-85 recovery tank, and vapor generator. The rupture disks on the first two must conform to Section VIII, Div. I, Part UG-127 of the ASME Boiler & Pressure Vessel Code (see Piping and Pressure Vessel Codes). However, Section I of the Code requires a safety relief valve on the vapor generator (Part PVG, paragraph PVG-12). A rupture disk may be installed between the safety valve and vaporizer provided the requirements of paragraph PVG - 12.3 are met.

The vent lines from the condenser and vapor generator go to a sparger at the bottom of the 750 gallon outdoor recovery tank that is normally half-filled with water (verbal information from Thermo Electron). Since Fluorinol-85 is completely miscible with water, the recovery tank can provide some absorption of the vent vapors. We recommend that this tank be protected from freezing and provided with a sight glass or level gauge.

The condenser rupture disk is set at 60 lbs., while that of the recovery tank is set at 45 lbs. Therefore, if the condenser disk ruptures, the recovery tank rupture disk may also blow. In addition, the vapor generator safety relief is set at 1,000 lbs., and if it blows, it will also cause the recovery tank vent to open. In fact, if this vent is not properly sized, the recovery tank may actually blow apart (it is rated at 150 lbs.). Furthermore, while the maximum condenser temperature is only 113° F, it is at 550° F in the vapor generator. This may vaporize some of the water in the recovery tank. Atmospheric release of Fluorinol-85 is certain to occur, since the sparger cannot function very efficiently under such conditions. For this reason, the recovery tank vent pipe must be elevated sufficiently to allow dispersion of the vent gases. A height of at least 30 ft. is recommended.

It is not recommended that additional vapor absorbers (such as a carbon cannister) be placed at the recovery tank outlet. Such devices may plug, or otherwise cause excessive back pressure in the safety vent system, and proper relief of high pressure is considered more important than a momentary release of Fluorinol-85 into the environment. (As noted under Safety Instrumentation recommendations, the automatic safety trip should be connected to the vapor generator high pressure alarm, rather than the high temperature alarm. This would mean a rapid shut-down of the system, and the removal of any cause of pressure rise.)

A.10. FLUORINOL SPILL TANK

During deluge operation, or spill cleanup, large volumes of contaminated water will be generated. An acceptable method of disposal is yet to be specified, but it will be necessary to have a holding tank, or sump, available that can temporarily contain this waste. The floor of the PCM building should be curbed, and slope toward a drain leading to the spill tank. The tank should be so located that it will not contaminate any drinking water supplies in the event of a leak.

At 70°F, the vapor pressure of trifluoroethanol above Fluorinol-85 liquid is estimated to be about 75 mm Hg. This corresponds to a vapor concentration of 10%, which is within the explosive limits. Therefore, if undiluted Fluorinol-85 is contained in a spill tank, a number of precautions would have to be taken to prevent a detonation when the hatch is removed and solution pumped out. To avoid this problem, Fluorinol spills should be washed down with copious amounts of water. Since water and trifluoroethanol are completely miscible, water acts to suppress the trifluoroethanol vapor pressure, and if sufficiently dilute, will bring the vapor concentration in the tank well below the LEL.

The spill tank should either be constructed of non-conducting material (e.g. lined concrete), or be electrically grounded. It should have a separate vent, external to the PCM building, and at least 5 to 10 ft. higher than the building roof, and be supplied with a man-hole cover and dip-stick port (for liquid level determination).

A.II. PERSONNEL PROCEDURES

An operating manual should be written before the facility is operated. This must include specific instructions concerning personnel response to fire, handling of Fluorinol-85 (including its addition to the system), use of protective equipment, spill clean-up, and emergency situations. If an alarm goes off, there should be no doubt in the mind of the operator as to his next course of action. Otherwise, all of the engineering safeguards may count for nothing.

At Thermo Electron headquarters in Waltham, MA, personnel were observed wearing rubber gloves and a full face mask with hydrocarbon filters whenever handling Fluorinol-85. These procedures should be continued. Furthermore, a supply of water must be available whenever Fluorinol-85 is handled, since it can penetrate intact skin (causing toxic effects), and also damage the eyes⁽²⁵⁾. If handling is anticipated to occur very infrequently, a water hose with spray nozzle could be brought over to the handling location, with another person stationed nearby to help in an emergency. Otherwise, a safety shower and eye wash must be installed.

A.12. SAFETY INSTRUMENTATION

Basically, the Thermo Electron system is instrumented for high pressure boiler and gas turbine operation, with additional safeguards for the working fluid (Fluorinol-85). Boiler and turbine safety instrumentation are listed below, followed by instrumentation for detection of Fluorinol-85 release into the work environment.

Boiler and Gas Turbine Instrumentation in Present Design

1. Fluid (Fluorinol-85) high/low flow alarm on feed pump discharge
 2. Vapor generator outlet high pressure and temperature alarms (temperature only connected to safety trip system - see below)
 3. Cooling water low flow and pressure alarms
 4. Condenser high pressure alarm
 5. Automatic safety trip system:
 - a. Feed pump off
 - b. Vapor valve closed to gas turbine
 - c. Vapor bypass valve opened to condenser
 - d. Diesel exhaust gas diverter valve closed (ND)
- NOTE: Valves fail in the appropriate position consistent with the safety trip system. (ND)
6. Turbine lube oil low level alarm, to safety trip
 7. Lube oil high temperature alarms, to safety trip
 8. Lube oil low pressure alarm, to safety trip
 9. Excessive axial or lateral vibration alarms on turbine, to safety trip
 10. Turbine high speed alarm, to safety trip

ND: Not documented. Verbal information from Thermo Electron Corp.

Fluorinol-85 Detectors

1. A Wilks (Division of Foxboro) Miran II Process Infrared Analyzer will be panel-mounted in the control center, with multipoint sensors (12), and strip chart recorder. This detector actually senses total hydrocarbons in the PCM building. Since trifluoroethanol vapor is nearly 3 1/2 times heavier than air, most of the sensors should be placed at ground-level, with another at the turbine output shaft. As presently conceived, the detector will activate an alarm at 5 and 10 ppm. (ND)

Although the accuracy of the Wilks analyzer is unknown, it should be at least $\pm 35\%$ up to 5 ppm, and $\pm 25\%$ thereafter.

It should be further noted that the odor threshold for ethanol is 10 ppm⁽⁶⁾. If we assume the same for trifluoroethanol, it means that odor is not a sufficient warning for personnel protection (recommended vapor concentration limit is 5 ppm⁽¹⁾). Hence, the need for a trifluoroethanol monitor.

2. Deluge system (ND) to operate on 20% of LEL (1.2 vol. % Fluorinol-85 vapor concentration) in the power conversion building. (Note: The saturation vapor concentration at 50° F is about 4%, and at 100° F 21%.)

ND: Not documented. Verbal information from Thermo Electron Corp.

At this time, we would recommend the following changes to the safety instrumentation:

1. The water pressure for the deluge system should be positively indicated and protected from freezing. Periodic checks of the system should be made to ensure operability. Activation of the deluge system should be alarmed, and initiate an automatic shutdown of the ORC.
2. The roof ventilator must be alarmed and initiate an automatic shut-down of the bottoming cycle installation in the event of loss of building ventilation.
3. The vapor generator discharge high pressure alarm should initiate an automatic system shutdown, rather than the high temperature alarm.

4. There should be a low level condenser alarm, set at 10% below the normal set-point, and connected to the safety trip system. In addition, the level indicator output should be connected to a strip chart recorder, rather than the magnetic tape currently indicated on the P&ID. A strip chart will provide a permanent visible record of declines in Fluorinol-85 inventory (the set-point inventory level should be continuously superimposed on the strip chart output). Instrument sensitivity should be at least 0.5% of total inventory. The only place for Fluorinol-85 to go is the environment, and leaks need to be found and repaired quickly (there are also strong economic incentives, at a Fluorinol cost of \$85/gallon).
5. The Fluorinol-85 recovery tank should have a pressure indicator in the control room.
6. The Fluorinol detectors should be alarmed at 2.5 and 5 ppm (rather than at 5 and 10 ppm as presently conceived).
7. Cooling water low flow, and condenser high pressure should also initiate an automatic system shutdown.
8. The waste heat gas diverter valves should have limit switches, and panel mounted lights when open. On system shutdown, if valves fail to close, an alarm should sound, and the valves closed manually. For that purpose, a pulley-and-chain system must be installed.
9. A stack gas temperature sensor should be installed in the stack, near the discharge opening. When it senses an excessive discharge temperature (e.g. 450° F), it should actuate the recommended vaporizer extinguisher (see Fire Protection), and simultaneously initiate an automatic shutdown of the ORC system.
10. A Fluorinol sensor should be placed in the exhaust stack to monitor any release of working fluid from the vaporizer (see Community Safety). The Fluorinol sensors in the PCM building actually operator on detection of hydrocarbons, and would therefore be unsuitable as stack monitors. The monitor used would have to be capable of withstanding continuous exposure to 683° F, with the same sensitivity as the Wilks analyzer (see above). The instack monitor should also sound a warning alarm at 2.5 ppm, and initiate an automatic shutdown of the facility at 5 ppm.

A.13. ELECTRICAL CODE⁽⁷⁾

Although Fluorinol-85 is not specifically listed in the National Electrical Code, ethanol is listed as a Class I, Group D chemical.

Division 2 locations are those in which hazardous liquids or vapors are normally confined within closed systems, from which they can escape only by accidental rupture. Or, in which hazardous concentrations of gases or vapors are normally prevented by positive mechanical ventilation. Since the Thermo Electron design confines Fluorinol-85 to a closed system and also provides for mechanical ventilation, it would be considered a Division 2 location.

Therefore, the electrical system should be consistent with a Class I, Group D, Division 2 location. We were informed verbally by Thermo Electron personnel that this is the electrical code designation used in their design.

A.14. PIPING AND PRESSURE VESSEL CODES^(8,9,10)

According to Thermo Electron, the ASME Boiler and Pressure Vessel Code (B&PVC), Section VIII, Div. I ("Pressure Vessels"), is used for the working vessels, and all piping in the system conforms to ANSI B31.1 ("Power Piping").

We were also informed verbally by Thermo Electron personnel that they leak test all welds with helium based on 1×10^{-5} cc/sec. This is the acceptable rate recommended by the ASME B&PV Code, Section V, "Non-Destructive Examinations, paragraph T-1053.1.

However, more information is required on the Codes and Standards used by Thermo Electron in their design, particularly regarding the specific sections and paragraphs adhered to, and the equipment tests to be applied.

The codes and standards for construction should include the following:

a) Overall Requirements

1. Welding and Brazing Procedures, Welders, Brazers, and Welding and Brazing Operators should be qualified in accordance with Section IX of the ASME Boiler and Pressure Vessel Code, 1977 edition, with Addenda applicable at the time of fabrication.
2. Structural welding shall be in accordance with the Structural Welding Code AWS D 1.1-1975, including revisions applicable at the time of fabrication.

b) Piping

1. All piping design and welding external to the vaporizer shall be in accordance with the requirements of ANSI B31.1 "Power Piping" 1977, except the cooling water piping, which shall be in accordance with B31.5 "Refrigeration Piping" 1974 (both with Addenda applicable at the time of fabrication).
2. Piping internal to the vaporizer shall be in accordance with paragraph PG-109 of ASME B&PV Code, Section I, 1977, with Addenda applicable at the time of fabrication.

c) Condenser/Regenerator

The Condenser/Regenerator shall be fabricated, tested, inspected and registered in accordance with the applicable requirements of the ASME B&PV Code Section VIII, Division I, 1977 with Addenda applicable at the time of fabrication.

d) Vaporizer

The Vaporizer shall be fabricated, tested, inspected, stamped, and registered in accordance with the applicable requirements of Part PVG of the ASME B&PV Code, Section I, 1977, with Addenda, and with the specific requirements listed below:

1. Inspection and Tests The Vaporizer shall be inspected and tested in accordance with the general requirements of Part PVG, and paragraph PG-90, and the specific requirements of paragraph PW-46, et al.

Inspectors shall be qualified in accordance with paragraph PG-91.

Hydrostatic tests shall be in accordance with paragraph PG-99 and PG-100. Interior of tubes shall be free from residual moisture following the completion of the hydrostatic testing.

Radiographic Inspection of Welds shall be in accordance with paragraph PW-11 and Article 2 of Section V and shall meet the requirements of paragraph PW-51, except as noted in PW-11.1.1 and PW-11.1.2.

