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FORMATION OF PCDFs UNDER "OPTIMIZED" COMBUSTION CONDITIONS FROM LOW-LEVEL PCB DIELECTRIC FLUIDS

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The Environmental Protection Agency (EPA) issued a final rule on August 25, 1982, authorizing indefinite use of certain electrical transformers containing polychlorinated biphenyls (PCBs). This rule is known as the PCB Electrical Use Rule. At that time, information available to the EPA indicated that fires involving electrical transformers were rare, isolated incidents. However, several recent transformer fires in buildings have brought into question EPA's earlier assumption. The Agency has therefore issued an Advance Notice of Proposed Rulemaking (ANPR) (USEPA 1984a) and proposed rule (USEPA 1984b) to gather data on the specific risks posed by fires involving electrical transformers that contain PCBs and also on mechanisms for mitigating or eliminating these risks. Depending upon the results of EPA's enelysis of these data, the Agency may propose further control measures on the use of this equipment.

This abstract describes the methods and results of a study, conducted in support of EPA's data gathering activities under the ANPR, of the potential for formation of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) from uncontrolled fires involving PCB-containing dielectric fluids.

At high temperatures, such as those in transformer fires, polychlorinated biphenyls (PCBs) react to form polychlorinated dibenzofurans (PCDFs) and other toxic by-products. The purpose of this study was to optimize conditions for PCDF formation in order to examine the potential for formation of PCDFs and polychlorinated dibenzodioxins (PCDDs) from combustion of selected PCB-containing dielectric fluids.

The study was conducted in three phases. In Phase 1, a bench-scale thermal destruction system, developed by MRI, was refitted with specific components installed to accommodate this study as shown in Figure 1. Then, a few test runs

were made under preliminary temperature and oxygen conditions to ensure an acceptable system blank. The concentrations of CO, CO_2, and O_2 in the effluent were monitored continuously. The entire effluent from the thermal destruction system was passed through an XAD-2 trap to collect PCDFs and other semivolatile organics. The XAD-2 trap and a rinse of connective tubing were Soxhlet-extracted and cleaned using column chromatography to isolate the PCDFs and PCDDs. All samples were analyzed for PCDFs (and PCDDs in Phase 3), using high resolution (capillary) gas chromatography/electron impact mass spectrometry (HRGC/EIMS) in the selected ion monitoring (SIM) mode. No PCBs or PCDFs were detected in the Phase 1 samples.

The Phase 2 experiments were conducted to determine the optimum temperature, oxygen, and residence time conditions for PCDF formation. The feed into the system was mineral oil spiked with three individual PCB congeners which form PCDFs by the four known reaction mechanisms. A statistical analysis of the results for 33 runs indicates that both temperature and oxygen have significant effects on the PCDF yield and that the interaction between temperature and oxygen is synergistic. The results indicate that the optimum values are a temperature of 675°C and an excess oxygen concentration of 8%. The residence time did not significantly affect the yield in the range of 0.3 to 1.5 s, although lower times appeared to yield less PCDFs. Since residence time does not appear to significantly affect the PCDF formation, 0.8 s was chosen as convenient for the Phase 3 runs.

In Phase 3, duplicate test runs were conducted with mineral oil and silicone oil dielectric fluids containing PCBs (Aroclor 1254) at concentrations of 0, 5, 50 and 500 ppm. A PCB askarel containing 70% Aroclor 1260 and a non-PCB askarel, containing mostly trichlorobenzene with some tetrachlorobenzene, were also tested in duplicate. PCDFs were found in all samples, except blanks, as shown in Figure 2. PCDDs were found in the samples from the trichlorobenzene runs and occasionally at low levels in some of the other samples. Up to 5,700 ng total PCDFs/mL of spiked feed oil or 4% conversion efficiency (PCBs to PCDFs) was observed for the mineral oil and silicone oil runs. The PCB destruction efficiencies calculated for the 5, 50, and 500 ppm runs ranged from 79 to > 99%. Up to 19,000,000 ng total PCDFs/mL feed oil (19 mg/mL) or 3% conversion efficiency was observed for the askarel fluid. Statistical analysis showed a linear relationship for PCDFs formed versus the amount of PCBs (Figure 3). Although not statistically different, about twice the quantity of PCDFs was formed from PCBs in silicone oil than from the corresponding mineral oil samples. All eight PCDF homologs were detected in the askarel runs with a maximum at the pentaCDF (Figure 4). With a few exceptions, only tri- through hexaCDFs were observed in the lower level runs, with a maximum generally at the triCDF homolog.

PCDFs and, to a lesser extent, PCDDs are formed from the trichlorobenzene dielectric fluid under the optimum PCB-to-PCDF conversion conditions. Up to > 110,000 ng total PCDFs/mL feed oil (> 0.004% yield) and 1,900 ng total PCDD/mL feed oil (0.0001% yield) were observed for the trichlorobenzene runs. The homolog distribution of PCDFs is similar to that found from feeding PCBs. The amount of PCDFs formed is one to two orders of magnitude lower than for the askarel, but substantially higher than that for dielectric fluid containing 500 ppm or less PCBs.

The results of this work indicate that the optimum conditions for PCDF formation from PCBs are near 675°C for 0.8 s or longer, with 8% excess oxygen. Under these

conditions, PCDFs are formed from mineral oil or silicone oil contaminated with PCBs at 5 ppm or greater. PCDFs are also formed from a trichlorobenzene dielectric fluid which contained no detectable PCBs.

Further work is focusing on identification and quantitation of other products from combustion of these samples, and on running samples of other dielectric fluids, including paraffinic hydrocarbons, ester hydrocarbons, and tetrachloroethylene.

