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Evaluation of Shipboard Formation of a Neurotoxicant (Trimethylolpropane Phosphate) from Thermal Decomposition of Synthetic Aircraft Engine Lubricant[1,2]

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ABSTRACT

MIL-L-23699 lubricants that are composed principally of trimethylolpropane triheptanoate (TMP) and tricresyl phosphate (TCP) have been shown to form a neurotoxicant, trimethylolpropane phosphate (TMPP), during pyrolysis and/or combustion. Mechanistically TMPP is thought to irreversibly inhibit the GABA-mediated inhibitory response and thereby produce epileptiform clonic/tonic seizures with convulsions followed by death. Thermal decomposition of MIL-L-23699 lubricant produces TMPP under laboratory conditions but this product has not been detected in the work place following actual fires. It is possible that thermal decomposition of these synthetic lubricants may result in contamination of an aircraft crash site or lubricant storage space aboard ship producing a dermal hazard to shipboard personnel involved in clean-up operations after a fire. This study has examined whether TMPP is produced during an actual shipboard fire by placing the synthetic lubricant in a fire environment aboard the ex-U.S.S.Shadwell, Mobile, Alabama. Efforts were made to create optimum conditions for formation of TMPP (as determined in the laboratory) and to duplicate the shipboard environment of the lubricant in order to simulate what might actually result if a fire occurred. Both biological and chemical analyses were performed on the thermally decomposed lubricant to ensure detection of the neurotoxic material. Under the conditions of this study, the formation of TMPP during a shipboard fire was confirmed.

INTRODUCTION

Synthetic lubricants available under Military Specification L-23699 (MIL-L-23699) are widely used in military as well as civilian aircraft. Depending on the manufacturer, the lubricant is prepared with a base stock of a polyol ester of trimethylolpropane (TMP) and/or pentaerythritol. A lubricity additive and metal deactivator is included (usually at a 1-3% concentration) to prevent interaction of the lubricant with the engine surfaces. This additive is often an organic phosphate (typically triaryl, most frequently tricresyl). The polyol ester component of the base stock may be varied to change the viscosity of the lubricant.

Thermal decomposition of MIL-L-23699, which contains the TMP ester base stock, can produce the potent neurotoxicant trimethylolpropane phosphate (TMPP) (1,2,3).The structure of this compound is shown in Figure 1. Those formulations of MIL-L-23699 which do not contain the TMP base stock or which do not contain a phosphate additive will not produce TMPP during thermal decomposition (2). The highly neurotoxic effect of TMPP (chemically, 4-ethyl-1-oxo-2,6,7-trioxa-1-phospha-bicyclo[2.2.2]octane) has been known for some time (4,5) and initial investigations were in regard to pesticide formulations. Its formation as a product of combustion was first discovered in an evaluation of polyurethane foam combustion (6). TMPP characteristically causes Grand Mal type epileptiform clonic/tonic seizures with convulsions, followed by death. Initial observations further suggest that the TMPP mechanism of action is related to its effectiveness as an antagonist of GABAergic receptors (7). The extreme toxicity of TMPP was demonstrated for both rats and mice in this laboratory (2,3).

The most likely routes of exposure to TMPP for personnel working around the thermally degraded lubricant are inhalation and dermal absorption. TMPP was not formed in lubricant under normal or excessive use conditions (2). Whether TMPP is an

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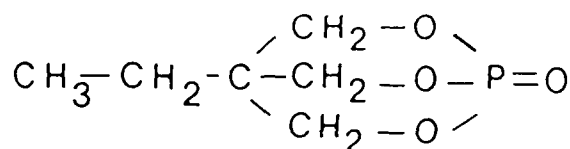
Figure 1. Molecular structure of Trimethylolpropane phosphate (TMPP).

inhalation hazard following decomposition of MIL-L-23699 has been addressed in two previous studies in different laboratories (8.9). In both studies rats exposed to smoke generated by pyrolysis of MIL-L-23699 showed no signs of neurotoxic insult during a thirty minute exposure using a Federal Aviation Administration (FAA) combustion chamber. These data suggest that TMPP precipitates from or condenses quickly out of the respirable atmosphere once it passes from the heat source to cooler ambient temperatures. However, these findings were preliminary and additional characterization of the inhalation hazard needs to be performed using more sensitive indices of toxicity such as EEG analysis. In another inhalation study using a different system for exposure, alteration of EEG was demonstrated at inhaled TMPP concentrations which were insufficient to produce observable tremors (6).

Of greater concern than the inhalation hazard is the possibility of intoxication through dermal exposure. Mice dermally exposed to thermally decomposed lubricant developed convulsive seizures. This finding suggests that a hazard may exist for clean-up personnel after a fire involving MIL-L-23699 lubricant, either as a result of the crash and burn of an aircraft or a shipboard fire.