2. Safety Valves and Rupture Disks shall be in accordance with part PVG, - paragraph PVG-12. Rupture disks may be installed between the safety-valves and vaporizer provided the requirements of paragraph PVG-12.3, et al, are met.
3. Stamping shall be in accordance with paragraphs PG-104 through PG-113 of Section I, B&PVC.

PART B

SUNDSTRAND CORP.

RANKINE BOTTOMING CYCLE FACILITY

AT

EASTON, MARYLAND

B.1. INTRODUCTION

At the present time, Sundstrand has two operational 600 kW Organic Rankine Bottoming Cycle (ORC) systems on utility diesel exhausts. One of these is located at Beloit, Kansas, and the other at Easton, Maryland. Another utility system is currently being installed at Homestead, Florida. Because of the constraints of time and budget, DOE decided that Vector Engineering should review only one of these sites for safety. Sundstrand recommended Easton, Maryland, as the preferred site, and this represents the focus of our report.

It is important to note, however, that safety studies are very site-specific. Many of the comments and recommendations in this report may not apply to another site.

As of November 16, 1979, Sundstrand had accumulated 4,400 hours of operating experience at Beloit, and 1,200 hours at Easton (the Easton unit was officially commissioned on September 10, 1979). In addition, Sundstrand has more than 15,000 hours of operating experience with a 100 kW ORC (which also uses toluene as the working fluid), and has been operating a 600 kW pilot unit at their headquarters in Rockford, Illinois, for the past three years.

At Easton, Sundstrand owns the equipment shown in Figure 2 (including the instrumentation and control cabinets), with the exception of the piping to and from the vaporizer. Easton Utilities (a municipal electrical generating company), owns the site, supplies the waste heat (via its diesel generator exhaust), and was responsible for the construction of the Power Conversion Module (PCM) building, and toluene spill tank, under recommendations received from Sundstrand. Easton Utilities has overall operational responsibility, but Sundstrand will maintain the equipment they own under a field testing agreement, until September 10, 1980. At that time, Easton Utilities must decide whether or not it wants to purchase the ORC unit.

On August 28, 1979, Vector Engineering personnel made a site visit to the Easton installation. This report is based on that visit, on technical documents received from Sundstrand (see Table 7), on a technical review conducted at the Rockford, Illinois, headquarters of Sundstrand, and on other published sources of information (see References).

B.2. PROPERTIES OF TOLUENE

Table 8 lists some pertinent physical properties of toluene. From a safety standpoint, its flammability is of most concern; and because it is immiscible with water, either foam, carbon dioxide, or dry chemical extinguishers must be used to fight a toluene fire (although a fine water spray can provide cooling and containment).

Regarding its toxicity ⁽¹²⁾:

"...commercial grades usually contain small amounts of benzene as an impurity. Acute poisoning, resulting from exposures to high concentrations of the vapors, are rare with toluene. Inhalation of 200 ppm of toluene for 8 hours may cause impairment of coordination and reaction time; with higher concentrations (up to 800 ppm) these effects are increased and are observed in a shorter time. In the few cases of acute toluene poisoning reported, the effect has been that of a narcotic, the workman passing through a stage of intoxication into one of coma. Recovery following removal from exposure has been the rule. An occasional report of chronic poisoning describes an anemia and leucopenia, with biopsy showing a bone marrow hypoplasia. These effects, however, are less common in people working with toluene, and they are not as severe."

"Exposure to concentrations up to 200 ppm produces few symptoms. At 200 to 500 ppm, headache, nausea, loss of appetite, a bad taste, lassitude, impairment of coordination and reaction time are reported, but are not usually accompanied by any laboratory or physical findings of significance. With higher concentrations, the above complaints are increased and in addition, anemia, leucopenia and enlarged liver may be found in rare cases."

The Threshold Limit Value (TLV) is 100 ppm by volume in air ⁽¹²⁾, which corresponds to a time-weighted average over an 8-hour day. The American Conference of Government and Industrial Hygienists (ACGIH) also recommends a maximum peak excursion for toluene of 1.5 times the TLV (or 150 ppm) for short term exposure ⁽¹²⁾.

The U. S. Labor Department's Occupational Safety and Health Administration (OSHA) has also proposed an 8-hour time-weighted vapor concentration of 100 ppm as a safe operating level for toluene ⁽¹⁵⁾, with a maximum allowable excursion to 200 ppm for 15 minutes (the existing standard is 200 ppm for 8 hours, with a maximum allowable excursion to 500 ppm). Regular medical check-ups and environmental monitoring would be required if the vapor concentration reached an "action level" of 1/2 TLV, or 50 ppm.

Table 9 summarizes the toxicity data.

Sundstrand has placed warnings regarding the handling of toluene in their operating manual for the Easton facility⁽¹⁶⁾. These include the use of rubber gloves and eye protection. In addition, a full face mask with organic vapor cartridges should be prescribed for confined spaces. (In poorly ventilated spaces, the toluene vapor concentration at 70° F can be as high as 25,000 ppm at equilibrium).

Toluene can also cause corneal damage, and accordingly OSHA requires⁽¹⁵⁾ eye wash facilities wherever toluene is handled. Since toluene handling should be a relatively rare occurrence at the Easton facility, a temporary eye wash may be substituted during those periods, by bringing a water hose over to the handling area, and turning on the water at low flow. Safety goggles should be worn at all times by personnel in the PCM building (even if on a cursory inspection).

It is important to note that the reagent grade toluene used in the system may contain benzene, which is a carcinogen⁽³⁰⁾. The benzene content could impose a more stringent limitation on emission of toluene into the work environment than the toluene itself. At the present time, the benzene content for the Sundstrand units is unknown, and is not analyzed for by the toluene manufacturer (Allied Chemical). However, a TSCA Interagency Testing Committee⁽¹⁷⁾ reports the following (p. IX-8):

"Benzene is a common contaminant of toluene. Highly purified toluene (reagent grade and nitration grade) contains less than 0.01% benzene as contaminant."

OSHA has recently promulgated an 8-hour time-weighted average exposure limit of 1 ppm benzene vapor (the pre-existing standard had been 10 ppm). This is now being litigated through the federal courts, and a suit brought by the American Petroleum Institute to revert to the 10 ppm standard is presently being heard by the U.S. Supreme Court⁽¹⁸⁾.

However, if we assume a benzene content of .01%, a toluene standard of 100 ppm corresponds to only .01 ppm benzene, which is far below even the 1 ppm limitation. Therefore, the toluene limitation remains as the operable toxicity criterion.

Toluene itself is listed among suspected carcinogens. The following is abstracted from the introduction to Reference 28:

"It must be reemphasized that the entry of a substance in the subfile does not automatically mean that it must be avoided. A listing does mean, however, that the

substance has the potential of being hazardous if misused and, therefore, care must be exercised to prevent tragic consequences. Thus, there will be found in the subfile many substances which are common in everyday life and are in nearly every household in the United States."

The introduction goes on to say that compounds are listed in the file if they have reported neoplastigenic (tumor-forming) or carcinogenic effects, or are of oncological interest. Since no neoplastigenic or carcinogenic effects are listed for toluene, the presumption is that it is on the list simply because of its "oncological interest". Therefore, unless quantitative data materializes which indicates otherwise, a toluene level at or below 100 ppm for 8-hour industrial exposure was considered "safe" for the purposes of this report.

The Occupational Safety & Health Manual (U.S. DOE Office of Fossil Energy Programs)⁽²⁹⁾ also has a chapter on the handling of carcinogens. However, although it is fairly specific regarding industrial hygiene practices associated with "known" carcinogens, it leaves open the treatment of "suspected" carcinogens (such as toluene).

B.3. TOLUENE DEGRADATION

Sundstrand ran two toluene degradation tests under high temperature conditions⁽¹⁹⁾. They found a total degradation of 0.8% after 1,000 hours at 700° F, and 0.04% after 1,000 hours at 600° F. However, neither the toluene purity, nor pressure, nor dissolved oxygen content, nor the material of which the container was made were specified.

Extrapolating the Sundstrand data on semi-log paper (log of degradation vs. temperature), the toluene degradation over 1,000 hours of operation at 500° F (the maximum toluene temperature at Easton) would be about 0.001%. If assumed to be linear with time, this would correspond to a degradation rate of 0.000001%/hr. This implies a toluene loss of only 1 gallon after about 10 years of continuous operation. The actual operating record, particularly an examination of any lube filter sludges, will provide the test of these predictions.

Sundstrand reports the degradation products during their tests⁽¹⁹⁾ to be hydrogen, xylene, bibenzyl, substituted diphenyl methane, and benzene. Based on the rate of toluene decomposition noted above, the concentration of these products is expected to be extremely low. Furthermore, none of them are corrosive to steel.

B.4. EXHAUST GAS ACID CONDENSATION

The minimum temperature of the waste heat exhaust gas in the Sundstrand design is 285° F. This is above the sulfuric acid dew point temperature of 236-248° F (see discussion in Section A.4). Therefore, during steady operation of the ORC system, no serious corrosion problems are anticipated. However, during start-ups, when the heat exchanger surfaces are cold, acid condensation could occur on the vaporizer tubes.

B.5 COMMUNITY SAFETY

Toluene itself is a fairly common atmospheric pollutant, with typical urban concentrations in the 2 to 10 ppb range. The principal source of emissions is automobile exhaust. In the atmosphere, toluene reacts with various oxidizing agents to produce the eye irritants associated with smog.

If a leak develops in the ORC vaporizer, toluene will contact the exhaust gas, which contains similar oxidizing agents (O_2 , NO_x). The maximum residence time for toluene in the stack would be 2.6 seconds (see Appendix IV for calculations), during which time the stack gas temperature would drop from $752^\circ F$ to $285^\circ F$ (the autoignition temperature of toluene is about $1,000^\circ F$). Below $1,000^\circ F$, the rate constants for toluene-oxygen reactions are so low⁽²⁰⁾ that essentially no degradation will occur during the 2.6 second stack residence time. Therefore, in the event of a toluene leak, all that is expected from a community standpoint is a marginal increase in the local smog potential.

At the present time, there is no official ambient limit for toluene. The proposed industrial limit is 100 ppm, as noted above. However, the industrial limit assumes an 8 hour exposure of a healthy worker. On the other hand, the community at large breathes its atmosphere 24 hours a day, and includes infants, the elderly, and the sick. Therefore, assuming a maximum tolerable community level of 1 ppm (this is below the odor threshold of 2 - 4 ppm⁽⁶⁾), dispersion calculations can be used to determine the maximum allowable stack discharge rate (see Appendix V). This turns out to be about 2.33 gpm, which amounts to the loss of the entire toluene inventory of 1,100 gallons in less than 8 hours. Such a high rate of loss would eventually be detected by the vaporizer and hotwell low level indicators, either of which would automatically shut down the system (see Safety Instrumentation) and divert the waste heat exhaust gas to the original diesel generator stack. However, a continuous indication of system inventory is essential to preventive maintenance, and a minimum requirement should be a continuous sight glass at the condenser hotwell (with a calibrated scale). The sight-glass should have upper and lower isolation stopcocks that can be opened to take a reading, but otherwise remain closed to avoid a leak if the glass breaks. At the present time, the hotwell has just 3 spot glasses rather than a continuous gauge. Even with a sight glass, operating personnel must be relied upon to periodically record the level in a data log (see Personnel Procedures). Although desirable, an automatic continuous recording of the toluene level is not considered essential, because a very rapid decrease in toluene inventory is required before there is any significant danger to the community.

A leak rate of 2.33 gpm (1,013 lb/hr) of toluene in a stack containing 99,932 lb/hr of exhaust gas amounts to a toluene concentration of 0.3 volume %, or 25% of the lower explosion limit (LEL). Therefore, such a leak rate does not present an explosion hazard.

(Note: The dispersion calculations were based on normal dispersion to a neutral or slightly unstable atmosphere over level terrain. Also required, as a rule-of-thumb, is that the stack be at least 1 1/2 times the height of nearby buildings, in order to prevent plume downwash. At the Sundstrand installation in Easton, Maryland, the terrain is fairly level, and the stack is about 1.6 times the height of the generator building.)

B.6. FIRE PROTECTION

At Easton, a fire hydrant is located approximately 20 feet from the eastern entrance to the PCM building, and about 40 feet total from the hotwell. This is deemed adequate from the standpoint of fire water availability.

The PCM building is constructed of steel sheet, and is internally insulated on all walls except those formed by the control room.

The control room is part of the PCM building and is constructed of cinder block with a concrete slab roof. All electrical conduits between the control room and the turbine area are now, or soon will be, sealed, in order to prevent toluene vapor from passing through the control room wall. The type of sealant, and procedures used, must conform to the National Electrical Code (see below). There are no doors between the control room and turbine area.

