DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH

NATIONAL INSTITUTE OF
ENVIRONMENTAL HEALTH SCIENCES
P.O. BOX 12233
RESEARCH TRIANGLE PARK, N.C. 27709

September 22, 1978

Dr. John F. Brown
Manager, Life Sciences Branch
Physical Chemistry Laboratory
Bldg. K-1, Rm. 3B35
GE Company
Research and Development Center
P.O. Box 8
Schenectady, NY 12301

RECEIVED
SEP 2 6 1978
J. F. BROWN JR.

Dear Dr. Brown:

The used and unused transformer fluids you provided have been analyzed and the detailed analytical data is included in the attached reports from Drs. Albro and Hass of our laboratories and Mr. Jack Weaver of the NC State nuclear services laboratories. The following summarizing comments are offered:

1. The total mixtures were analyzed in several ways including gas chromatography, infrared (IR), ultraviolet (UV) and nuclear magnetic resonance (NMR) spectroscopy, and neutron activation analysis (NAA) for gross characterization.

2. The gross characterization revealed that the unused fluid was a simple mixture of Aroclor 1254 and trichlorobenzenes. The used fluid on the other hand was an extremely complex mixture of chlorobenzenes, PCB's and other aromatics as determined by gas chromatographic techniques. The PCB mixture did not resemble any Aroclor suggesting that significant alterations and rearrangements have occurred during its use. A developmental radioimmunoassay method for PCB's provided a fingerprint which most closely resembled that of an Aroclor 1260 standard. This type of assay may ignore much of the rearranged PCB's present.

3. The neutron activation analysis revealed that both mixtures were approximately 60% by weight chlorine. Trace amounts (ppm) of bromine were found with the level in used fluid being about twice that in unused fluid. Trace amounts of iron found were also somewhat higher in used fluid. Tin was obscured in this analysis by the large concentration of chlorine and bromine and could not be accurately quantitated.

4. A fractionation scheme was devised based on our previous experience with these types of compounds, especially the Yusho Oil mixture. For both used and unused fluids the total recovery of starting materials accounted for in the fractions was greater than 80%. The fractions were

subjected to combined gas chromatography-mass spectral (GC-MS) analysis for more specific structural information (only about 10% of fraction 48 was submitted for analysis since this fraction contained most of the total material).

5. As expected, most fractions are complex mixtures of isomeric and homologous chlorinated aromatic hydrocarbons (indicating chlorine scrambling) as outlined in the attached report. The major differences were the presence of a much higher level of chlorinated biphenyl ethers and a large amount of hydroxy triphenyl stannane in the used fluid. In addition, several other compound classes are represented here albeit at much lower levels including straight chain and polynuclear aromatic hydrocarbons, brominated hydrocarbons, phthalates, thiazoles, chlorinated terphenyls, and methyl substituted chlorinated terphenyls (or chlorobenzylbiphenyls). No chlorinated quaterphenyls (biphenyl dimers) were detected in either sample.

6. The presence of the stannane in used fluids is probably derived from the tetraphenyl tin additive used as stablizer some time ago, and as you pointed out, would suggest that this is a very old fluid indeed.

7. The finding of some chlorinated dibenzofuran level in the unused fluid is not surprising. The presence of high levels of chlorinated diphenylethers which obscure the chlorinated dibenzofurans in the used fluid is somewhat surprising, but there may be a logical explanation.

8. One can only speculate on this at the moment, but it is likely that the diphenylethers present in the used oil are derived from hydrolysis and/or oxidation and coupling of the various chlorobenzenes present since their formation from biphenyls would require breakage of the strong biphenyl pivot bond. Undoubtedly, there are some chlorinated dibenzofurans present, but reactions leading to their formation would have to compete with those depleting available oxygen sources to form diphenylethers. There is also evidence from other studies suggesting some thermal instability of the chlorinated dibenzofurans. Therefore, the net result may be an attenuation of dibenzofuran formation. If these mechanisms are operating, one would also expect chlorinated phenols and possibly chlorinated biphenylols as intermediates. Failure to detect these compounds would suggest their occurrence only in steady state concentrations.