Synthetic engine lubricants containing TMP esters and TCP are ubiquitous. In addition to their current functions, new uses for high temperature synthetic lubricants have recently been found by Air Force laboratories, thus increasing the probability of their deployment in military aircraft. In reaction to these engineering findings, a "Warning Message" has been released regarding the use of synthetic lubricants at temperatures which may cause their thermal degradation (10).

Thermal decomposition of MIL-L-23699 has been shown to produce TMPP under laboratory conditions, but this neurotoxicant has not been detected in the work place following actual fires. Whether personnel involved in clean-up following a fire with these synthetic lubricants are at risk of intoxication has therefore not been established. The objective of this study was to assess whether TMPP is formed from combustion of the MIL-L-23699 synthetic lubricant (TMP ester base stock) during an actual fire aboard ship by placing the lubricant in a fire environment aboard the ex-U.S.S. Shadwell. The conditions needed for optimum formation of TMPP were determined in laboratory studies and then applied to the shipboard environment.

MATERIALS AND METHODS

Chemicals

Lubricant: The synthetic lubricant evaluated in this study was provided by the Aero Propulsion Laboratory, Fuels and Lubricants Division, Wright-Patterson Air Force Base, OH. This lubricant, which was used in both laboratory and shipboard studies, was selected from the qualified products available under Military Specification MIL-L-23699 and was known to have the trimethylolpropane carboxylic acid ester base stock formulation with organophosphate additive. The specific composition of the lubricant used is proprietary information and cannot be reported.

Authentic standard: A standard of TMPP was needed to allow identification of the neurotoxicant in the thermally decomposed lubricants. This standard was prepared using methods previously described (11,12) and the synthesized standard authenticated by previously described electron impact mass fragmentation patterns (13) and melting point analysis. All other chemicals used in this study were of reagent grade quality.

MSD = Mass Selective Detector

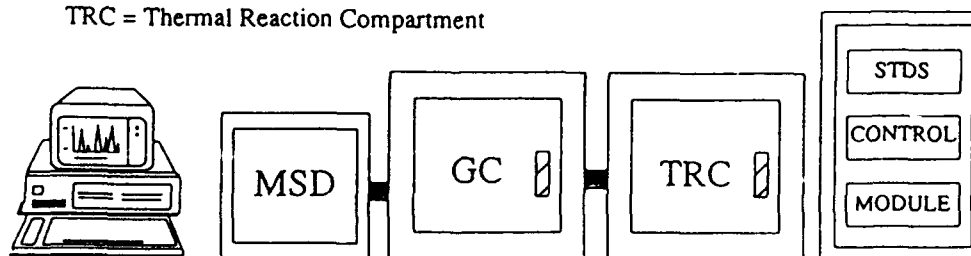GC = Gas Chromatograph

TRC = Thermal Reaction Compartment

Figure 2. Diagram of system for thermal diagnostic studies.

Laboratory Studies

Formation of TMPP during thermal decomposition of MIL-L-23699 lubricant was characterized in the laboratory over a temperature range of 300 to 800 °C using a System for Thermal Diagnostic Studies (STDS). This System was developed at the University of Dayton Research Institute, Dayton, OH and was marketed as the Model 1000 System. This analytical instrumentation (schematically shown in Figure 2) is composed of a thermal reaction compartment consisting of a modified Lindberg furnace and quartz reaction cell with associated flow and temperature controllers, a 5890 Hewlett-Packard (Hewlett Packard Co., Avondale, PA) gas chromatograph, a 5970B Hewlett-Packard mass selective detector (MSD), and a 59970 MS Hewlett-Packard ChemStation with associated gas chromatographic software and a mass spectral library. The conditions used for the thermal reaction compartment, the gas chromatograph, and the MSD are listed in Table 1.

Table 1: Thermal Diagnostic System Conditions and Operating Parameters.

Thermal Reaction Compartment (TRC)

TRC Oven:	100 °C to 300 °C at 25 °C/min
TRC Injector:	225 °C
Lindberg Furnace:	300 °C to 800 °C
Sample Size:	0.5 uL
Sample Residence Time:	5 sec
TRC to GC Transfer Line:	300 °C

Gas Chromatograph (GC)

Initial Temperature:	-50 °C
Temperature Program Rate:	8 °C/min
Final Temperature:	300 °C
GC to MSD Transfer Line:	320 °C
Column:	30 m DB5, 0.25 mm ID, 0.1 um film thickness
Carrier gas:	Helium

Mass Selective Detector (MSD)

Ion Source Potential:	70 eV
Selected Ion Monitoring:	149,150,151,163,178
Scan Range:	35 to 550 amu
Scan Speed:	427 amu/sec
Resolution:	1 amu

Typically, the lubricant sample, prepared in toluene, was injected onto a quartz wool injector which had been equilibrated at 100 °C. After allowing time for the more volatile solvent to be removed from the lubricant, the thermal reaction compartment was rapidly heated from 100 to 300 °C causing the sample to pass into the reaction cell. The residence time of the sample in the reaction cell (i.e., period of thermal decomposition) was controlled at 5 sec for each sample by adjusting the temperature and flow of the carrier gas. Residual sample and decomposition products were cryogenically focused at the head of the gas chromatographic column at - 50 °C. The sample was then fractionated by gas chromatography and the degradation products identified by Selective Ion Monitoring with a Mass Selective Detector. The gas chromatographic temperature program was the same for all samples. To determine the formation of TMPP under conditions of combustion and pyrolysis, reaction cell gases of air and helium were used, respectively.