In the event of an explosion in the turbine area, it will be preferentially relieved via the open garage door on the West side of the building (see PCM Building Ventilation). Also, the turbine has a containment ring that minimizes the possibility of flying metal due to a disc failure.

For the above reasons, the type of construction at Easton appears to be adequate to protect control room personnel and safety equipment from fires and explosions in the turbine area.

The vaporizer is protected by CO₂ extinguishers. These are positioned at three locations inside the exhaust stack, facing the outside of the vaporizer tubes. The CO₂ cylinders are housed in the turbine area of the PCM building, and the extinguishing system is activated by a high temperature (450° F) sensor in the stack exhaust. This system is intended to snuff out any fire that develops as a result of a toluene leak from the vaporizer, and CO₂ discharge will automatically shut-down the system and divert the exhaust gases to the original generator stack.

It should be noted that a fire at the vaporizer is unlikely, since it requires at least a double system failure: (1) a leak, and (2) a source of ignition. Furthermore, the oxygen content of the stack gas may not be high enough to support combustion.

There is also a CO₂ extinguisher system being installed in the turbine area of the PCM building. Four spray headers are located at the ceiling level, activated by four

temperature sensors, also located at ceiling level. The sensors first close the main garage door on the western side of the building. After a 40 second delay, the CO₂ nozzles are opened. As with the vaporizer CO₂ system, the CO₂ cylinders are all located inside the turbine area of the PCM building. The building extinguisher system is not connected to the auto safety shut down circuit for the ORC unit.

Besides the garage door, there are two other doors to the PCM building that are supposed to remain closed when the building is empty. However, during our visit of August 28th, one of these doors was already open when we arrived, and remained open during our visit.

We, therefore, recommend the following:

- (1) The CO₂ cylinders should be placed in a separate metal-roofed shed alongside the PCM building, or inside a separate control room structure, in order to isolate the means of fire protection from a potential fire source. If a fire starts in the turbine area of the PCM building, it may damage or rupture the cylinders and prevent their proper operation.
- (2) Openings (doors, vents, etc.) into the turbine area of the PCM building must be closed off in the event of a fire, in order for the CO₂ extinguishing system to function effectively. The exhaust fan and inlet air damper (recommended in PCM Building Ventilation) must be linked with the CO₂ system. If a fire occurs, the exhaust fan must stop, and the inlet air damper must close, in order for the CO₂ concentration to build up enough to blanket the fire. Personnel must be warned to evacuate the building. The exit door must be self-closing.
- (3) The PCM building CO₂ extinguishers should also initiate an automatic shut down of the ORC unit on CO₂ discharge.
- (4) There should be a dry chemical fire extinguisher (rated 3-A; 20-B:C, or better) in the control room, and two others in the turbine area of the PCM building.
- (5) "NO SMOKING" signs should also be placed outside the PCM building, adjacent to each entrance to the turbine area and control room (on our visit, of August 28, 1979, only one sign was observed, and that was inside the turbine area).
- (6) A fire blanket must also be placed inside the PCM building for additional personnel protection.
- (7) Combustible materials (other than the working fluid) should never be stored or allowed to accumulate in the PCM building.

B.7. PCM BUILDING VENTILATION

At Easton there is no mechanical ventilation of the PCM building. The only means of ventilation is a motor operated garage door on the west wall, which is supposed to remain open at all times. "At all times" includes the winter months, with the possibility of snow blowing into the PCM building. "At all times" includes periods when the ORC system is not operating. This implies that all water lines inside the PCM building must be freeze-protected. Sundstrand has informed us verbally that the cooling tower sump is heated, and the cooling water is continuously circulated through the main generator building and PCM building. However, during ORC shutdown, the gearbox cooling water will remain stagnant in the lines and must be freeze-protected. Leaving the garage door open during winter would also seem to negate one of the purposes of the PCM building (for winter protection), and also would negate the effect of the building electric heaters.

In addition to being the sole means of PCM building ventilation, the garage door also is the sole means of venting the toluene spill tank (see below).

For these reasons, it is recommended that a roof-mounted exhaust fan be installed, with a minimum capacity of 2,900 cfm. Such a fan could accommodate a daily loss rate of 1.25% of the toluene inventory and still maintain the PCM building at 100 ppm (see Appendix VI for calculations). The fan must be linked with a motor operated damper (preferably at floor level) to allow fresh air to sweep the building (and also to avoid a negative building pressure). Both fan and damper motor must conform to a Class I, Group D, Division 2 location (see Electrical Code). The garage door would then remain closed, and the inlet air damper and exhaust fan would shut on CO₂ extinguisher discharge (see Fire Protection).

B.8. NON-CONDENSIBLE VENT

As non-condensable gases accumulate in the main condenser, a vacuum pump removes them via a separate water-cooled toluene vapor condenser (steel wool in the discharge line acts as a mist eliminator). The vacuum pump then vents out an 8 inch pipe that rises about 2 ft. above the PCM building roof level. Upstream of the vacuum pump discharge line is a rupture disk (also in the same 8 inch vent line), set at 15 psig (195°F) $\pm$ 0.75 psi.

The vent pipe height is inadequate for proper dispersion of released toluene. (Note that toluene is more than 3 times heavier than air, and the intake for the cooling tower fan (which is not spark-proof) is located approximately 30 feet from the base of the vent pipe.) This vent pipe should be at least 6 ft. higher (24 ft. above the ground).

B.9. OTHER VENTS

There are also two safety valves on the vaporizer separator set at 500 psig (550° F). These valves vent to atmosphere through a short pipe which ends about 2 ft. below the roof of the main generator building, and about 10 ft. away from it. This is likely to cause downwash of the toluene vapors in the event of a release, and their accumulation at ground-level. The air intake ports for the diesel generators are also located at ground-level, approximately 25 ft. from the base of the vaporizer (the air intake fans are probably not spark-proof).

Although we had initially recommended that the separator vent pipes be raised at least 10 ft. above the generator building roof level (12 ft. above their present height), Sundstrand states that such an increase in height would generate unacceptable mechanical moments on the primary structure due to shock wave propagation (the present vent pipe was designed utilizing paragraph 31.1 of the Power Piping Code). In light of this, since the risk of danger due to vapor downwash is small in any case, we have decided to drop our initial recommendation.

B.10. TOLUENE SPILL TANK

The floor of the PCM building is sloped toward a central drain, which runs into a 1,500 gallon underground concrete tank. The exhaust stack also drains condensate or rain water via a weighted valve into this tank. The location of the spill tank should be such as to avoid drinking water contamination in the event of a leak. It is not known if the present location conforms to this safeguard.

At the present time, this tank is vented through the 12" drain line from the PCM building (assuming the drain line is never completely filled with toluene). Again, this emphasizes the need for a building vent fan. At a temperature of 70° F, the vapor space above the liquid in the spill tank will have an equilibrium concentration of 2.5 volume %. This is within the explosive limits. Diluting the toluene with water will not reduce the equilibrium vapor concentration because water and toluene are immiscible. Extreme caution must, therefore, be exercised whenever the top hatch is removed following a spill. Hatch bolts should be non-sparking, and non-sparking tools should be used to remove it (the tank itself is made of concrete and need not be grounded). The local fire department should be notified whenever this tank is to be opened for pump-out, no smoking must be strictly obeyed, and the tank pumped out with an explosion-proof self-priming pump, into a tank truck for ultimate disposal. Such disposal must of course be accomplished in an environmentally sound manner.

No one should be allowed to enter the tank unless a flammable vapor meter shows the atmosphere to be outside the explosive limits, and (a) the oxygen content is at least 18% by volume, or (b) a self-contained breathing apparatus is used. Whenever someone enters the tank, there must always be someone else above at grade level holding a life-line in case of emergency.

Furthermore, since the spill tank vents through the PCM building, the ORC unit must remain off, and no one should be allowed in the PCM building until the tank is emptied. The hatch cover on this tank should also be gasketed to prevent ignition of any leaking toluene vapors above ground.

B.11. PERSONNEL PROCEDURES

OSHA requires⁽¹⁵⁾ an employee training program wherever toluene is stored, handled, or used. This program is to include information on the toxicity and flammability of toluene, use of protective equipment, and hazardous or emergency procedures. The latter is extremely important. Entering the toluene spill tank would be one hazardous condition for which specific procedures must be communicated to operating personnel. Emergencies would involve a toluene spill, excessive vapor concentration, or fire; and specific procedures must also be developed for these contingencies. There should be no doubt in the mind of the operator as to his course of action during an emergency. Such procedures do not yet exist in the operating manual⁽¹⁶⁾, although in discussions with Sundstrand, they have suggested including the following (abstracted from p. 46218 of Reference 15):

"Steps to be taken if toluene is released or spilled: Large amounts of water spray should be used to flush the spills. Do not flush toluene into a confined space, such as a sewer, because of explosion danger. Remove all ignition sources. Ventilate enclosed places. Persons not wearing protective equipment should be restricted from areas of spills until clean-up has been completed."

It should be noted, however, that there is presently no fire hose near the PCM building with which to provide "large amounts of water spray", and the only location to which toluene can be flushed in the PCM building is the spill tank, which is a "confined space".

Sundstrand has also suggested following Section 1910.94(d)(11)(ii-v) of Title 29 of the Code of Federal Regulations (Occupational Safety and Health Standards), which contains provisions for entering vessels containing hazardous vapors (such as an emptied spill tank).

The response of the central utility plant operators (located about a mile away in Easton) to emergency situations must also be clearly specified and subjected to safety review. In general, the Organic Rankine Cycle (ORC) equipment control room is left unmanned. Whenever an alarm goes off in the control room, another one goes off at the central utility plant. The usual procedure seems to be (as observed on our August 28th visit) that the central plant operator then calls the maintenance room of the auxiliary facility at which the ORC is located (the control room does not have a phone), and a local maintenance man goes over to the control room to see what the problem is. All of this takes time. What if the central plant operator calls and gets no response? What if he

calls, the local maintenance man checks the control panel, and never returns the call? It will be at least another 10 minutes or more before someone can get from the central utility plant to the ORC facility. These procedures must be carefully considered, and responses to various contingencies must be clearly specified to operating personnel at both locations.

In addition, we recommend the following with regard to present practices:

- (1) For both safety and environmental reasons, any detection of toluene loss under constant operating conditions (noticed by a sinking inventory) should be immediately followed up by location of the leak, and correction. Personnel must log the toluene level in the condenser hotwell at least once every 8 hours (see Community Safety).
- (2) When replacing filter cartridges, the system must be shut down, and any toluene that's drained, along with filter sludge and used cartridges, must be disposed of in an environmentally acceptable manner.
- (3) During toluene filling, the operating manual⁽¹⁶⁾ has grounding procedures for the fill container (to PCM frame with 1/8 to 1/4 inch copper wire). In addition (see also p. 46219 of Reference 15):
 - (a) 2 people must be present at all times.
 - (b) Use non-sparking tools to open the toluene container.
 - (c) The toluene supply container should have two top openings--one for the vent, and one for the flexible fill hose.
 - (d) The fill hose should be made of non-soluble plastic (such as Teflon) in order to avoid sparking.
 - (e) The recommended PCM building roof ventilator should be on.
 - (f) Water should be available in the PCM building via a water or fire hose.
 - (g) Step (6) (p. 5 - 8) of the operating manual⁽¹⁶⁾ should be replaced with the following:
 6. Shut off hand valve at fill connection.
 7. Remove flexible hose from toluene container and let drain.
 8. Disconnect hose at fill connection and replace cap. Remove ground wire from PCM frame and remove toluene container from area.

In order to minimize the amount of air being sucked into the system, the hand valve must be shut off as soon as a "soda straw" sucking noise is heard from the supply drum.

- (4) On low CO₂ cylinder pressure, a "CO₂ Discharge" light is illuminated on the PCM control cabinet door (for vaporizer extinguishers only). However, this indication is not associated with any alarm. Since the control room is generally unmanned, the CO₂ system pressure (at the cylinder regulators) must be logged every 8 hours, along with the toluene hotwell level (see item (1) above). If not already present, pressure gauges must be installed on the cylinders for this purpose.

In discussions with Sundstrand, they have suggested installing a low pressure switch on the PCM building CO₂ cylinders that would (along with the switch for the vaporizer CO₂ cylinders) actuate a master warning light at both the on-site and central generating plants. If this is associated with the alarm horn, it would represent an acceptable alternative.