9. In comparing the used transformer fluid with the used heat exchange mixture (Yusho Oil) with which we have some experience, there are some key differences. Apparently chlorobenzenes were not added to the PCB mixture used in this heat exchanger as is apparently the practice also for their use in capacitors. This eliminates the competing oxygen depletion reaction leading to diphenylethers and, therefore, one would expect enhanced dibenzofuran formation or at least greater ease in their

detection. Model experiments involving heating (although at high temperatures) of PCB mixtures or purified isomers in the presence of oxygen support this enhancement possibility.

10. The apparent absence of quaterphenyls or biphenyl dimers in the used transformer fluid (would expect them to have eluted in fraction 2A) may point out yet another difference in the two mixtures. There is probably much more surface area in heat exchangers which could encourage more metal catalysis such as with copper if copper tubing is used. This could also serve to scavenge for oxygen, thereby attenuating dibenzofuran formation while facilitating non-oxygen metal catalyzed free radical reactions such as dimerization of biphenyls to form quaterphenyls. We have confirmed the presence of large amounts of quaterphenyls in Yusho oil.

11. In considering the more complex PCB pattern found in the used fluid, this may reflect a thermodynamic tendancy toward more symmetrical and structured PCB isomers having lesser degrees of ortho substitution; although there are probably both kinetic and thermodynamic influences on these reactions. There is no evidence to support this, but the alterations are most likely to occur through dechlorinations involving the more sterically crowded ortho chlorines. The more symmetrical and non-ortho substituted PCB's tend to be more acutely toxic; the 3,4,5,3',4',5'-hexa and 3,4,3',4'-tetra compounds representing two extremes in this regard. The PCB pattern in Yusho oil was similarly complex with isomer and homolog content primarily in the tetra to octa range.

12. Toxicologically then the used transformer fluid and the used heat exchange fluid (Yusho Oil) would be expected to have some similarities but yet some differences. Similarities would be expected with respect to the presence in both of the toxic chlorinated dibenzofurans and possibly symmetrical/non-ortho substituted PCBs. Differences would be expected with the relatively non-toxic chlorinated diphenylethers and the unknown (but probably predictable) toxicity of biphenyl dimers and certain chlorinated benzenes.

13. In addition to the hazard of handling used transformer fluids associated with some existing levels of chlorinated dibenzofurans present, the greater concern may be associated with increased levels from transformation after disposal since dibenzofurans can readily be formed from diphenylethers under photochemical conditions and their (diphenylethers) further thermo- or photooxygenation could ultimately lead to the even more toxic chlorinated dioxins. Of course, the real degree of hazard would depend (among other things) on the balance of reactions both forming and degrading these compounds.

14. I think there is now evidence at least in support of considerable alteration/rearrangement of these mixtures under actual use conditions. It seems safe to say also that the general tendency is toward more oxygenated chloroaromatic content in addition to a much more complex mixture of the non-oxygenated chloroaromatics. This is almost certain to be a more biologically active mixture, both qualitatively and quantitatively as based on the many studies with the commercial mixtures and members of the individual compound classes without regard to their synergistic properties.

15. General population exposure would be dependent on the fate and distribution of these compounds in the environment either from accidental leakage or deliberate attempts at their disposal in the environment. Fate and distribution studies will be further complicated by the necessity to deal with even more complex and difficult to simulate modified mixtures of this type.

As I indicated in our recent telephone conversation (9/19/78) concerning this data, there are probably representative trends and patterns identified here which deserve publication. After you have had an opportunity to review and evaluate the data in some detail, I would like to consider this matter further. In the review and evaluation process, if you should have any questions, please do not hesitate to contact me directly.