The stability of authentic TMPP, free of lubricant components, was evaluated using the same conditions and parameters as those for the MIL-L-23699 lubricant, except TMPP was prepared in methanol and the reaction cell gas was limited to air only. The injection volume was 4 Ul (5% TMPP stock solution) and the range of reaction cell temperatures was from 300 to 550 °C

Shipboard Tests

Experimental Design: Shipboard tests were conducted aboard the ex-U.S.S. Shadwell (14) which is maintained and operated as a fire test research vessel by the Navy Technical Center for Safety and Survivability in Mobile, AL. A diagram of the ship's spaces for the portside wing wall where the fire was staged is shown in Figure 3. Compartments used for the study were designated as Berthing 2 and Ricer 2. The fire was created in the lower Berthing 2 compartment, with conductive heat transfer to the upper Ricer 2 compartment. Ricer 2 was chosen as the compartment to contain the lubricant based upon maximum compartment temperature determinations in previous studies; the maximum temperature achieved in this compartment was 583 °C, which was close to the optimum temperature of 525 °C.
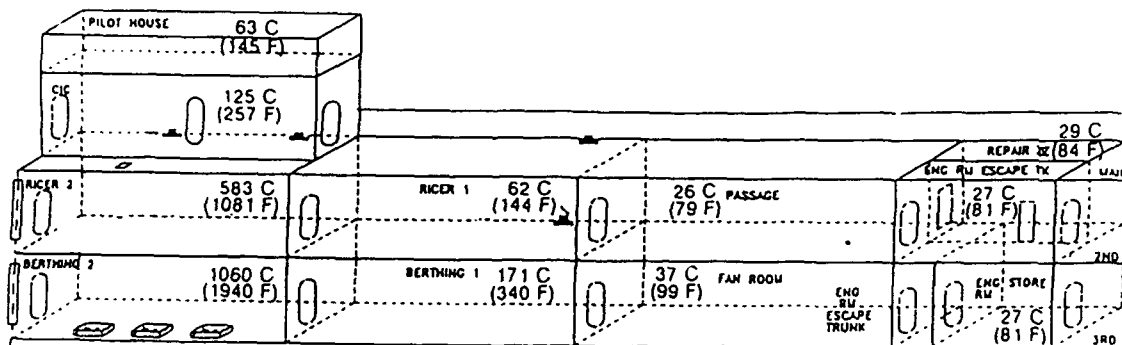
Figure 3. Diagram of ex-U.S.S. Shadwell's compartments showing maximun temperatures achieved during a fire in Berthing 2.
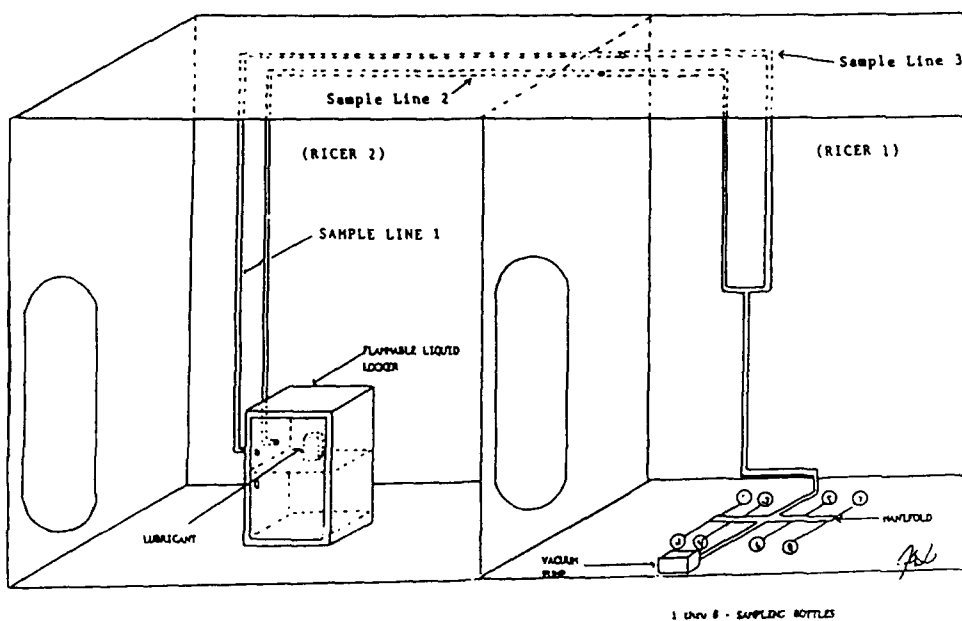

Figure 4. Diagram of flammable storage cabinet placement in the Ricer 2 compartment.