- (5) Although no operator is routinely designated to occupy the PCM building, the maximum allowable exposure should be 200 ppm for 15 minutes (see Properties of Toluene). This is well above the odor threshold of 2-4 ppm⁽⁶⁾. Therefore, 200 ppm will constitute a "strong" toluene odor, but so will 1,000 ppm or 12,700 ppm (the lower explosion limit). What action, then, should be taken by operating personnel when they detect a "strong" toluene odor in the PCM building? The sniffer is calibrated from 0 to 100% of LEL (or 0 to 12,700 ppm), with an accuracy of $\pm 3\%$ of scale (± 381 ppm). Therefore, the sniffer cannot be relied upon to detect a toluene level of 200 ppm. Furthermore, the definition of a "strong" odor is highly subjective. We, therefore, recommend that if anything above a faint odor is noticed, personnel should not be allowed in the PCM building without a cannister mask with full facepiece, and the leak must be found and corrected as soon as possible. Even with a cannister mask, care must be exercised that the cannister is fresh, and its absorptive ability is not exceeded (if toluene odor is detected through the mask, the wearer must exit from the PCM building). Cannister and mask must conform to OSHA specifications (30 CFR 11.90 (r) (1-3)). On our visit to Easton (8/28/79), we did not detect any toluene odor with the equipment running.
- (6) If a leak develops in the PCM building, the vapor concentration will rise until automatic shutdown is initiated. This presently occurs at 75% of LEL, although we recommend this be changed to 20% of LEL (see Safety Instrumentation). However, a system shutdown may not stop the leak. The present PCM building CO₂ extinguisher system only operates on heat

detection. If the toluene vapor concentration rises within the explosive limits, the presence of a spark will result in a detonation before the extinguisher system has a chance to function. That spark may be generated simply because the portions of the PCM building not supplied by Sundstrand (i.e. anything besides the Power Conversion Module) do not conform to the National Electrical Code (see Electrical Code).

If the "sniffer" initiates automatic shutdown at 20% of LEL as recommended, there may be time for personnel to enter the PCM building with hydrocarbon cannister masks (full face mask) to repair the leak. If this is done, the recommended ventilation fan (see PCM Building Ventilation) must be operating, and there must be close monitoring of the "sniffer" reading. If the toluene vapor concentration reaches 50% of LEL, all personnel must be evacuated, and the building left to ventilate. Even with complete conformance to the NEC, a spark could still be generated by the shoe nails, tools, or static charge associated with the maintenance crew. Only if ventilation reduces the vapor concentration back below 50% of LEL should personnel consider reentering the turbine area. Needless to say, if the sniffer gauge isn't functioning properly, no one should be allowed in the building.

SAFETY INSTRUMENTATION

There is a safety trip system which automatically initiates either an emergency or normal shutdown of the ORC system. An emergency shutdown is sequenced as follows:

- (1) Diverter valves closed, waste heat gas bypasses the vaporizer.
- (2) Shut-off valve to turbine is closed.
- (3) Main breaker opened.
- (4) Liquid level control valve closed.
- (5) Throttle valve to turbine closed.
- (6) Condenser vacuum pump to shut down.
- (7) Initiate spindown timer; after 5 minutes, boost pump and lube pump are shut off.

The following system safeties automatically initiate an emergency shutdown. These sensors also have an individual indicator light on the control panel, and activate a common alarm horn—an alarm also sounds in the main control room of the central utility plant located about a mile away in downtown Easton:

- + turbine overspeed (10230 rpm)
- + turbine lubricant (i.e. toluene) underpressure (15 psig)
- + turbine bearing high temperature (200° F)
- + no cooling water flow
- + condenser overpressure (10 psig)
- + gearbox lubricant (DTE heavy medium oil) overtemperature (155° F)/
underpressure (16 psig, start -- 18 psig, run)
- + module not connected — An internal continuity check determines whether or not the analog control modules are connected to their electrical connectors. System shutdown prevents operation when a module is not properly connected.
- + ground fault, overcurrent, reverse power

In addition, there are system safeties which actuate a "normal" shutdown. This is automatically sequenced as follows:

- (1) Diverter valves closed, waste heat gas bypasses the vaporizer.
- (2) Initiate 12 second timer, to allow diverter valves to close. (In the procedures received by Vector, no system response is indicated if the diverter valves fail to close, except for a warning light and alarm (see below). We recommend that failure of the diverter valves to close must automatically initiate an emergency shutdown).

In response to this recommendation, Sundstrand states the following (see Table 7, item 7 (e)):

"Failure of the diverter valves automatic control should not trigger an emergency shut-down. Under an "emergency" shutdown, the emergency shut-off valve is immediately closed containing all the fluid energy in the vaporizer. Continued application of heat will probably cause activation of the vaporizer vent and subsequent venting of toluene. However, if the "normal" shut-down is utilized, the unit continues to run, dissipating the fluid energy. The warning light will then generate action by the operator to manually close the diverter valve, allowing the unit to be completely shutdown."

However, if the diverter valves fail to close, there is no "normal" shutdown. In fact, there is no shutdown at all. Heat will continue to vaporize the toluene, which will continue to drive the turbine, as in the normal operating mode. Since the ORC control room is generally unmanned, the amount of time it would take to manually close the diverter valves is unknown. Furthermore, a "normal" shutdown may be initiated by fire (CO₂ extinguisher discharge), or an excessive toluene vapor level in the PCM building ("sniffer" alarm), both of which Vector considers to be more dangerous than the temporary venting of toluene from the vaporizer safety relief valve.

- (3) If the diverter valves close, the vaporizer will begin to cool, and the turbine will coast down. According to information received from Sundstrand, a turbine coastdown will eventually cause a reverse power flow in the generator, which will initiate an emergency shutdown (see last item in list of emergency shutdown safeties). This may require several minutes, from detection of a failure to complete shutdown of the ORC system.

The following sensors initiate a normal shutdown:

- + turbine underspeed (8370 rpm)
- + vaporizer overtemperature (510° F)/overpressure (500 psig)
- + separator low level (16 inches)
- + hotwell low level (18 inches, to prevent boost pump cavitation)
- + CO₂ extinguisher discharge (at stack discharge temperature of 450° F)
- + toluene high vapor concentration detected (by the "sniffer") in the turbine area; 3 floor level detectors, and another at the turbine output shaft, actuate a warning light on the control panel at 65% of the lower explosion limit (LEL), and initiate automatic shut down at 75% of LEL (9525 ppm). Sniffer accuracy is $\pm 3\%$.

The following merely illuminate a warning light on the PCM control panel. They do not initiate auto shut-down, or actuate the alarm. Furthermore, since the control room is generally unmanned, the effectiveness of warning lights is questionable:

System Warnings

- + system and turbine lubricant (i.e. toluene) filter high pressure (40 psig)
- + gearbox lubricant low level
- + vaporizer (separator) toluene high level
- + high condenser pressure (5 psig)
- + low generator power (50 kw)
- + circuit breaker trip on cogenerator electrical output
- + heat source ready -- The system will not function unless the source used to heat the toluene is above 600⁰ F. The system cannot be started while the indicator remains off.
- + shut off trip test (safety test) - Pushbutton on the annunciator panel is pressed to verify operation of the system shutdown circuitry. If the shutoff valve fails to operate, the indicator remains illuminated.
- + Not Auto--one or more of the system valves or pumps is being operated in the manual mode.
- + one of the two exhaust gas diverter valves (individual warning lights) is not closed on normal system shut-down (i.e. exhaust gas is still going to the vaporizer); 12 seconds after shutoff switch is activated, if valve is still not closed, local alarm is activated at the open valve.
- + sniffer detects toluene vapor concentration in PCM building at 65% of LEL (8255 ppm).

The main control room of the central utility plant a mile away can also remotely shut-down the ORC unit (according to verbal information received from on-site operator).

In addition to the recommendation made above with regard to the "normal" shutdown procedure, we recommend the following:

- (1) With installation of a roof ventilator (see PCM Building Ventilation), loss of ventilation should be added to the list of emergency shutdown sensors.
- (2) The "sniffer" should actuate a warning light at 10% (rather than 65%) of LEL, and automatic shut down at 20% (rather than 75%) of LEL. A local sensor reading of 75% does not guarantee that the vapor concentration is below the LEL everywhere in the PCM building.

In response to this recommendation, Sundstrand states the following (see Table 7, item 7 (e)):

"Strong exception is taken to the recommendations of this paragraph. 1) The three sensors or "sniffers" are located on the floor of the building. Because of the characteristics of toluene (heavier than air), it is essentially guaranteed that the vapor concentration at the floor level will be the greatest; 2) A system shutdown at a 20% of LEL signal could trigger unnecessary nuisance shutdowns; 3) The PCM building is unmanned, therefore the major purpose of the toluene vapor warning/shutdown safeties is to warn the operator of leaks and shutdown if they are significant.

"It is suggested that to alleviate the concern of not recognizing small leaks, the warning light be actuated at 20% LEL. The shutdown should be actuated at the present 75% LEL. This will provide operator warning of minor leaks, shutdown of more significant leaks, and minimum of nuisance shutdowns."

However, a vapor concentration of 20% of LEL is equivalent to 2540 ppm. This is 25 times greater than the TLV. At the recommended building vent rate of 2900 cfm (see PCM Building Ventilation), it would take a toluene leak rate of 2533 lb/day (1/3 of the total system inventory) to reach such a vapor concentration. Therefore, an automatic shutdown at 20% of LEL should not constitute a "nuisance" shutdown.

In addition, the sniffer is calibrated from 0 to 100% of LEL ($\pm 3\%$). Therefore, 20% of LEL is 7 times the instrument sensitivity.

- (3) If it does not already do so, the condenser pressure should register on a gauge in the ORC control room.

B.13. ELECTRICAL CODE⁽⁷⁾

Toluene is listed in Table 500-2 (p. 70-350) of the National Electrical Code-as a Class I, Group D chemical.

Division 2 locations are those in which hazardous liquids or vapors are normally confined within closed systems, from which they can escape only by accidental rupture. This is consistent with the Sundstrand installation at Easton, Maryland.

Therefore, the electrical system should be for a Class I, Group D, Division 2 location. The Power Conversion Module is designated as such in a Sundstrand Energy Systems brochure⁽²¹⁾. However, the electrical system in the rest of the PCM building (lights, fans, switches, etc.) does not conform to the Code (it is simply designated as "vapor proof"). All electrical equipment in the PCM building must conform to a Class I, Group D, Division 2 location, as per the NEC. This must also apply to electrical equipment (cables) and seals between the turbine area and control room (see Fire Protection).

B.14. PIPING AND PRESSURE VESSEL CODES^(8, 9, 10)

The following information was received from Sundstrand regarding the Power Conversion Module:

- (1) All welding was done by qualified welders to Section IX (1977 edition) of the ASME Boiler and Pressure Code (B&PVC), including 1977 addenda in effect when the unit was built.
- (2) All structural welding was done in accordance with structural welding code AWS D 1.1 - 1977.
- (3) Welds requiring nondestructive methods of examination were done by qualified Level II inspectors (Section V of the 1977 ASME B&PVC, in effect when units were built).
- (4) All external piping to the Vaporizer is in accordance with the requirements of ANSI B 31.1 "power piping" (1977), with 1977 addenda.
- (5) All piping internal to the Vaporizer is in accordance with paragraph PG 109 of ASME B&PVC, Section I (1977), with 1977 addenda.
- (6) The condenser/regenerator is fabricated, tested, inspected and registered in accordance with the applicable requirements of the ASME B&PVC, Section VIII, Division I (1974).
- (7) The Vaporizer is fabricated, tested, inspected, stamped, and registered in accordance with the applicable requirements of the ASME Part PVG of the ASME B&PVC, Section I (1977), with the 1977 addenda.
- (8) The Vaporizer is inspected and tested in accordance with the general requirements of Part PVG, and Paragraph PG-90, and the specific requirements of paragraph PW-46. Inspectors are qualified in accordance with Paragraph PG-91.
- (9) Hydrostatic tests are in accordance with Paragraph PG-99 and PG-100.
- (10) Radiographic inspection of welds in accordance with ASME B&PVC, Section I (with reference to Section V, Article 2, PW-11).
- (11) Leak testing is in accordance with ASME B&PVC, Section V, Article 10. The test is run by the boiler manufacturer.

- (12) Vaporizer safety valves and rupture disks are in accordance with ASME B&PVC, Section I, Part PVG, Paragraph PVG-12. The requirements of Paragraph PVG-12.3 are met, allowing the installation of rupture disks. The condenser rupture disk is in accordance with Section VIII, Div. I, Part UG-134 (this should be UG-127).
- (13) Stamping is in accordance with PG-104 through PG-113, of Section I, ASME B&PVC.

