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November 13, 1984

Dr. John Craddock
Monsanto Company
800 North Lindbergh Boulevard
St. Louis, MO 63166

Dear John:

As we discussed on the telephone recently, MRI has strong experience in the investigation of the combustion or pyrolysis of organic materials. I have included several reprints and brochures which highlight this experience. One of these enclosures is the paper submitted to Chemosphere, which describes the preliminary results of our investigations into the products formed from PCB-containing and other dielectric fluids under fire conditions. I will send you a copy of the more detailed EPA report when it is published in December.

With regard to our discussion about further investigations of the products from certain dielectric fluids, I believe that MRI has the best combustion facility and the broadest capabilities available. My general approach to an investigation for Monsanto would follow the general design used in our EPA study. The conditions would first be optimized using model compounds. This would ideally involve a known, unambiguous reaction from the starting material (e.g., a trichlorobenzene isomer) to a target product (e.g., a PCDD). Using a factorial design and statistical analysis of the data, the optimum conversion conditions would be found. Using the optimum conditions, various real samples (e.g., technical products, field samples, used oils, etc.) would be combusted. The combustion products would be identified, quantitated, and the conversion efficiency calculated. Alternatively, conversion efficiency under other (i.e., nonoptimum) conditions could be measured. If it is important to Monsanto, MRI could also investigate other issues, such as the effects of additives or contaminants. Needless to say, the study would be designed to meet Monsanto's data objectives.

We are most enthusiastic about the possibility of continuing our work in this important area and look forward to further discussions. As you know, you are invited to visit MRI at any time and see our facilities. I look forward to seeing you at the EPRI meeting in December and also to discussing this matter further.

Sincerely,

Mitchell D. Erickson
Principal Chemist

MDE/sp

Enclosures

cc: J. Going

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# PCDF FORMATION FROM PCBs UNDER FIRE CONDITIONS

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and

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Electrical transformer fires can cause extensive smoke damage, especially when PCBs are involved. At high temperatures, such as those in transformer fires, polychlorinated biphenyls (PCBs) can react to form polychlorinated dibenzofurans (PCDFs) and other toxic by-products. The U.S. EPA is considering additional regulations to minimize the risk of these PCB transformer fires. To provide background information to EPA, MRI has studied the thermal decomposition of PCBs This study was undertaken to optimize conditions for PCDF formation and to study the potential for formation for 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 (Figure 1), located at MRI, was refitted with specific components installed to accommodate this study. 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. The optimization was performed using a partial factorial design at three nominal temperatures, 450°C, 600°C, and 750°C, three oxygen concentrations, < 1%, 4%, and > 10%; and three residence times, 0 3, 0.8, and 1 5 s Intermediate values were used in subsequent runs to approach the optimum. A statistical analysis of the results for 33 runs

MONS 214207

indicates that both temperature and oxygen have significant effects on the PCDF formation 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 All Phase 3 runs were made at 675°C for 0.8 s with 8% excess oxygen. 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 (Figures 2 and 3) 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 waste feed or 4% conversion efficiency (PCBs to PCDFs) was observed for the mineral oil and silicone oil runs Up to 19,000,000 ng total PCDFs/mL waste feed (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 4). Although not statistically different, about twice as many PCDFs were 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. 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 waste feed (0.004% yield) and 1,900 ng total PCDD/mL waste feed (0.0001% yield) were observed for the trichlorobenzene runs. The homolog distribution of PCDFs is similar to that formed from PCBs. The amounts of PCDFs formed were 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, currently underway, is focusing on identification and quantitation of other products from combustion of these samples, and on running samples of other dielectric fluids.

The work upon which this publication is based was performed on Contract No 68-02-3938 with the U.S. Environmental Protection Agency A more detailed report was published as EPA Report No EPA 560/5-84-009