A schematic drawing of the arrangement of the flammable cabinet, lubricant can and sample collection lines is shown in Figure 4. One quart of lubricant, contained in a screw-top, rectangular metal can, was placed in Ricer 2 inside a benchtop size flammable locker (Product No. RA-1199, Laboratory Safety Supply, Janesville, WI). The cabinet was set on the steel deck. This design mimicked actual storage of the lubricant at work stations aboard Naval aircraft carriers in the fleet (15).

The flammable locker was modified (not illustrated in Figure 4) to contain calorimeters for measurement of heat flux, type K inconel-sheathed thermocouples to detect temporal changes in temperature at three locations in the cabinet, and gas sampling lines for monitoring the contents of the cabinet at different temperatures. A series of 8 grab samples were collected by remotely operated solenoid valves attached to stainless steel collection bottles located outside the compartment. In addition, a video camera was placed adjacent to the cabinet vent hole to film the condition of the can during the fire. The camera was protected in a water-cooled housing and all temperature sensitive equipment such as cables wrapped in Fiberfax[R](Manville Corp., Denver, CO) and heat reflective aluminum foil.

The Ricer 2 compartment was similarly equipped with thermocouples for measuring temperatures outside the flammable cabinet, video and infra red camera equipment for monitoring the compartment environment. No combustible material, except for the test material was placed in the compartment. Gas analyzers were used to continuously measure O_2, CO_2, and CO during the test.

Conditions: To achieve the desired temperature inside the double walled flammable cabinet, it was necessary to cut a 1 ft^2 hole in the deck above Berthing 2 to allow sufficient heat to transfer into Ricer 2. The source of ignition of the fire in Berthing 2 was n-heptane (5 gallons) poured into two 2 ft X 2 ft pans. Once started, the fire was maintained by remotely pumping diesel fuel into the pans. To achieve a maximum temperature inside the flammable cabinet of 515 °C, a burn time of approximately 45 min was required. This temperature reading was obtained from a thermocouple attached to the lubricant can inside the cabinet. The fire in Berthing 2 was extinguished by turning off the flow of diesel fuel. With water cooling of the exterior bulkheads of the compartments, a period of approximately 2 hours was required before the compartment was cool enough to allow re-entry and sample collection.

Sample collection: Once the compartment and cabinet were cooled to ambient conditions, samples were collected from the exterior and interior of the cabinet using methanol soaked gauze pads. The sample collection lines were sectioned into three pieces and rinsed with methanol to remove lubricant which had escaped the lubricant can. All samples, the lubricant can, and grab sample bottles were brought back to the laboratory for chemical and biological assay for TMPP. After samples had been collected, the cabinet, compartment and collection lines were decontaminated by treatment with 1 M NaOH; TMPP is hydrolyzed by treatment with strong alkali.

Analysis of collected samples: All samples were extracted from their containers with methanol, filtered to remove particulate material, and the methanol removed by rotoevaporation in a water bath. The homogenous oil samples were then reconstituted in acetone (5/100 dil) for gas chromatographic analysis. All analyses were performed using a Hewlett-Packard 5890 GC/NPD Chem Station (Model 7376 Autosampler) using a 30 meter x 0.53 mm bonded wide-bore (SPB-1, 100% CH_3, 1.5 um) fused-silica capillary column # 034606A (Supelco, Inc., Bellefonte, PA). Splitless injections (1 uL) were performed. The injector zone temperature was 300 °C, the oven programmed from 50 °C (1 min) to 250 °C (5 min) at 20 °C/min, and the detector temperature kept at 275 °C. Quantitative analysis of TMPP in the reconstituted samples was accomplished by the external standard method using peak-areas standard-curve data obtained from TMPP authentic standard samples in acetone. The minimum detectable level for TMPP in the present study was 1 ng/ml.

TMPP Confirmation by Bioassay and GC/MS analysis

Bioassay. Both B6C3F1 mice and Fischer 344 rats were maintained (in separate colonies) for bioassay of neurotoxicity. These species had been used for toxicity testing with TMPP in previous investigations (2, 3). All animals were maintained in cages with water and laboratory chow provided ad libitum. Application of combusted lubricant was both dermal and by intraperitoneal injection.

GC/MS: The STDS was used in a "non-reactive" mode to confirm the presence of TMPP in shipboard samples. The thermal reaction compartment and cell were held at 300 °C, the reaction gas was helium, and the cell residence time was 2 seconds. The sample and solvent were allowed to pass onto the gas chromatographic column simultaneously to minimize loss of analyte. All other GC and MSD conditions were the same as those listed in TABLE I.