PART C

MECHANICAL TECHNOLOGY INC.

RANKINE BOTTOMING CYCLE INSTALLATION

AT

ROCKVILLE CENTER, NY

C.I. INTRODUCTION

Mechanical Technology Inc. (MTI) has designed and built a 500 KW Rankine Bottoming Cycle (RBC) at the power house operated by the Village of Rockville Center, New York. Figure 3 is a schematic of their system. It operates on a combined steam/Freon-II cycle.

On September 26, 1979, Vector Engineering personnel made a site visit to the MTI installation. At that time, the unit was not operational, pending repairs and adjustments. The following analysis is based on that visit, and on additional documents received from MTI (see Table 10).

Since safety studies are very site-specific, some of the comments and recommendations in this report may not apply to another site.

C.2 STEAM/FREON-II (Trichlorofluoromethane)

Of course, steam is entirely non-toxic and non-flammable. Freon-II is also non-flammable, and non-toxic up to vapor concentrations of 1,000 ppm^(12, 14). Higher concentrations (60,000 ppm) can cause narcosis and anaesthesia. Table II is a summary of Freon-II toxicity.

C.3. FREON-II DEGRADATION

The primary danger from Freon-II occurs on exposure to heated surfaces ($\sim 1,000^{\circ}\text{F}$ or higher), or open flames⁽²²⁾. Toxic decomposition products (including hydrofluoric acid and phosgene) can then result. However, the hottest surface in continuous contact with Freon-II in the MTI system is only at 215°F . This occurs in the tubes of the Freon vaporizer, where heat is supplied by condensing steam. The entire Freon system is several hundred feet distant from the primary waste heat boiler, where steam picks up heat from the diesel exhaust gases. Maximum surface temperatures in the waste heat boiler do not exceed 450°F .

Another potential source of danger is reaction of the Freon with zinc, magnesium, or aluminum⁽²²⁾. However, the MTI system is constructed entirely of carbon steel and copper.

Therefore, Freon-II is expected to remain stable under the conditions prevalent in the MTI system.

C.4. EXHAUST GAS ACID CONDENSATION

The MTI system has the highest exit gas temperature 320°F , and should therefore have the least problem with sulfuric acid condensation (which is expected to occur between $236\text{-}248^{\circ}\text{F}$ -- see discussion in Section A.4.)

Furthermore, steam is the working fluid in the stack vaporizer. Even if corrosion occurs, it will only release steam out the exhaust stack.

Therefore, in the MTI system, considerations of sulfuric acid condensation are inconsequential from a safety standpoint.

C.5. COMMUNITY SAFETY

Because of the relative safety of both steam and Freon-11, no community safety problems are anticipated, provided that Freon-11 holding vessels are protected from excessive heat during a fire. This means having enough fire water available to act as a coolant.

C.6. FIRE PROTECTION

A fire in the immediate vicinity of Freon holding vessels could cause high internal pressures. In order to protect the vessels from rupturing, rupture disks and safety valves are provided (see Pressure Relief Vents). However, large discharges of Freon-11 from these vents, in proximity to open flames, presents the possibility of forming such toxic decomposition products as hydrofluoric acid and phosgene. Therefore, in the event of fire, it is essential that Freon-11 holding vessels receive copious supplies of fire water to keep them cool and minimize discharges.

At Rockville Center there are two fuel oil storage tanks approximately 50 ft. away and two fire hydrants within 150 ft. of the RBC. This is considered to be adequate availability of fire water. Also, the RBC building is made of metal, with fiberglass insulation, and does not normally contain flammable materials. This building houses the turbines, Freon feed tank, and control room (separated by a metal wall).

Combustible materials should never be stored or be allowed to accumulate within 20 feet of the RBC building, and a multipurpose dry chemical fire extinguisher should be located there, with a minimum rating 1-A; 5-B:C.

During the winter months (December 15 to March 15), the RBC building is sealed up and placed under a low nitrogen blanket to prevent condensation damage to the electrical system. A warning light is illuminated in the main power plant control room when the nitrogen supply runs low. The RBC is not operated during this period because of low, intermittent availability of exhaust gas from the diesel generators which function in a peaking mode.

C.7. RBC BUILDING VENTILATION

The volume of the RBC building is 1695 ft^3 ($8'2'' \times 20'9'' \times 10'$ high).

Ventilation for the RBC building is provided by four 18" square louvered panels and one 18" diameter fan. The fan and two louver panels are located at the rear of the turbine section of the building, and the other two shutters are located on the front wall of the control room portion of the building, just below the roof. The fan discharges air from the turbine section of the building to the outside. Fresh air is drawn in through the control room and thence into the turbine section. The 18" fan has a capacity of approximately 2800 cfm, which can exchange all of the air in the building in 36 seconds.

This is more than adequate. The minimum ventilation requirement is 510 cfm (see Appendix VII). A vent rate of 2800 cfm would be capable of maintaining the air in the RBC building at the 1000 ppm TLV even with a Freon-11 leak rate of 1437 lb/day (corresponding to a loss of approximately 1/3 of the total system inventory per day).

However, in any future installations, it is recommended that the louvered panels be installed at floor level. This would improve natural convection in the event of fan failure, and also sweep the floor with fresh air. Freon-11 is almost 5 times denser than air, and will settle to the floor in the event of a leak.

C.8. PRESSURE RELIEF DEVICES

These include the following:

- (1) A safety valve on the steam boiler preheater inlet line, located approximately 30 feet above the roof of the main power plant (set at 80 psig).
- (2) A safety valve on the steam boiler superheater inlet line, located approximately 30 feet above the roof of the main power plant (set at 80 psig).
- (3) A safety valve on the steam boiler superheater outlet line, located approximately 15 feet above the roof of the main power plant (set at 80 psig).
- (4) A safety valve on the steam entrainment separator located approximately 30 feet above the roof of the main power plant (set at 80 psig).
- (5) A safety valve on the water receiver tank, located just above the roof of the machinery house, approximately 15 feet off the ground (set at 20 psig).
- (6) A burst disk on the steam condenser, located approximately 15 feet off the ground (set at 27 psig).
- (7) A safety valve on the Freon condenser, located approximately 12 feet off the ground (set at 50 psig).
- (8) A double burst disk installation on the vapor discharge line from the Freon entrainment separator, set at 107 psig. This installation provides over-pressure protection for the entrainment separator vessel, and discharges relieved vapor to the Freon condenser if the burst disk ruptures.
- (9) A double burst disk installation on the Freon receiver tank, set at 30 psig, which discharges to the Freon condenser if the burst disk ruptures.

The maximum Freon vapor pressure during normal operation is 75 psig; and maximum steam pressure is 45 psig.

These devices are considered to be adequate from a safety standpoint.

C.9. FREON-II SPILLS

Freon-II has a normal boiling point of 24° (or 75° F). Furthermore, at Rockville Center the system is not operational during the winter months, because the RBC operates off what are essentially peaking generators.

Therefore, during most of its operation Freon-II will be exposed to temperatures near the boiling point, and will vaporize rapidly in the event of a spill. If, for example, the Freon feed receiving tank were to rupture, the RBC building would quickly fill with vapor, and the falling Freon inventory would actuate an alarm in both the RBC and main power plant control rooms. The system could then be shut down, and personnel wearing self-contained breathing apparatus would open the doors to the RBC building to facilitate venting (note that the roof vent fan would be operating during this time to exhaust the Freon vapors).

If a rupture were to occur while the system is moth-balled for the winter (see Fire Protection), it would probably go unnoticed until operation was resumed in the spring. Therefore, before restarting the unit after a long down-time, the roof fan must be turned on and the doors to the RBC building opened to facilitate venting.

In the future, we recommend that the Freon feed receiving tank be placed outdoors.

If a massive rupture of one of the Freon holding vessels were to occur in cold weather, some of it could enter the nearby storm sewer, and travel to the Rockville Center treatment plant. However, this eventuality is not expected to result in any safety hazard. The treatment plant must simply be notified and power plant personnel warned to stay away from the immediate area of the spill until it visibly dissipates.

C.10. PERSONNEL PROCEDURES

An operating manual must be written and adhered to, including emergency procedures. Emergencies would involve fire, or rupture of a Freon-containing line or vessel. Emergency procedures must be very specific and leave no room for personnel indecision. Everything must be done automatically, as in a fire drill.

Since the RBC control room is generally unmanned, particular attention must be paid to the response of the main power plant control room operators to an alarm, or emergency situation, at the RBC.

Whenever personnel enter the RBC building, the large doors should be left open with the vent fan on. Two people should always be present during maintenance or repairs.

When the RBC building is opened up after winter mothballing, it should be allowed to ventilate for at least 15 minutes (25 air changes) before personnel enter (see also RBC Building Ventilation, and Freon-II spills).

Regarding personnel protection, it was noticed during our visit of September 26, 1979, that some of the steam containing surfaces in the RBC building were uninsulated. We recommend that all surfaces at a temperature of 150° F or higher be insulated. Furthermore, rubber gloves and a full face mask with cannister should be worn whenever handling liquid Freon.

If a Freon leak were to occur in the RBC building at a rate of (e.g.) 70 lb/hr, even with the exhaust fan pulling at 2800 cfm, the Freon-II concentration in the building would rise to 60,000 ppm in 3.6 hours. At that concentration, a worker could experience narcosis and anaesthesia. In 3.6 hours the total loss of Freon from the system would be 250 pounds, or 6.3% of total system inventory. At 100,000 ppm, after 6 hours at a leak rate of 70 lb/hr, the Freon-II concentration in the RBC building would be lethal. At that time the total loss of Freon would be 420 lb, or 10.5% of system inventory (a low level alarm is not activated until there is a 20% reduction in inventory). MTI writes (see Table 10, item 3):

"All MTI staff members who have worked with the Rockville Center binary system agree that Freon II does have a distinctive odor. The existence of relatively small leaks has been quickly detected merely by odor. In a telephone conversation with Dr. Hans Borchardt of the Refrigeration Section of E. I. duPont de Nemours & Co.,

it was learned that the Material Safety Data Sheet for Freon 11 (issued by DuPont to OSHA) states that the material has a "slight, ethereal odor". It is extremely unlikely that a worker could enter an area where the atmosphere contained 60,000 ppm of Freon and not detect the odor of Freon....

"It should be restated that, from a safety standpoint, the MTI Freon system is very similar to large water chiller units using Freon 11 employed in many large buildings for air conditioning. These systems have been in commercial service for many years and represent a well developed body of technology and standard operating practice. It is not standard practice with such systems to install or employ a Freon detector unit for personnel protection."

However, in order to keep track of the Freon inventory, we recommend that the sight glass reading on the Freon Feed Receiving Tank be logged once per shift. In order to do this, a scale (e.g. a rule) should be permanently fixed behind the sight glass. A falling inventory should be immediately corrected.

If personnel smell the "ethereal odor" of Freon on entry to the RBC building, they should immediately evacuate, open the large doors on the side of the building, and allow the building to ventilate for at least 15 minutes (with the fan on). If an odor is still detected, personnel should wear cannister masks before reentering to repair the leak.

C.II. SAFETY INSTRUMENTATION

The safety instrumentation includes 3 step indicator lights (low low, low, & high) on the controllers, and panel mounted warning lights with control room annunciator. The following sensors have both alarm and trip levels. At the trip level, the turbines and entire vapor generating system automatically shut down:

- + low control air pressure
- + cooling tower low level
- + cooling water low flow
- + diesel exhaust high pressure
- + steam condensor high pressure
- + Freon condensor high pressure
- + feedwater receiving tank low level
- + Freon feed receiving tank low level
(3200 lb, or 80% of normal inventory)

The following sensors also have an automatic shut down of the turbines, but allow the rest of the vapor generating system to remain in operation (with vapor bypassing the turbines):

- + lube oil sump low level
- + lube oil high temperature
- + lube oil low pressure
- + turbine high vibration
- + turbine overspeed
- + generator breaker open

The following sensors are alarmed, but do not initiate an automatic shut down.

- + steam drum high/low level
- + steam hotwell high/low level
- + Freon condenser high/low level
- + Freon drum high/low level

The control room also has a panel light when the damper control valves are open and the following gauges:

- + Freon condenser pressure/temperature
- + Freon vapor supply pressure/temperature
- + steam condenser pressure/temperature
- + steam supply pressure/temperature

In addition, there is an instrument gauge which indicates turbine speed.