Sincerely,

James D. McKinney, Ph.D.
Head, Chemistry Section, EBCB

Attachments

cc: Dr. Moore, AD, RRP, NIHES
Dr. Albro
Dr. Hass
Dr. Cox

783263

GENP 010452

(10)

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTE OF HEALTH

TO : Drs. McKinney and Hass

DATE: March 3, 1978

FROM : Dr. Albro

SUBJECT: Preliminary Examination of Transformer Fluids

1. GC Chromatograms, IR spectra, NMR spectra (proton), and UV spectra of the fluids have been obtained.

2. "New" transformer fluid appears to be a simple mixture of Aroclor 1254 and trichlorobenzene (mixture of 1,2,4- and 1,2,3-). No tetrachlorobenzene was found except a trace.

3. Neither of the fluids contain mineral oil or silicone oil.

4. "Old" transformer fluid is an extremely complex mixture of mono-, di-, tri- and tetrachlorobenzenes, polychlorinated biphenyls and other aromatics. The PCB mixture does not resemble any Aroclor, although a mixture of 1242, 1254 and 1260 might come close. Even then one could probably not exactly simulate this pattern, and it appears more likely that alterations and rearrangements have occurred.

P.W. Albro

Phillip W. Albro, Ph.D.

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH

TO : Head, Chemistry Section
Group Leader, Specialty Instrumentation

DATE: 8/21/78

FROM : Group Leader, Anal. Biochem. and Immunochem.

SUBJECT : Possibility of Chlorophenols in Transformer Fluid

By spiking transformer fluid with known amounts of 2,4,5-trichlorophenol, it was determined that it would easily be possible to detect chlorophenol in the fluid down to 1% by weight, using the infrared peaks at 2.8-2.9 and 7.75 μ. Nevertheless, no chlorophenols were detectable in either "new" or "used" transformer fluid.

PWA for PWA.

Phillip W. Albro, Ph.D.
Research Chemist

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH

TO : Head, Chemistry Section

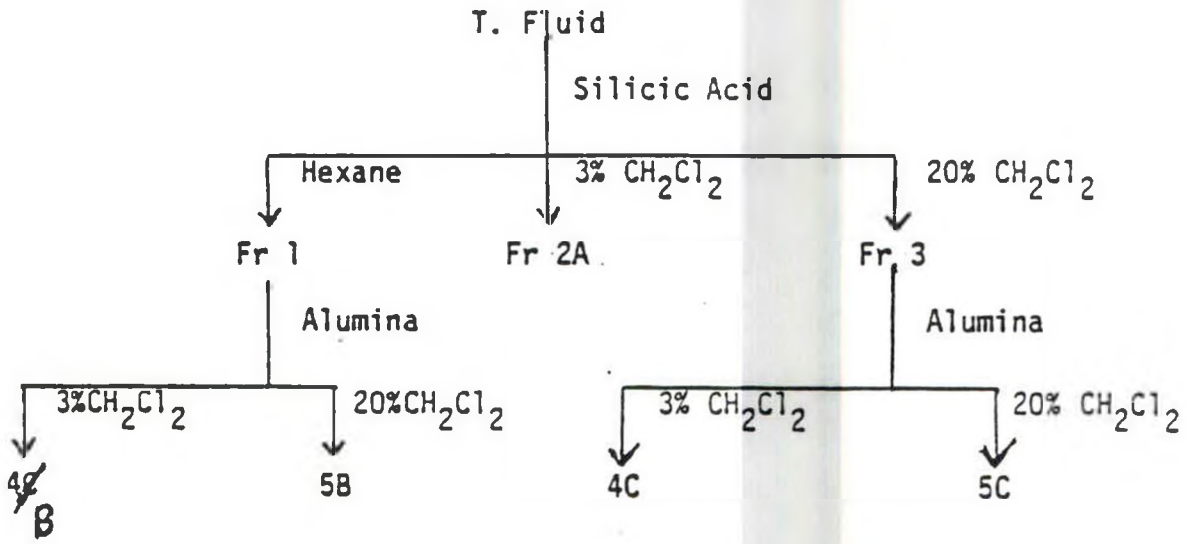
DATE: August 4, 1978

Through: Research Chemist
Research Chemist

FROM : Chemist

SUBJECT : Transformer Fluid Analysis

Ten samples of transformer fluid which had been fractionated were received from Dr. P. W. Albro. The fractionation scheme and sample weights were:



Sample Wts. (mg)

F.N.	Old T.F.	New T.F.
2A	14.3	1.6
4B	151.7	170.4
4C	3.1	2.3
5B	--*	4.7
5C	0.4	0.6

* <0.1 mg

started with 1 ml each (a 1.5 g)
old 4B actually 1.25 g
new 4B " 1.20 g

783266

GENP 010455

The samples were analyzed by GC-MS on OV 17 100/8°/280°, scanning from 100-600 amu @ 1000 resolution. For each fraction a 10 µg aliquot was analyzed, except Old 5B - 5% of this sample was analyzed.

The major differences between the two samples were:
1. Old T.F. contained a much higher level of chlorinated biphenyl ethers.
2. Old T.F. contained a large amount of hydroxy triphenyl stannane in F.N. 4C, as compared to New T.F.

Limited mass searching for the molecular ion cluster of chlorinated dibenzo furans and dioxins revealed the presence of several hexachlorodibenzofurans in one fraciton, New T.F. - 4B. Hexachlorodibenzofuran standards were not available for quantitation. However, comparison with 2,3,7,8 and 2,3,4,7,8 tetra and pentachlorodibenzofuran standards allows a crude estimate of 10 ppm, assuming a linear response and unity slope for different isomers.

The old T.F. samples contained large amounts of chlorinated diphenylethers. Loss of two chlorines from a given chlorodiphenylether generates an ion of identical mass as a chlorodibenzofuran. This obscures the presence of chlorinated dibenzofurans and raises their detection level to the level of the chlorodiphenylethers. In the old T.F. samples, this was approximately the 0.2% level.

F.N. 2A

Complex Mixture of Cl-Biphenyls and Cl-Benzenes

Component	# Isomers Old	New
$C_7H_{15}Cl$	(1)	(1)
Tri Cl-Benzene	(2)	-
Tetra-Cl-Benzene	(2)	(2)
Biphenyl	(1)	-
Mono-Cl-BP	(2)	(2)
Di-Cl-BP	(2)	(2)
Tri-Cl-BP	(7)	(4)
Tetra-Cl-BP	(5)	(7)
Penta-Cl-BP	(4)	(7)
Hexa-Cl-BP	(5)	(5)
Hepta-Cl-BP	(1)	(2)
Octa-Cl-BP	(2)	(2)
Hexa-Cl-BP ether	(3)	-
Hepta-Cl-BP ether	(3)	(2)
Octa-Cl-BP ether	(3)	(1)
$C_{10}H_{11}Br_3$ isomers	-	(2)

$C_{16}H_{34}$ hydrocarbon large component

783268

F.N. 4C

Old	New
Two major components:	One major component:
1) $C_{16}H_{34}$ Hydrocarbon	$C_{16}H_{34}$ Hydrocarbon
2) Hydroxy Triphenyl Stannone $C_{18}H_{16}OSn$	Several PCB's - primarily 5 and 6 Cl's

	# Isomers	
Component	Old	New
Mono-Cl Biphenyl	(1)	-
Di-Cl Biphenyls	(2)	-
Tri-Cl Biphenyls	(6)	(1)
Tetra-Cl Biphenyls	(5)	(3)
Penta-Cl Biphenyl	(1)	(5)
Hexa-Cl Biphenyls	(3)	(6)
Hepta-Cl Biphenyls	(2)	(2)
Octa-Cl Biphenyl	(1)	(1)
Hexa-Cl-Biphenyl ether	(2)	-
Hepta-Cl-Biphenyl ether	(3)	-
Octa-Cl-Biphenyl ethers	(2)	-
Phthalates	(3)	-
$C_8H_7Br_3$	-	(2)
$C_{10}H_{11}Br_3$	-	(2)

Old	New
Alkyl Thiazole (mw=155)	Alkyl Thiazole (mw-155)
$C_{14}H_{10}$ Hydrocarbons	$C_{14}H_{10}$ Hydrocarbon
$C_{16}H_{10}$ Hydrocarbons	$C_{18}H_{14}$ Hydrocarbon

783269

GENP 010458

F.N. 4B

Both old and new were a complex mixture of Cl-Benzenes and Cl-Biphenyls.