RESULTS AND DISCUSSION

Laboratory STDS Studies

Both formation and decomposition of TMPP in MIL-L-23699 lubricant under high temperature conditions were evaluated using the STDS (see methods). Sample residence time in the thermal reaction cell for both studies was 5 sec.

TMPP formation: Figure 5 depicts the production of TMPP from synthetic lubricant at varied temperatures. No attempt to quantitate actual amounts of TMPP formed was made in STDS studies; data are depicted as area counts only. Under the conditions employed, the optimum temperature for formation of TMPP was approximately 525 °C, and formation of TMPP did not occur below 350 °C. These findings compare favorably with previously reported values (2).
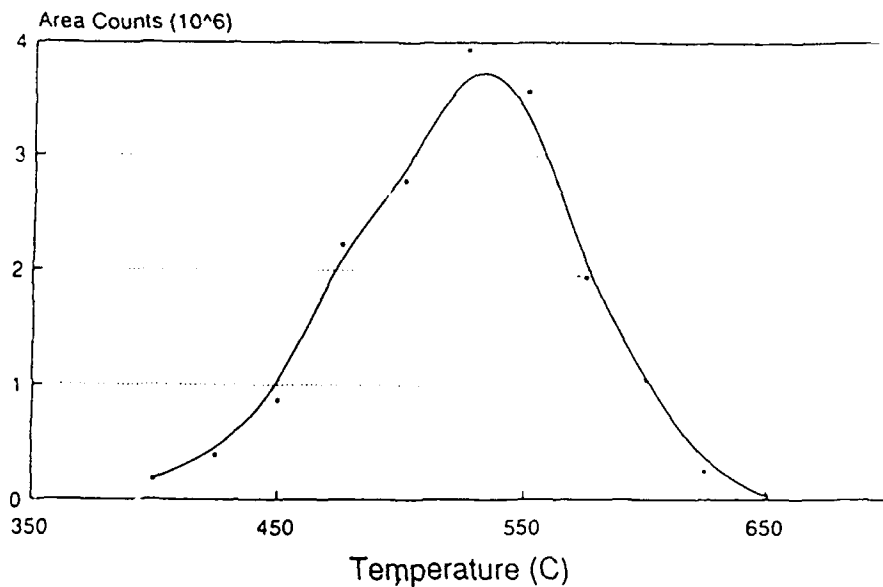
Figure 5. Production of TMPP from MIL-L-23699 lubricant at different temperatures.

Comparison of TMPP formation in an oxygen (air) and non-oxygen (He) environment is depicted in Figure 6 In the absence of oxygen, the production of TMPP was approximately six fold higher, suggesting oxidative decomposition of the compound in air atmospheres. The Figure shows total ion chromatograms; the convoluted peak shapes arise from coeluting species that are not detectable in the selective ion monitoring mode. These coeluting species influence the chemistry of the column stationary phase and therefore the resolution of the TMPP analytical peak. A scan across the retention time range of the peak showed spectral purity
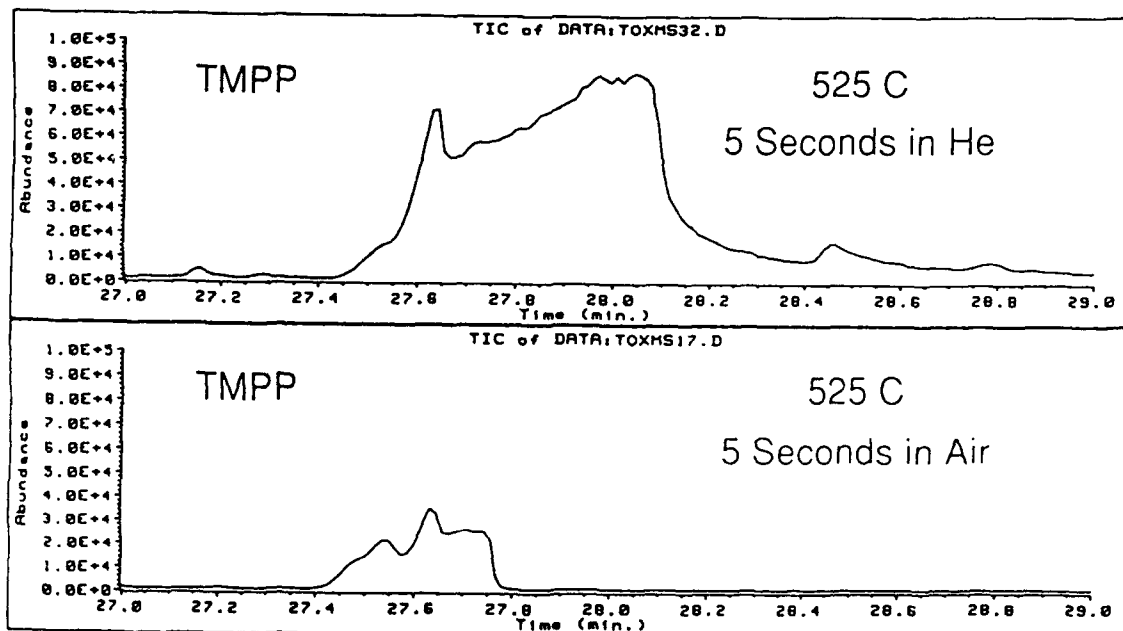

Figure 6. Production of TMPP in atmospheres of air and helium at constant temperatures.