We were told by the utility plant superintendent that the control panel was supposed to be checked every 1/2 hour.

There are additional indicator lights in the main generator building, located below the diesel exhaust stacks. These lights are for the damper control valves (open/closed/intermediary), and steam boiler isolation valves (open/closed). Manual switches to control these valves are also located at the same position, along with an exhaust gas temperature gauge.

The hot gas damper control valves are pneumatically actuated butterfly valves installed on the outlet of the original exhaust silencers of the diesel engines. These valves are closed to force exhaust gas through the steam boiler when the RBC is active. The valves open to allow gas flow through the silencers to atmosphere when the RBC is off line. Failure of the valve actuator system or loss of pneumatic system pressure causes the valves to assume the open position. Open force under this condition is provided by large helical tension springs. When the valves are open, some hot exhaust gas can continue to pass through the steam boiler.

Two manually operated isolation damper valves are also installed in series between each diesel exhaust duct and the steam boiler. An atmospheric vent port is also installed between each pair of isolation dampers. This allows complete isolation of either or both engine exhaust systems from the steam boiler, with essentially zero leakage of exhaust gases across the isolation barriers.

All three sections of the steam boiler (economizer, vaporizer, and superheater) have safety valves installed, set to relieve at 80 psig. If the system were shut down and hot exhaust gas continued to flow through the steam boiler, steam pressure would increase to 80 psig, the safety valves would lift, and steam would be vented to atmosphere until residual water in the boiler was exhausted. At that time, the safety valves would reseal and the boiler tube metal temperature would gradually increase to the exhaust gas temperature of about 500° F. This is neither hazardous nor injurious to the waste heat boiler.

The main generator plant control room is located approximately 275 ft. from the RBC unit. It has the following indicator lights for the MTI system:

- + turbine shut-down
- + malfunction
- + PCM building overtemperature
- + low N₂ supply to gearbox, and for winter mothballing of the RBC (see Fire Protection)

In addition, it has a duplicate alarm, manual shut-down switch, and intercom with the RBC control room.

The only recommendation we would make regarding safety instrumentation is that failure of the RBC building exhaust fan be added to the annunciator panel.

C.12. ELECTRICAL CODE⁽⁷⁾

Since both steam and Freon-II are non-flammable, the RBC is classified as a non-hazardous area and does not require special electrical equipment.

C.13 PIPING AND PRESSURE VESSEL CODE^(8,9,10)

The following codes and standards were used by MTI:

a) Overall Requirements

1. Welding and Brazing Procedures, Welders, Brazers, and Welding and Brazing Operators were be qualified in accordance with Section IX of the ASME Boiler and Pressure Vessel Code (B&PVC), 1977 edition, with Addenda current at the time of fabrication.
2. Structural supports for piping are welded in accordance with the applicable requirements of American Welding Society Codes current at the time of fabrication. (This should be AWS D1.1-1975, with applicable revisions.)
3. Nondestructive Methods of Examination, and Standards used for these examinations, were in accordance with Section V of the ASME B&PVC, 1977, with Addenda current at the time of fabrication.

b) Piping

1. All piping design and welding external to the steam vaporizer is in accordance with the requirements of ANSI B31.1 "Power Piping" 1977 with Addenda current at the time of fabrication.
2. Piping between the code-stamped waste heat boiler assembly and associated isolation and safety valves carries a "PP" stamp and was fabricated in accordance with paragraph PG-109 of ASME B&PVC Code, Section I, with Addenda current at the time of fabrication.

c) Pressure Vessels

The Freon condenser, steam condenser/Freon vaporizer, Freon entrainment separator, Freon receiver tank, water receiver tank and steam hotwell were all fabricated, tested, inspected and registered as unfired pressure vessels in accordance with the requirements of ASME B&PV Code, Section VIII, with Addenda current at the time of fabrication. The Freon vapor generator was treated as a Section VIII system, since it is not "A pressure vessel in which an organic fluid is vaporized by the application of heat resulting from the combustion of fuel...". The MTI Freon vaporizer derives heat from the condensation of steam. (The preceding quotation is in the preamble to ASME B&PV Code Section I.)

d) Waste Heat Steam Boiler

The waste heat steam boiler was fabricated, tested, inspected, stamped and registered in accordance with the applicable requirements of the ASME B&PV Code Section I with Addenda current at the time of fabrication.

Safety valves for the economizer and vaporizer sections of the waste heat steam boiler were selected and installed in accordance with paragraph PG-67 of Section I. Safety valves for the superheater section were selected and installed in accordance with paragraph PG-68.

REFERENCES

- (1) Trifluoroethanol Product Bulletin (1979), from Halocarbon Products Corp., 82 Burlews Court, Hackensack, NJ 07601.
- (2) Fluorinols, technical information bulletin from Halocarbon Products Corp. (March 15, 1978).
- (3) Engel, P. K., Silvestrini, R., & Thompson, R. E., "Corrosion and Fouling Potential in Diesel Exhausts", presented at the Winter Annual Meeting of ASME in San Francisco, Calif. (December 10 - 15, 1978).
- (4) Verbal information from Ted Gleichman of PSE&G (11/6/79).
- (5) Heat Exchanger Fouling and Corrosion Evaluation, Phase I, Topical Report, Exhibit III-B, by L. Kindlimann & R. Silvestrini under U.S. DOE Contract No. DE-AC03-77ET11296 (April 30, 1979).
- (6) Leonardos, G., Kendall, D., and Barnard, N., "Odor Threshold Determinations of 53 Odorant Chemicals", JAPCA, 19, pp. 91-95 (1969).
- (7) National Electrical Code, National Fire Protection Association No. 70-1978, Chapter 5 (1978).
- (8) ASME Boiler and Pressure Vessel Codes, 1977 edition, Sections I, II, V, VIII, IX, American Society of Mechanical Engineers.
- (9) Structural Welding Code, AWS D1.1-1975, American Welding Society.
- (10) ANSI Piping Codes B31.1 Power Piping, 1977, and B31.5 Refrigeration Piping, 1974 - American National Standards Institute.
- (11) A report from Hazards Research corp. (Denville, NJ) to Halocarbon Products Corp. (Hackensack, NJ) on "Flammability Studies on Fluorinol-61 and Fluorinol-85", HRC Report No. 3344 (9/19/74).
- (12) Dangerous Properties of Industrial Materials, 4th Edition, by N. Irving Sax (1975).
- (13) Chemical Engineers' Handbook, 3rd Edition, edited by John H. Perry, p. 1868 (1950).
- (14) Registry of Toxic Effects of Chemical Substances, National Institute for Occupational Safety and Health, Pub. No. 76-191 (1976).
- (15) Occupational Exposure to Toluene, OSHA, Federal Register, 40 (No. 194), 46206-46219 (October 6, 1975).
- (16) Operation and Service Manual, for the Model ORC600B01 Organic Rankine Cycle (ORC) Waste Heat Power Generation System, Part Number 725003 (Easton, Maryland Unit), Sundstrand Energy Systems Bulletin 550 (January 1, 1979).
- (17) Initial Report of the TSCA Interagency Testing Committee to the Administrator, Environmental Protection Agency, NTIS Publication No. PB-275, 367 (Oct. 1977).

- (18) C&EN (October 22, 1979), p. 19.
- (19) Toluene, An Organic Working Fluid, by Sundstrand Aviation (4/29/70, revised 5/8/70).
- (20) Lee, K. C., Jahnes, H. J., & Macauley, D. C., JAPCA, 29, p. 749 (1979).
- (21) Power Generation Through Waste Heat Recovery (600 KW or 900 HP), Sundstrand Energy Systems Brochure No. 9014824 (undated).
- (22) Freon Compounds and Safety, Product Information Bulletin S-16, E. I. DuPont de Nemours & Co. (1969).
- (23) Fire Protection Guide on Hazardous Materials, NFPA, 6th edition (1975).
- (24) Workbook of Atmospheric Dispersion Estimates, by D. Bruce Turner, U. S. Public Health Service, Pub. No. 999-AP-26 (1969).
- (25) Final Reports on Trifluoroethanol from Hazelton Laboratories Inc. (Falls Church, VA) to Halocarbon Products Corp. (Hackensack, NJ): (a) "Acute Oral Administration--Rats; Acute Inhalation LC50--Rats" (2/24/65), (b) "Acute Dermal Application--Rabbits" (4/20/65), (c) "Acute Eye Irritation--Rabbits" (1/3/68), (d) "Subacute Inhalation Gonadal Toxicity Evaluation of Trifluoroethanol" (5/15/75).
- (26) Calculations by Dr. Joseph Bozzelli of the New Jersey Institute of Technology (Newark, NJ).
- (27) Industrial Ventilation, American Conference of Government and Industrial Hygienists, 15th edition (1978).
- (28) Suspected Carcinogens, 2nd edition, National Institute for Occupational Safety and Health (1976).
- (29) Occupational Safety and Health (OSH) Manual, U.S. Dept. of Energy, Office of Fossil Energy Programs, Order ETF 5480.1, Chapter VII, "Carcinogens" (8/15/79).
- (30) Sullivan, J. L., et al, "Monofluoroacetate and Trifluoroethanol as Testicular Poisons in the Rat", Toxicology and Applied Pharmacology, 45, p. 291 (1978). Abstract only.
- (31) Cascorbi, H. F., Rozman, R. S., & Meyer, F. J., "Animal Toxicity of 222--Trifluoroethanol", Toxicology and Applied Pharmacology, 15, pp. 83-91 (1969).
- (32) Trifluoroethanol, by S. Silberstein, Brookhaven National Laboratory Publication BNL-50964 (October, 1978).
- (33) Chemical Reaction Engineering, 2nd edition, by Octave Levenspiel (1972).
- (34) Silvestrini, R., "Heat Exchanger Fouling and Corrosion," CEP, pp. 29-35 (December 1979).

FIGURE 1

THERMO ELECTRON 440 kW
ORC SCHEMATIC

NOTE: Toluene Flow Rate = 41,200 lb/hr
Toluene Inventory = 1,100 gallons

FIGURE 2

600 KW ORC SCHEMATIC

FIGURE 3 MTI SYSTEM SCHEMATIC

TABLE I

TECHNICAL DOCUMENTS PROVIDED BY
THERMO ELECTRON

- (1) Process & Instrument Diagram, Subsystem Test Phase, Drawing No. 029-03-000, Revision B (4/4/78).
- (2) Process Schematic, entitled "Combined Diesel/Organic Rankine-Cycle Engine with Cooling Tower".
- (3) Vapor generator design conditions (Table 5.10 from an unknown report).
- (4) An undated drawing of the stack configuration.
- (5) A copy of a Thermo Electron internal memorandum, dated 8/17/78, from A. Zakak to E. Nalewak on "ORCS Test Lab. Facility and Fluorinol-85 Flammability Characteristics".
- (6) A copy of a Thermo Electron internal memorandum, dated 10/30/78, from A. Zakak to E. Nalewak, on "F-85 Flammability Characteristics".
- (7) A report from Hazards Research Corporation (Denville, NJ) to Halocarbon Products Corp. (Hackensack, NJ) on "Flammability Studies on Fluorinol-61 and Fluorinol-85," HRC Report 3344 (9/19/74).

TABLE 2⁽¹¹⁾

FLUORINOL-85 PHYSICAL PROPERTIES

Composition	85 mole % trifluoroethanol, 15 mole % water
Mol. Wt.	87.74
b.p. at 1 atm.	74.4° C (166° F)
Liq. density at 70° F	1.35 g/cm ³
Flash point (closed cup)	92° F
Flash point (open cup)	109° F
Autoignition temp.	480° C (896° F)
Explosive range in air (at 150° F and 1 atm.)	6% (LEL) to 38% (UEL)
Quenching diameter at 1% excess above LEL (150° F, 1 atm.)	1.25 inches
Minimum inert gas requirement	13% CO ₂
Maximum safe air gap (150° F, 10%)	0.28 inches
Minimum ignition energy (1% above LEL)	1200 millijoules
Maximum explosion pressure (12.5% in air)	97 psia
Maximum rate of pressure rise (12.5% in air)	490 psi/sec

TABLE 3

COMPARISON OF FLAMMABILITY DATA

	<u>Boiling Pt. at 1 atm. (° F)</u>	<u>Flash Pt. (Closed Cup) ° F</u>	<u>Autoignition Temp. (° F)</u>	<u>Heat of Combustion at 25° C (k cal/g mole)</u>	<u>Explosive Range (Vol. %)</u>	<u>ORC System Inventory (Pounds)</u>
Fluorinol-85 ⁽¹¹⁾	166	92	900	-179	6 - 38	4000
Ethanol ^(12,13)	173	54	700	-328	3.3 - 19	----
Toluene ^(12,13)	231	40	1000	-934	1.3 - 7.0	8000
Steam	212	-----Non-Flammable-----				----
Freon-11	75	-----Non-Flammable-----				4000

TABLE 4
TRIFLUOROETHANOL TOXICITY DATA

<u>Route</u>	<u>Parameter</u>	<u>Animal</u>	<u>Dosage</u>	<u>Reference</u>
Intraperitoneal	LD50	Rat	195 mg/kg	14
"	"	Mouse	350 mg/kg	14
Oral	"	Rat	240 mg/kg	25
"	"	Mouse	366 mg/kg	14
Dermal	"	Rabbit	1670 mg/kg	25
Intravenous	LDLO	Dog	400 mg/kg	14
Inhalation	LC50	Rat	550 ppm/6 hrs (6600 ppm/30 min)*	25
"	LC50	Rat	4850 ppm/2 hrs (19400 ppm/30 min)*	30
"	LC50	Mouse	16000 ppm/10 min (5333 ppm/30 min)*	31

* Assumes concentration x time = constant.
Calculated on this basis to facilitate comparison.