MONS 214208

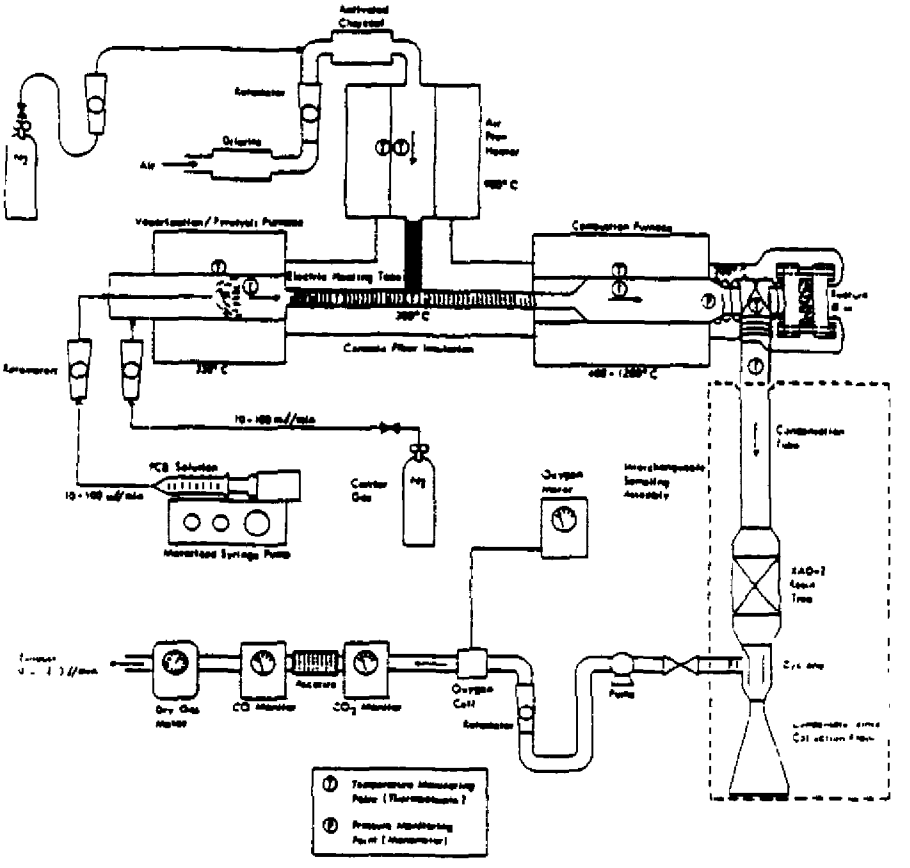


Figure 1 - MRI Laboratory-Scale Combustion System

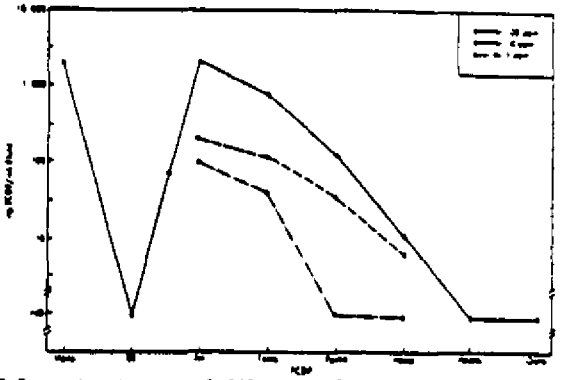


Figure 2 - PCDF Formation in Mineral Oil by Homolog. Closed symbols are averages of two values; open symbols are single determinations; missing points are no data.

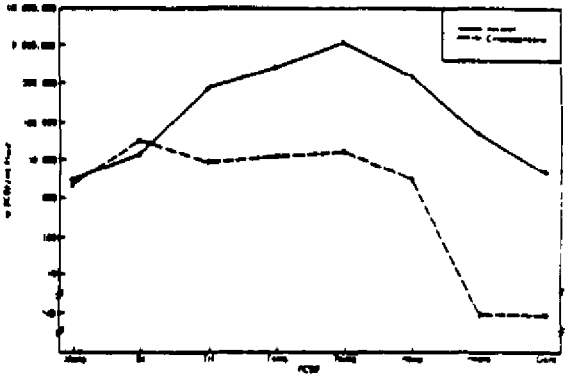


Figure 3 - PCDF Formation from PCB Askarel and Trichlorobenzene Fluid. Closed symbols are averages of two values; open symbols are single determinations.

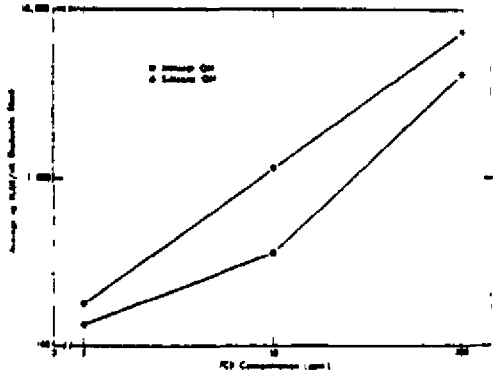


Figure 4 - Average PCDF Formation Versus PCB Concentration for Phase 3