Thermal stability of TMPP: The loss of TMPP from authentic standard samples in the thermal reaction cell at varied temperatures is shown in Figure 7. Temperatures above 475 °C produce a very rapid decomposition with no detectable TMPP present at 500 °C. These data seem inconsistent with data indicating maximum production at 525 °C (Figure 5) and total decomposition at 650 °C. Possible explanations for this discrepancy may be that lubricant components provided some unknown means of protection against the

elevated temperatures and thus insulated the TMPP molecule from thermal decomposition. In the absence of lubricant, the TMPP molecule received all of the thermal energy, resulting in its destruction. Whether the lubricant provides insulating properties for TMPP was not examined. Alternatively, the lubricant components provided a precursor pool for the continued formation of the TMPP product which resulted in higher levels of the compound. Lastly, the reaction time for the formation of TMPP may be such that TMPP was formed at the very end of the 5 sec residence time and was removed from the cell before it could decompose.
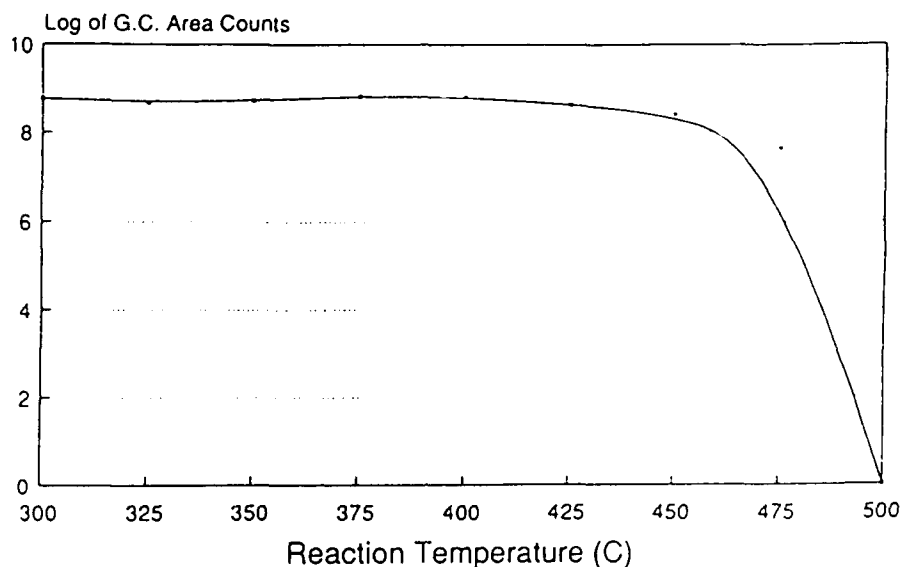

Figure 7. Stability of TMPP with increasing temperature.

Knowing the temperatures at which formation and thermal decomposition of TMPP occurs in the lubricant matrix is important from the standpoint of TMPP hazard evaluation. In this regard, our laboratory recently received an inquiry as to whether TMPP might be formed in power plants using spent synthetic lubricant as a fuel source (16). Since the power plant furnace temperatures were in excess of 1000 °C, the use of spent lubricant in this application was considered safe with regard to TMPP production.

The thermal decomposition of TMPP standard resulted in the formation of a broad-based, unresolved peak of non-chromatographable material. Within this complex mixture, two products were tentatively identified (based on total ion chromatograms) from the MS library as 3-methyl-2-methylene-3-butene-1-ol and 2,3-dimethyl-1-pentene with hit qualities of 90 and 86 %, respectively. The amount of these substances relative to the amount of TMPP initially injected was not quantifiable.
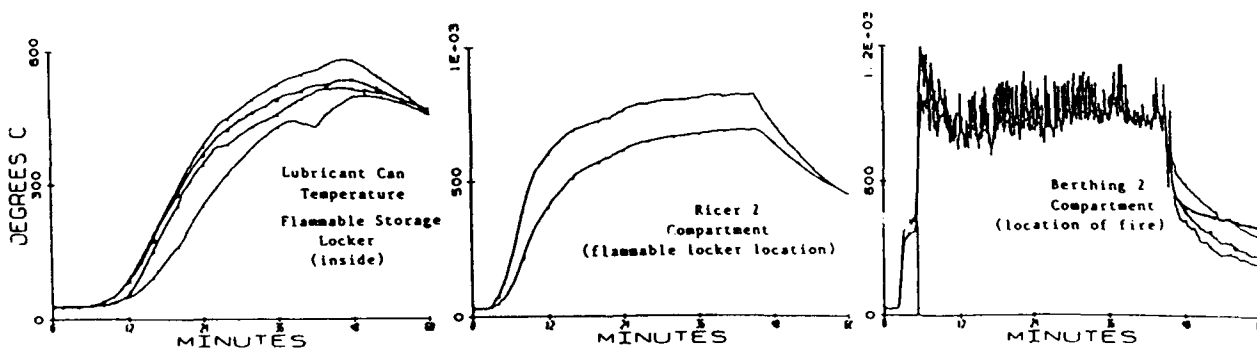