TABLE 5⁽²⁶⁾

THEORETICAL GAS PHASE DISSOCIATION

OF PURE TRIFLUOROETHANOL

(Calculated using transition state theory⁽³³⁾, based on
the weakest bond energy being 86 kcal/gmole)

<u>T(° F)</u>	<u>% Dissociation</u>
80	6×10^{-5}
260	.002
440	.020
620	.080
1,340	.100

TABLE 6A

TOXICITY OF TRIFLUOROETHANOLREACTION PRODUCTS

<u>Compound</u>	<u>TLV (ppm)</u>	<u>Intraperitoneal (mg/kg)</u>		<u>Oral (rat, LD50, mg/kg)</u>
		<u>Mouse</u>	<u>Rat</u>	
Trifluoro Acetic Acid	---	150 (LDLO) ⁽¹⁴⁾	---	200 ⁽¹⁴⁾
Trifluoroethanol	5 ⁽¹⁾	350 (LD50) ⁽¹⁴⁾	195 (LD50) ⁽¹⁴⁾	240 ⁽²⁵⁾
Hydrofluoric Acid	3* ⁽¹²⁾	---	25 (LDLO) ⁽¹⁴⁾	80 (guinea pig, LDLO) ⁽¹⁴⁾
Phosgene	.05** ⁽¹²⁾	---	---	---

* Ceiling concentration is 6 ppm.

** Maximum allowable concentration.

TABLE 6B

TOXICITY OF TRIFLUOROETHANOL REACTION PRODUCTS⁽¹⁴⁾INHALATION (Xppm/Ymin)

Compound	Human (TCLO)	Human (LCLO)	Monkey (LC50)	Dog (LCLO)	Cat (LC50)	Rat (LC50)	Rabbit (LC50)	Guinea Pig (LC50)	Mouse (LC50)
Hydrofluoric Acid	110/1	50/30	1780/60	---	---	1276/60	314/420 (LCLO)	4327/15	456/60
Phosgene	25/30	---	1087/1	79/30	1482/1	50/30 (LCLO)	3211/1	141/30	110/30
Carbonyl Fluoride	---	---	---	---	---	360/60	---	---	---
Trifluoroethanol	---	---	---	---	---	550/360 ⁽²⁵⁾	---	---	16000/10 ⁽³¹⁾

INHALATION

(Above data normalized to Xppm/30 min, by
assuming concentration x time = constant)

Hydrofluoric Acid	4	50	3560	---	---	2552	4392 (LCLO)	2163	912
Phosgene	25	---	36	79	50	50 (LCLO)	107	141	110
Carbonyl Fluoride	---	---	---	---	---	720	---	---	---
Trifluoroethanol	---	---	---	---	---	6600	---	---	5333

TABLE 7

SUNDSTRAND TECHNICAL DOCUMENTS
UTILIZED IN THIS REPORT

1. Operation and Service Manual, for the Model ORC600B01 Organic Rankine Cycle (ORC) Waste Heat Power Generation System, Part Number 725003 (Easton, Maryland, Unit), Sundstrand Energy Systems Bulletin 550 (January 1, 1979).
2. Toluene, An Organic Working Fluid, by Sundstrand Aviation (4/29/70, revised 5/8/70).
3. Power Generation Through Waste Heat Recovery (600 KW or 900 HP), Sundstrand Energy Systems Brochure No. 9014824 (undated).
4. The following drawings:
 - a. 600 KW ORC Bottoming System Schematic EP 2613-340 (showing flow rates, temperatures, pressures, and partial instrumentation), undated.
 - b. ORC-600 Installation Typical Toluene Sump Design, Sketch No. MG-778-2 (Rev. A), 10/10/77.
 - c. Easton Utilities, Power Plant No. 2 Site Plan, April 1975.
 - d. Easton Utilities, 600 KW ORC Site Plan, Dwg. No. I-77319-01, Jan. 1978.
5. 3 undated color photographs of the Easton installation (Numbers 129805-3, 129802-3, and unnumbered aerial view).
6. 4 undated information sheets on the 600 KW system entitled:
 - a. "Safety Features", and "Why Toluene?" (both excerpted from Brochure No. 9014764).
 - b. "600 KW Organic Rankine Cycle Waste Heat Power Conversion System", by R. M. Cheek and P. D. Lacey (No. 9013784).
 - c. "Development and Performance of a 600 KW Organic Rankine Cycle Waste Heat Power Conversion System", by R. M. Cheek, et al.
7. 5 letters from R. H. Guedet dated:
 - a. 7/31/79, giving stack dimensions and exhaust gas temperatures, and materials of construction, at Easton, MD.
 - b. 8/17/79, giving the exhaust gas mass flow rate at Easton.
 - c. 8/31/79, giving toluene "sniffer" settings, toluene experience with 100 KW systems, and codes and standards for construction.
 - d. 10/3/79, clarifying a number of statements in the Operating and Service Manual.
 - e. 1/18/80, providing comments on Vector's Draft Final Report.

TABLE 8

TOLUENE PHYSICAL PROPERTIES (12,13,15,23)

liquid density at 68° F	0.866 g/cm ³
formula	C ₇ H ₈
molecular weight	92.13
normal boiling point	110.4° C (231° F)
lower explosive limit in air	1.27% by volume
upper explosive limit	7.0% by volume
flash point (closed cup)	40° F
autoignition temperature	947 - 1026° F
underwriter's laboratory classification *	75 - 80

* ULC Flammability Scale:

ether	100
gasoline	90 - 100
ethyl alcohol	60 - 70
kerosene	30 - 40
paraffin oil	10 - 20

TABLE 9

TOLUENE TOXICITY⁽¹⁴⁾

TLV: 100 ppm (8 hour time-weighted average) ^(12, 15)
200 ppm = maximum allowable short-term (15 min.) exposure ⁽¹⁵⁾

<u>Route</u>	<u>Parameter</u>	<u>Animal</u>	<u>Dosage</u>
Oral	LD50	rat	5000 mg/kg
Skin	LD50	rabbit	14000 mg/kg
Intraperitoneal	LD50	rat	1640 mg/kg
"	LDL0	rat	800 mg/kg
Subcutaneous	LDL0	rat	5000 mg/kg
Inhalation	LC50	mouse	5300 ppm
"	LCL0	rat	4000 ppm/4 hr.
"	TCLO	human	100-200 ppm

TABLE 10

Technical Documents Supplied by Mechanical Technology, Inc.

1. Letter from Robert K. Rose of MTI dated 7/18/79, including diesel generator discharge temperatures and general materials of construction.
2. Freon Compounds and Safety, Product Information Bulletin S-16, E. I. DuPont de Nemours & Co. (1969).
3. The following MTI drawings:
 - (a) Layout sketch No. 79P25-23
 - (b) Piping & Instrument Diagram, No. 340E105 (2/10/77)
 - (c) Plot Plan, No. 340E223 (10/31/77)
 - (d) Steam Boiler & Ducting Assembly, No. 340E064, sheets 1 & 2 (1/20/77)
 - (e) Ground Installation, No. 340E198, sheets 1 & 2 (8/1/77)
4. Letters from John Meacher dated December 26, 1979, and January 2, 1980, which included detailed explanations of the ventilation system, pressure relief devices, safety instrumentation, and piping and pressure vessel codes used by MTI.
5. A Material Safety Data Sheet on Freon-11 (forwarded from DuPont).

TABLE II

Freon-11 Toxicity^(12, 14)

Threshold Limit Value (= OSHA Time Weighted
Average for 8 hour day)

1,000 ppm

LCLO (inhalation - rat)

100,000 ppm/20 min.

LCLO (inhalation - guinea pig)

10,000 ppm/1 hour

TABLE 12
DOUBLE-RISK FAILURE MODE ASSESSMENT

1st System Failure	Present System Response			2nd System Failure	Present System Response			Recommendations		
	Thermo Elec.	Sundstrand	MTI		Thermo Elec.	Sundstrand	MTI	Thermo Elec.	Sundstrand	MTI
Line rupture or leak of working fluid in PCM bldg.	1) If vapor concentration reaches TLV (5 ppm), alarm sounds.	1) None at TLV (100 ppm).	1) None at TLV (1000 ppm)	1) Low-level vapor detector inoperative	1) Odor detected at about 10 ppm (above TLV)	1) Not applic. (no detector)	1) Not applic. (no detector)	1) Condenser low-level alarm (with auto safety trip), & level monitor. If odor is noticed, personnel must wear respiratory protection.	1) If anything above a faint odor is noticed (2-4 ppm), personnel must wear respiratory protection in PCM bldg.; continuous sight-glass installed, with periodic log.	1) None: Freon-11 has a slight ethereal odor; low-level alarm provides sufficient warning
	2) If vapor conc. reaches 12,000 ppm (20% of LEL), deluge system is activated	2) If vapor conc. reaches 9,525 ppm (75% of LEL) auto syst. shutdown is initiated	2) Non-flam. fluids used (no LEL)	2) Extinguisher system inoperative	2) Low level vapor detector & odor tell personnel of rising vapor concentration	2) Not applic. (exting. syst. only operates on heat detection). Detonation could occur since rest of PCM bldg. does not conform to Nat.Elec.Code	2) Not applic. (non-flam. fluids)	2) None: since elec.code conforms to hazardous location a source of ignition would rep. a 3rd level failure	2) Rest of PCM bldg. must conform to NEC; personnel procedures must be specified as in Sec. B.11	2) None: non-hazardous location
	3) Bldg. vent. capable of maintaining atmosphere inside PCM bldg. at 5 ppm w/leak rate to 0.1 gal/hr, or at 12,000 ppm w/leak rate up to 4 gpm	3) No mech. ventilation--open garage door only	3) Exhaust fan rated at 2800 cfm can maintain RBC bldg. at 1000 ppm w/leak rate up to 1437 lb/day	3) Exhaust fan inoperative	3) Low level vapor detec. & odor indic. rising vapor conc.; deluge activated	3) Not applic. (no fan)	3) Vapor conc. rises; odor; low fluid level alarm	3) Auto syst. shutdown on fan failure	3) Exhaust fan on PCM bldg. rated at 2,900 cfm; to initiate auto syst. shutdown on fan failure	3) Alarm on fan failure

Continued.....

TABLE 12 (Continued)
DOUBLE-RISK FAILURE MODE ASSESSMENT

1st System Failure	Present System Response			2nd System Failure	Present System Response			Recommendations		
	Thermo Elec.	Sundstrand	MTI		Thermo Elec.	Sundstrand	MTI	Thermo Elec.	Sundstrand	MTI
	4)No provision for spill containment	4)Underground concrete spill tank & collection system	4)Freon-11 boils at 75°F; liquid could enter storm sewer but is not hazardous	4)Spill tank ruptures	4)Not applic. (no spill tank)	4) Toluene seeps into ground	4)Not applic. (no spill tank)	4)Lined concrete or metal tank needed w/ approp.design for spill containment & collection.Location chosen to avoid contamin. if leak occurs	4)Spill tank location chosen to avoid drink-water contam. in the event of a leak	4)None:Freon-11 evaporates quickly & presents no hazard to drink.water
Line rupture or leak of working fluid in PCM bldg.	—	—	—	5)Someone smoking in PCM bldg.	5)Fluorinol-85 could become involved (with potential production of toxic fumes)	5)CO ₂ extinguishing sys. operates on heat detection, but this is not rapid enough to contain a detonation if explosive limits are exceeded	5)None:Working fluids non-flammable, & combustible materials are not normally installed in bldg.	5)Deluge system to operate on heat detection	5) Personnel procedures must be specified as in Sec. B.11	5) None

Continued.....

