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Building K-1, Room 3B35
January 15, 1979

UNP 010405

Dr. James D. McKinney
NIEHS, Chemistry Section
POB 12233
Research Triangle Park
North Carolina, 27709

Dear Dr. McKinney:

I'm sorry to be engaged in such a slow-moving dialog on the PCB/PCDF analysis issue, but your letter and data package of Dec. 4 took two weeks to get here, and I couldn't get our mass spectrometrists to go over them with me until after the holiday season. However, now that we've been able to put together the various pieces from your Sept. 15, Nov. 15, and Dec. 4 communications, I think we have a better feeling for the situation. In addition, I have been able to get back to our transformer people for further info on the sample. Here's what's turned up:

1. Origin of "used" transformer fluid. In my letter of February 15, 1978, I indicated that the sample I'd sent had come from a single industrial transformer that had had 20 years of heavy duty service, but could have been refilled an unknown number of times over the years. I've now learned that this identification was incorrect: the particular sample that Dr. R.C. Osthoff passed on to me, and which I passed on to you, was a blend of 3-4 old samples of used oil, prepared for Osthoff by Dr. W.A. Fessler, with the intent of enabling the detection of any PCDF's that might have been present in any of them. Dr. Fessler also tells me that the phenyl tin stabilizer was used up until 1963, not 1953, so that the observed composition (Aroclor 1260, trichlorobenzene, trachlorobenzene, phenyl tin) can be dated pretty well to the 1953- period.

2. Identification of $C_{12}H_2Cl_6O$ Species. I think we're all agreed now that there is probably some species in new transformer fluid fraction New T.F.-4B having the empirical formula $C_{12}H_2Cl_6O$, but that neither its chromatographic behavior (not adsorbed on silica, strongly adsorbed on alumina) nor its fragmentation pattern are those expected of a hexachlorodibenzofuran. You indicated at the end of your Nov. 15 letter that you did not feel that further chemical characterization was justified. In this case, would you be willing to send us some part of your fraction New T.F.-4B? Since we got

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started on this problem, we too have acquired a high resolution mass spectrometer, and our mass spectrometrists, Dr. W.V. Ligon, has become personally curious about the question and would like to take a crack at it if you would be willing to share your sample.

3. Model Candidates for Forming PCDF's. In your Dec. 4 letter, you indicated surprise at not having found PCDF's, in view of their reported formation under "model" conditions. The only thermal oxidation experiments that I'm aware of are those of Rappe, which involved heating to 550-850°C. These would not seem to meaningfully model processes that might occur in a transformer operating at 20-95°C, so perhaps I missed something. Would it be possible to send me a reference to the "model" conditions you alluded to?

4. Identifications of "Hydrocarbons". In Don Harvan's memo to you of August 4, he identified a number of minor components as hydrocarbons, phthalates, thiazoles, bromine compounds, etc. including one prominent single species denoted a C₁₆H₃₄ hydrocarbon. As regards the latter, we note again that this material appears in fractions (those strongly adsorbed on silica) which are "wrong" for a saturated aliphatic hydrocarbon; moreover, I know of no likely source of molecularly pure C₁₆H₃₄ species. Reasonable alternatives having the same molecular weight would include diallyl adipate, vinyl dodecanoate, and t-butyl-phenyl-phenol. Do I conclude correctly that all of your "hydrocarbon", phthalate, bromo compound, etc. identifications are based upon low resolution molecular weight alone, and hence are purely suggestive rather than definite?

5. Identification of C₁₂H₁₀-xCl_xO Species. - In all your letters you have referred to these species, which were quite prominent in the old transformer fluid, as polychlorinated diphenylethers (PCDPE). I note from Donald Harvan's memo of 9/18/78, however, that these species were soluble in base, and were identified as polychlorinated diphenylethers rather than the isomeric polychlorinated biphenols solely on the basis of failure to silylate. What immediately comes to mind is that (a) failure to undergo silylation would not be unexpected for a heavily substituted phenol; (b) solubility in aqueous base is really pretty conclusive evidence for having a phenol rather than an ether; (c) a slow hydrolysis of highly chlorinated biphenyls to polychlorinated biphenols at 20-95° in a system containing H₂O and

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various metal oxides would certainly not be implausible; a parallel, though predictably slower, conversion of the polychlorinated benzenes could also have been going on but without ever bringing the polychlorinated phenol level within 1-2 orders of magnitude of P.W. Albro's 1% detection limit. In short, the data that you sent me really argues pretty strongly that the species you're looking at are biphenols rather than diphenyl ethers. I recognize that there may be other pertinent data which somehow failed to get bundled up for the mailing to Schenectady. If so, I'd appreciate hearing about it.

Thanks again for your assistance.

Sincerely yours,

John F. Brown, Jr.

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