Figure 8. Temperature profiles for the flammable storage locker and compartments during the fire aboard the Ex-U.S.S. Shadwell

Shipboard Tests

Profiles of temperature versus time for the flammable cabinet and the compartments are shown in Figure 8. The interior of flammable cabinet increased in temperature at a much slower rate than the surrounding Ricer 2 compartment. Within the compartment, the maximum temperature achieved was above 700 °C. Based on the results of laboratory studies (Figures 5 and 6) any TMPP which may have escaped into this compartment atmosphere was most probably thermally degraded to non-neurotoxic products. The percent concentration of O_2, CO_2, and CO within Ricer 2, as a function of time, are shown in Figure 9. The source of CO_2 and CO within this compartment was most likely the diesel fuel used to conduct the fire rather than the synthetic lubricant. Based on laboratory findings, the observed decrease in percent O_2 concentration should have enhanced the production of TMPP.
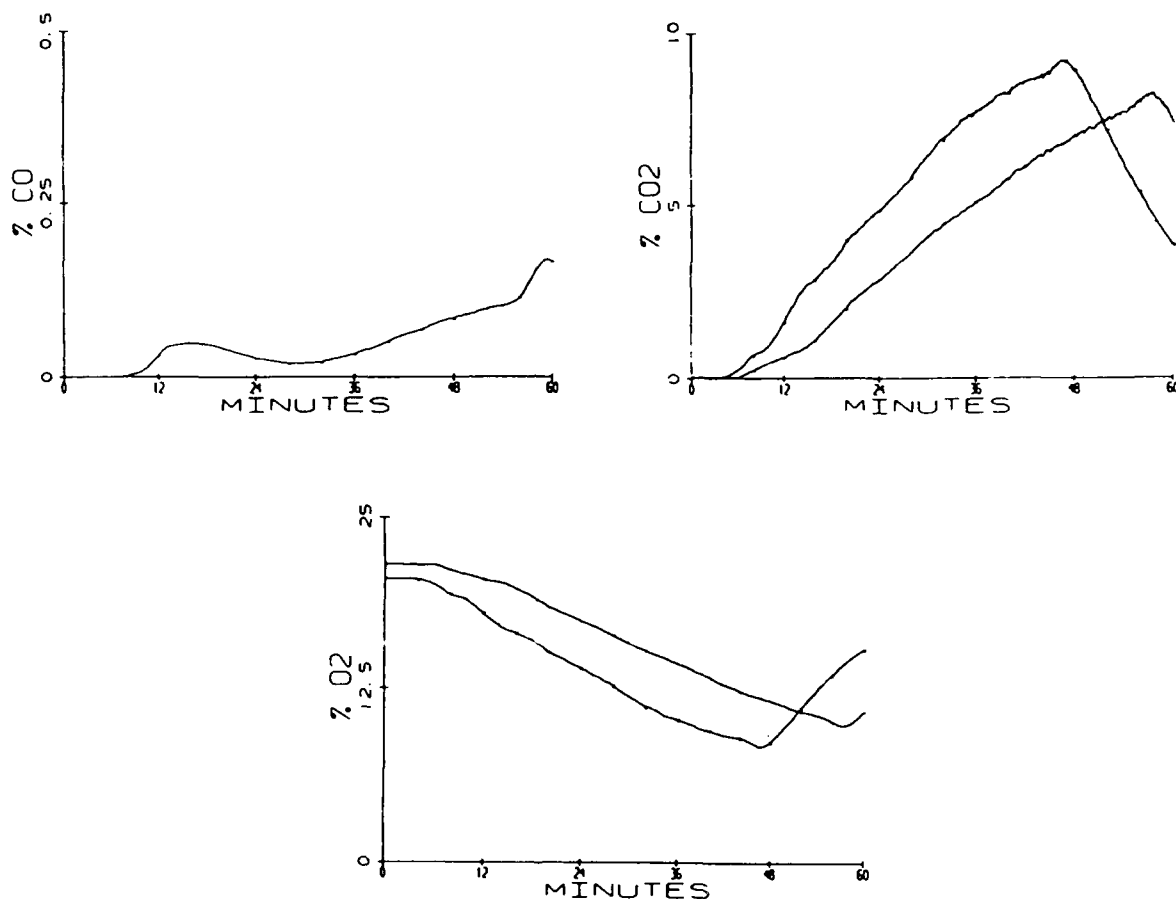

Figure 9.The concentration of CO, CO_2, and O_2 in Ricer 2 compartment as a function of time.