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REFERENCES

USEPA. 1984a. Polychlorinated biphenyls (PCBs); manufacture, processing, distribution in commerce and use prohibitions; usa in electrical transformers. Advanced notice of proposed rulemaking. (49 FR 11107D-11083).

USEPA. 1984b. Polychlorinated biphenyls (PCBs); manufacture, processing, distribution in commerce and use prohibitions; use in electrical transformers. Proposed rule. (49 FR 39966-39989).

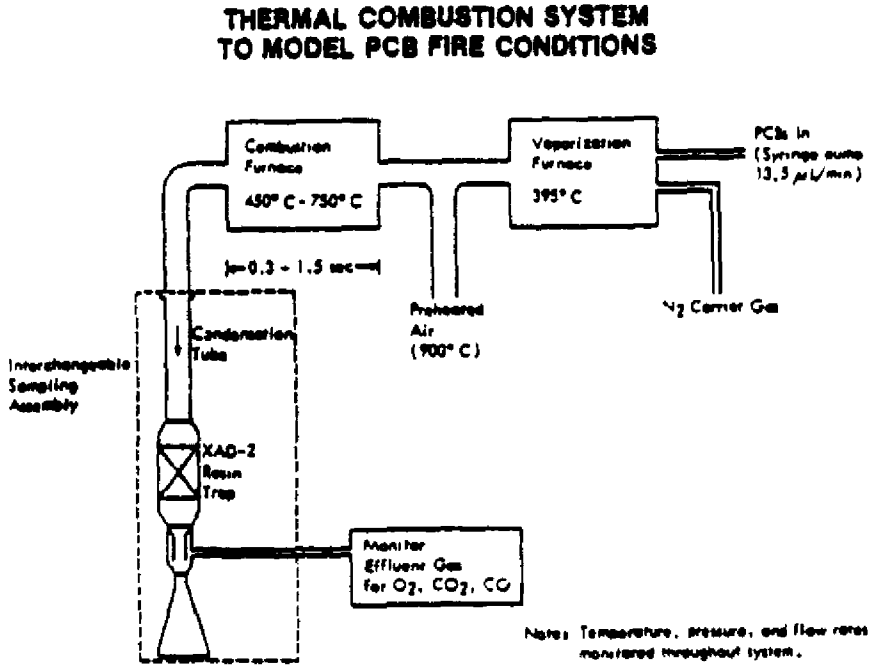

Figure 1

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PCDF FORMATION VERSUS PCB CONCENTRATION

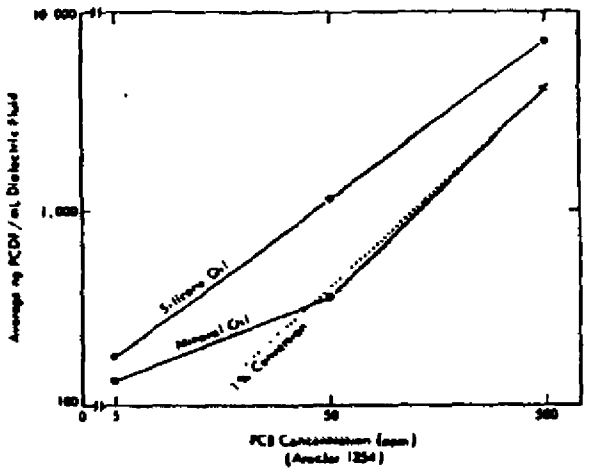

Figure 3

PCB ASKAREL

(70% Aroclor 1200, 30% Trichlorobenzene)

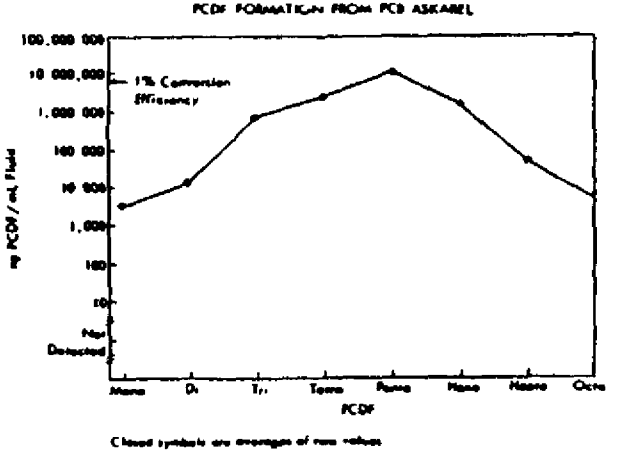

Figure 4

TETRA CDFs

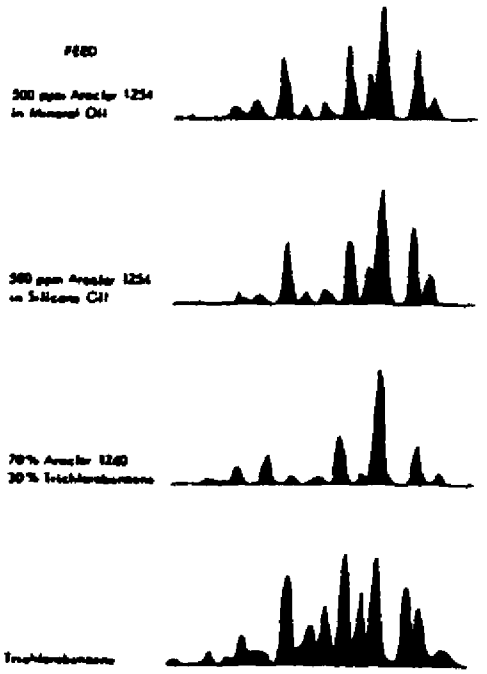

Figure 2. Tetrachlorodibenzofurans formed from various matrices. Note similar isomer distribution for the TCDFs formed from PCBs. Consistent patterns were noted for the other homologs.

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