TABLE 12 (Continued)
DOUBLE-RISK FAILURE MODE ASSESSMENT

1st System Failure	Present System Response			2nd System Failure	Present System Response			Recommendations		
	Thermo Elec.	Sundstrand	MTI		Thermo Elec.	Sundstrand	MTI	Thermo Elec.	Sundstrand	MTI
Rupture of condenser vapor space	Air sucked in; vacuum pump on non-condensable removal system attempts to keep pace with inflow.		Normal condens. operating pressure is greater than one atmosphere, so no air is sucked in.	Vacuum pump unable to keep pace; condenser pressure rises toward 14.7 psia.	None: Vapor concentration in condenser passes into explosive range, but source of ignition would constitute a third failure mode.		Not applic. (fluid is also non-flammable).	Condenser pressure should register in ORC control room.	If it does not already do so, condenser pressure should register on a gauge in the ORC control rm.	None
Rupture of working fluid line in vaporizer	Loss of vaporizer pressure will cause the turbine to coast down; condenser level will drop; working fluid will be released into the environment.			In-stack ignition source	Fire could result, with potential release of toxic fumes.	CO ₂ extinguisher sys. will go on; unit will shut down.	None: Steam is the only working fluid in the exhaust stack.	1) Install. of CO ₂ exting. system on the vaporizer. 2) Heat detector in stack to activate CO ₂ system. 3) In-stack F-85 detector.	None: Sight-glass already recommended to record falling inventory.	None
Emergency occurs requiring sys. shutdown	Waste heat gas diverter valves must close.		Diverter valves flip open under spring action.	Valves fail to close.	Unknown	Panel light & local alarm at open valve.	Not applic. (panel lights indicate valve position)	Must have panel light & alarm, with manual method for closing valves.	None: Valves can be closed manually.	None: (Syst. also has manually operated isolation valves)

TABLE 13

FLUORINOL-85 DEGRADATION TESTS AT 600° F⁽²⁾

a) With no additives:

<u>Metal</u>	<u>Time (hrs.)</u>	<u>% Decomp.</u>	<u>Remarks</u>
Cast iron	1724	0.25	metal black; liq. light yellow
Steel A-335-P5	2005	0.03	metal black; liq. pale yellow

b) With carbon steel:

<u>Additive</u>	<u>Time (hrs.)</u>	<u>% Decomp.</u>	<u>Remarks</u>
Humbletherm 500	1771	0.07	metal black; liq. colorless
0.1% stearic acid	1771	0.05	"
0.5% Catalin & 0.2% octanoic acid	1722	0.21	"

APPENDIX I

FLUORINOL

DISPERSION CALCULATIONS

As given in Reference 24, the applicable dispersion equations are as follows:

$$X = \frac{Q \times 10^6}{\pi \sigma_y \sigma_z U} \exp \left[-\frac{1}{2} \left(\frac{H}{\sigma_z} \right)^2 \right]$$

$$H = h + \Delta H$$

$$\Delta H = \frac{1.65 V_s D}{U} \left[1 + 1.81 \frac{\Delta T}{T_s} D \right]$$

$$\Delta T = T_s - T_a$$

Where X = plume centerline, ground-level concentration (10 min. avg.) at wind speed U and downwind distance X ($\mu\text{g}/\text{m}^3$)

Q = discharge rate of pollutant (g/sec)

σ_y, σ_z = dispersion parameters, in meters (functions of downwind distance X). For "C" (neutral, or slightly unstable) atmospheres:

$$\begin{aligned} \sigma_y &= 0.20 X^{.91} \\ \sigma_z &= 0.11 X^{.91} \end{aligned}$$

U = wind speed (m/sec)

H = effective stack height (m)

h = actual stack height (m)

ΔH = plume rise (m)

V_s = stack discharge velocity (m/sec)

D = stack discharge diameter (m)

T_s = stack discharge temperature ($^{\circ}\text{K}$)

T_a = average ambient temperature ($^{\circ}\text{K}$)

If this equation is differentiated with respect to U , and set equal to zero, an expression will be obtained for the wind speed (U_c) that will result in a maximum ground-level concentration of pollutant.

Similarly, if it is differentiated with respect to X , and set equal to zero, an expression will be obtained for the downwind distance (X_c) at which the ground-level concentration will be a maximum.

Substitution of U_c and X_c into the equation for X gives the ground-level concentration (X_c) which is maximized both with respect to wind speed and downwind distance.

It is, therefore, the highest ground-level concentration theoretically possible:

$$X_c = \frac{1.95 \times 10^4 Q}{h V_s D \left[1 + 1.81 \frac{\Delta T}{T_s} D \right]}$$

The following two parameters were taken from a Thermo Electron drawing (see Table I, item 4):

$$h = 25 \text{ Ft.} = 7.62 \text{ meters}$$

$$D = \frac{4(8 \times 1)}{2(8 + 1)} = 1.78 \text{ ft.} = 0.542 \text{ meters}$$

$$T_s = 383.7 \text{ }^\circ\text{K} (231 \text{ }^\circ\text{F})$$

$$T_a = 293 \text{ }^\circ\text{K} (68 \text{ }^\circ\text{F}) \text{ assumed}$$

$$\text{stack gas density } (\rho_s) = \frac{PM}{RT_s} = \frac{(1 \text{ atm}) (29 \text{ lb/lb mole})}{\left[\frac{0.7302 \text{ atm ft}^3}{\text{lb mole } ^\circ\text{R}} \right] (691 \text{ }^\circ\text{R})} = 0.0575 \text{ lb/ft}^3$$

$$V_s = \frac{50,988 \text{ lb/hr of exhaust gas}}{\rho_s (8 \times 1) \text{ ft}^2 (3600 \frac{\text{sec}}{\text{hr}}) (3.2808 \frac{\text{ft}}{\text{m}})} = 9.39 \text{ m/sec}$$

$$X_c = 416 \text{ } \mu\text{g/m}^3 (0.1 \text{ ppm})$$

$$Q = 1.02 \text{ g/sec} = 8.09 \text{ lb/hr} (0.72 \text{ gal/hr})$$

$$\begin{aligned} \left(\frac{8.09}{50988} \right) \left(\frac{29}{100} \right) &= .000046 \text{ mole fraction in stack gas} \\ &= 46 \text{ ppm} \end{aligned}$$

APPENDIX II

CALCULATION OF MAX. FLUORINOL-85 RESIDENCE

TIME IN EXHAUST STACK

$$\text{Max. stack cross-section} = 36 \text{ ft}^2$$

$$\text{Min. stack velocity} = \frac{50988 \text{ lb/hr}}{(36 \text{ ft}^2) (.0575 \text{ lb/ft}^3) (3600 \text{ sec/hr})}$$

$$= 6.84 \text{ ft/sec}$$

$$\text{Max. stack length} = 49 \text{ ft}$$

$$\text{Max. time in stack} = 7.2 \text{ seconds}$$

APPENDIX III

CALCULATION OF MAX. ALLOWABLE FLUORINOL LOSS RATE AT PROPOSED BUILDING VENT RATE OF 1 cfm/ft³

$$\text{PCM Building Volume} = 15,750 \text{ ft}^3 \text{ (35' x 25' x 18' high)}$$

$$\text{F-85 Vapor Volume at 5 ppm} = .0788 \text{ ft}^3$$

$$\text{F-85 Vapor Density at 68}^{\circ} \text{ F} = .228 \text{ lb/ft}^3$$

$$\text{Total F-85 in Building Air} = .0179 \text{ lb}$$

Since the vent rate means one turn-over of building air every minute, it can handle an evaporation rate of .0179 lb/min, which represents a daily loss of 0.65% of the total Fluorinol-85 inventory.

APPENDIX IV

CALCULATION OF MAXIMUM TOLUENE RESIDENCE

TIME IN EXHAUST STACK

Stack consists of a 12 ft. long, 8 ft. diameter section; followed by a 21 ft. long, 5 2/3 ft. diameter section; followed by a 32 ft. long, 3 ft. diameter section. Therefore,

$$\begin{aligned} \text{Max. Time} &= \frac{(.0533 \text{ lb/ft}^3) (3600 \text{ sec/hr})}{99,932 \text{ lb/hr}} \left[(12 \text{ ft}) \frac{\pi}{4} (8 \text{ ft})^2 \right. \\ &\quad \left. + (21 \text{ ft}) \frac{\pi}{4} \left(5 \frac{2}{3}\right)^2 + (32 \text{ ft}) \frac{\pi}{4} (3 \text{ ft})^2 \right] \\ &= 2.6 \text{ seconds} \end{aligned}$$

APPENDIX V

TOLUENE

DISPERSION CALCULATIONS

Using the same equation for maximum ground-level concentration developed in Appendix I:

$$X_c = \frac{1.95 \times 10^4 Q}{h V_s D \left[1 + 1.81 \frac{\Delta T}{T_s} D \right]}$$

At Easton, MD:

$$h = 70 \text{ Ft.} = 21.34 \text{ meters}$$

$$D = 3 \text{ ft.} = 0.914 \text{ meters}$$

$$T_s = 413.7^\circ \text{ K } (285^\circ \text{ F})$$

$$T_a = 293^\circ \text{ K } (68^\circ \text{ F}) \text{ assumed}$$

$$\text{stack gas density } (\rho_s) = \frac{PM}{RT_s} = \frac{(1 \text{ atm}) (29 \text{ lb/lb mole})}{\left[\frac{0.7302 \text{ atm ft}^3}{\text{lb mole } ^\circ \text{R}} \right] (745^\circ \text{ R})} = 0.0533 \text{ lb/ft}^3$$

$$V_s = \frac{99,932 \text{ lb/hr of exhaust gas}}{\rho_s \left[\frac{\pi}{4} (3 \text{ ft})^2 \right] (3600 \frac{\text{sec}}{\text{hr}}) (3.2808 \frac{\text{ft}}{\text{m}})} = 22.45 \text{ m/sec}$$

$$X_c = 3830 \text{ } \mu\text{g/m}^3 \text{ (1 ppm)}$$

$$Q = 127.6 \text{ g/sec} = 1013 \text{ lb/hr (2.33 gpm)}$$

APPENDIX VI

CALCULATION OF REQUIRED PCM BUILDING VENT RATE

(SUNDSTRAND SYSTEM)

Minimum ventilation requirements call for 2 cfm/ft² of floor area⁽²⁷⁾. The PCM building is 40' x 24' x 16' high. Therefore, the minimum ventilation rate should be 2 x 40' x 24' = 1920 cfm. With a 50% safety factor, the design rate should be 2900 cfm.

This corresponds to one air change in the PCM building every 5.3 minutes.

PCM Building Volume	=	15,360 ft ³
Toluene Vapor Volume at 100 ppm	=	1.536 ft ³
Toluene Vapor Density at 68° F	=	0.239 lb/ft ³
Total Toluene in Building Air	=	0.367 lb

With one air turnover every 5.3 minutes, the above vent rate could tolerate a leak rate of 0.367 lb/5.3 min (or 100 lb/day), and still maintain the air in the PCM building at 100 ppm. This leak rate corresponds to a daily toluene loss of 1.25% of the total system inventory.

APPENDIX VII

CALCULATIONS OF REQUIRED RBC BUILDING VENT RATE

(MTI SYSTEM)

Minimum ventilation requirements call for 2 cfm/ft² of floor area⁽²⁷⁾. The RBC building is 20'9" x 8'2" x 10' high. Therefore, the minimum ventilation rate should be 2 x 20.75 x 8.167 = 339 cfm. With a 50% safety factor, the design rate should be 510 cfm.

Actual ventilation rate equals 2800 cfm.

This corresponds to one air change in the RBC building every 0.6 minutes.

RBC Building Volume	=	1695 ft ³
Freon-11 Vapor Volume at 1000 ppm	=	1.695 ft ³
Freon-11 Vapor Density at 68°F	=	0.356 lb/ft ³
Total Freon-11 in Building Air at 1000 ppm	=	0.604 lb

With one air turnover every 0.6 minutes, the above vent rate could tolerate a leak rate of 0.604 lb/0.6 minutes (or 1437 lb/day), and still maintain the air in the RBC building at 1000 ppm. This leak rate corresponds to a daily Freon-11 loss of about 36% of the total system inventory.