Although the integrity of the metal can within the cabinet was maintained during the test, the lubricant escaped as a vapor through the spaces between the threads on the screw cap top. Only a very small amount of oil (< 3.5 ml) remained in the can following the fire. There was no visible sign of liquid oil in or outside the cabinet, but the cabinet was blackened by a lubricant residue which resembled tar. The cabinet atmosphere sampling lines contained the largest amount of spent lubricant. No TMPP was obtained from the stainless steel collection bottles and therefore the level of TMPP formation for any particular temperature could not be determined. The lubricant was vaporized at the high temperatures of the fire and condensed back to liquid (containing TMPP) in the cooler surrounding areas. This physical behavior is consistent with that observed in the laboratory and indicates that inhalation of a vapor or suspended aerosol of TMPP by emergency personnel is unlikely. However, dermal contact with thermal decomposition products is a realistic possibility

Lubricant Analysis

Table II lists the sample collection sites, the volume of lubricant collected, and the concentration of TMPP detected (GC/NPD analysis) for the respective samples. The data depict a gradient of deposition of TMPP from high concentration (can residue) to low concentration in collection sites farther away from the original position of the unburned lubricant (see Figure 4).

TABLE II: Amounts of TMPP from Shipboard Collection Sites.

Sample Site	Collection Volume (ml)	Lubricant TMPP Conc. (mg/ml)
Cabinet surface	0	None Detected
Can residue	3.5	2.1
Sampling line 1	2.6	0.39
Sampling line 2	2.0	0.31
Sampling line 3	1.9	0.12
Manifold for gas collection	4.3	0.01
Approx. total volume =	14.3	

Samples were collected and analyzed as described in the Methods section.

Bioassay: Initial attempts to detect TMPP in the lubricant samples by demonstrating neurotoxicity in mice through both dermal and i.p. administration of the neat pyrolysed oil failed to show characteristic tremors and convulsions. However, the GC retention time (NP Detector) for a compound in the burned lubricant matched the retention time of the TMPP authentic standard. Based on peak area, the amount of the unknown component present in the pyrolysed oil was quantitated using a TMPP standard calibration curve. Assuming that the unknown compound was indeed TMPP, an aliquot of the spent lubricant containing enough TMPP to elicit a convulsive response was prepared for injection by dissolving it in an equal volume of dimethyl sulfoxide. The convulsive dose was calculated based on a previously reported bioassay lethal dose value of 0.5 mg/kg (2). The sample used for bioassay was 1 ml of the extracted, filtered residue from the can (TMPP concentration = 2.1 mg/ml). The solution was injected intraperitoneally into a male Fischer 344 rat, and the characteristic convulsions produced by TMPP were observed within 3 minutes.

GC/MS confirmation: TMPP was confirmed in shipboard samples by direct comparison of their mass fragmentation patterns with those of known standards. The mass fragmentation patterns were generated in the selected ion monitoring mode, scanning mass ions at 149, 150, 151, 163, and 178 amu as previously described (2).

Bioassay and GC/MS confirmation of TMPP in the thermally degraded lubricant prove that TMPP production is possible during a shipboard fire involving MIL-L-23699 synthetic lubricant. Should such a fire take place, the amount of TMPP formed will depend upon the specific environment with regard to oxygen concentration and temperatures. The fact that TMPP formation was demonstrated, makes it necessary that personnel involved in post-fire cleanup be informed as to the potential hazard.

SUMMARY

The results of this investigation demonstrated the formation of TMPP from MIL-L-23699 lubricant following a shipboard fire. In the laboratory, optimum formation occurred at approximately 525 °C in an oxygen-free atmosphere. The presence of oxygen in air appeared to limit, but not prevent the formation of TMPP. The temperature range for production of TMPP is relatively narrow, from approximately 350 to 650 °C. At temperatures above 650 °C, TMPP was destroyed. In the shipboard fire, TMPP was only found in samples collected from the flammable storage cabinet atmosphere.

The results of this study suggest that the formation of TMPP during ship or aircraft fires is a significant potential hazard. To assess the degree of risk for ship's personnel, further study of the conditions required for TMPP formation, the limitations for spread of the neurotoxicant, and the logistics of use (units of issue, amounts on board, whether other applications of the formulation are active, etc.) of MIL-L-23699 lubricant are required.

ACKNOWLEDGEMENTS

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Glossary

EEG (electroencephalogram or electroencephalography)
FAA (Federal Aviation Administration)
GC/MS (gas chromatographic/mass spectral or spectrometry)
MIL-L-23699 (military specification L-23699)
MSD (mass selective detector)
MS (mass spectrometer)
TCP (tricresyl phosphate)
TMPP (trimethylolpropane phosphate)
TMP (trimethylolpropane)
STDS (System for Thermal Diagnostic Studies)