

Building K-1, Room 3B35
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Dear Dr. McKinney:

Many thanks for your letter of September 22 describing your analyses of used and unused transformer fluids, and your tentative conclusions regarding their implications.

These findings and conclusions raise a number of questions that I believe should be straightened out before we make any attempt to get the story into the published literature: some that we will have to work on from this end, and some that I'd like to pass back to you.

1. Evidence for Chlorine Redistribution. You reported finding broader distributions of both chlorinated benzene and chlorinated biphenyl homologs in the used oil than in the fresh sample, and possibly different isomer distributions as well. Your suggestion that this implies a redistribution of chlorines on the aromatic rings would be of considerable chemical significance. As best I can tell, going back through all available volumes of Beilstein and modern surveys of Friedel-Crafts type reactions as well, no such redistribution has ever been reported in the organic chemical literature. This is not to say that it couldn't happen, since no one has ever tried the experiment of gently heating an aromatic chloride with phenyl tin plus traces of copper, zinc, iron, oxygen, etc. for 20 years, but it would represent a new type of reaction.

As I pointed out in my letter of February 13, one has no way of knowing what the transformer owner's maintenance crew did to maintain the level of dielectric fluid in their transformer during the 20+ years that it was in service. However, if periodic additions were required to replace leakage or over-zealous sampling, these additions could well have included Aroclors 1242, 1254, and 1260, and any available chlorobenzene mixture as well. Thus, the observation of a broadened homolog distribution is not significant unless it turns out to be clearly broader than that present in any of the PCB's and chlorinated benzenes in commercial use since the early '50's.

What would be significant is a change in isomer contents from the rate-controlled distributions present in all of the initial families of PCB homologs towards equilibrium-controlled distributions in the "used" fluid. You mentioned concern for such changes in distribution both in your letter and over the phone, but I didn't see any concrete support for altered isomer distributions in your analyst's report. Did I miss something? If you still have the original chromatograms and identifications we would be very interested in having copies so as to be able to assess the evidence for alterations in either homolog or isomer distributions.

2. Evidence for Formation of Polychlorinated Diphenyl Ethers in Use. As best I can determine from your chemist's August 4 report of analyses of Dr. Albro's F.N. 2A fractions, polychlorinated diphenyl ethers (PCDPE's) were found in the unused as well as the used oil, implying that they must have been present at least partly as contaminants in one of the ingredients used. Unfortunately, we don't know the actual contamination levels of either the fluid originally placed in the transformer or of the make-up fluids added over its lifetime. As best I can determine from the old-timers around here, there was at least some production of PCDPE's by Dow in the early 1950's, but no one can recall whether it ever got used in dielectric fluids. I've also not yet been able to find out whether there is any data on PCDPE levels in commercial polychlorinated benzenes, but will continue to keep asking around the Company. Unless we can turn up something definite along these lines it may be difficult to figure out whether there actually was an increase in PCDPE in service.

3. Evidence for PCDF's in Unused Oil. - I am a little confused here by some seemingly contradictory statements, and wonder if you could help me out. Your chemist's letter of August 4 states that limited mass searching for the molecular ion cluster of chlorinated dibenzofurans revealed the presence of several such species in new transformer fluid fraction 4B, and estimated a content of roughly 10 ppm for this family of homologs. This is a surprising number, since fraction 4B should have been depleted in PCDF's relative to the starting material, and other homologs should have been present as well, implying a total PCDF content in the initial sample of new fluid that would be somewhat upwards of 100 ppm. Other reports of PCDF's in unused Aroclor 1254 of recent manufacture have run in the 0.5-1.0 ppm range. I also note that your chemist's next statement is that a PCDPE gives the same mass peak as a PCDF, and that his report on the next fraction off his original column, New T.F. 2A, described the species seen as PCDPE's rather than PCDF's. I certainly agree that any discrimination between PCDF's and PCDPE's

in a situation like this would be pretty difficult. My question is, under what circumstances can the distinction be made at all? Does your chemist really have evidence that New T.F. -4B contains PCDF's but not PCDPE's, and New T.F.-2A contains PCDPE's but not PCDF's, or did it somehow happen that the peaks got called one way one day and the other way on another? We are obviously quite disturbed by this, since a 100 ppm level of PCDF's in new Aroclors implies an exposure hazard that no one had been aware of previously; and if PCDF's really are unanalysable in the presence of PCDPE's, then we're stuck with no way to assess their presence in used oils in our service shops.

In short, any further information or clarification that you could supply as regards either the question of isomer distribution or PCDF/PCDPE discriminability would be most welcome. Other than that, I found both the reported data and your comments most interesting. We are deeply appreciative of your efforts to date, and hope that some rationalization of the remaining ambiguities will soon emerge.

Sincerely yours,

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