	# Isomers	
Component	Old	New
Di-Cl-Benzene	(1)	(2)
Tri-Cl-Benzenes	(3)	(3)
Tetra-Cl-Benzene	(2)	(2)
Penta-Cl-Benzene	(1)	-
Hexa-Cl-Benzene	(1)	-
Di-Cl-Methyl Benzene	-	(1)
Tri-Cl-Methyl Benzene	-	(1)
Mono-Cl-Biphenyl	(1)	-
Di-Cl-Biphenyls	(3)	-
Tri-Cl-Biphenyls	(5)	(2)
Tetra-Cl-Biphenyls	(5)	(6)
Penta-Cl-Biphenyls	(5)	(6)
Hexa-Cl-Biphenyls	(4)	(5)
Hepta-Cl-Biphenyls	(5)	(1)
Octa-Cl-Biphenyls	(3)	-
Hexa-Cl-BP ether	(2)	-
Hepta-Cl-BP ether	(2)	-
Octa-Cl-BP ether	(1)	-
Nona-Cl-BP ether	(1)	-

F.N. 5B

Old	New
Major Component:	Major Components:
Phthalate	4,5,6-Cl-PCB's

Component	# Isomers Old	New
Tri-Cl-Benzene	-	(2)
Tetra-Cl-Benzene	-	(1)
Tri-Cl-BP	(3)	-
Tetra-Cl-BP	(5)	(4)
Penta-Cl-BP	(3)	(5)
Hexa-Cl-BP	(4)	(5)
Hepta-Cl-BP	(3)	(3)
Octa-Cl-BP	(3)	(1)
Mona-Cl-BP	(1)	-
Hepta-Cl-BP ethers	(2)	-
Octa-Cl-BP ether	(1)	-
$C_{12}H_{16}$ Hydrocarbon (Several (6) components to base peaks 163)		
$C_{14}H_{10}$		

F.N. 5C

Both samples were primarily (>90%) one component, a $C_{16}H_{34}$ hydrocarbon.

Other identified components were:

$C_8H_7Br_3$
$C_{10}H_{11}Br_3$
4 - Phthalates
2 - $C_{16}H_{10}$ polynuclear aromatic hydrocarbons
1 - $C_{18}H_{12}$ polynuclear aromatic hydrocarbons

Don Harvan

Don Harvan

GENP 010461

783272

DHEW/PHS/NIH/NIEHS/RRP/EBCB/SIG

MASS SPECTROMETRY FACILITY

TO: HEAD , CHEMISTRY SECTION , EBCB

THRU: RESEARCH CHEMIST

FROM: CHEMIST

SUBJECT: TRANSFORMER FLUID ANALYSIS

FRACTION 2A OF THE TRANSFORMER FLUIDS (SEE MEMO OF 8/4/78 FOR FRACTIONATION SCHEME) WERE ANALYZED BY DIRECT PROBE ANALYSIS FOR TERPHENYLS AND QUATERPHENYLS

THE SAMPLE OF OLD TRANS. FL. CONTAINED OCTA, NONA, DECA, UNDECA AND DODECA CHLORO-TERPHENYLS. THE SAMPLE OF NEW TRANS. FL. CONTAINED HEPTA, OCTA, AND NONA- TERPHENYL. THIS SAMPLE ALSO CONTAINED MATERIAL WHOSE ELEMENTAL COMPOSITION, AS DETERMINED BY EXACT MASS MEASUREMENT, WAS C19 H9 CL7. THIS WOULD CORRESPOND TO A METHYL-HEPTA CHLORO-TERPHENYL , OR A HEPTA CHLORO-BENZYL BIPHENYL. AN OCTA-CHLORO ANALOG OF THIS MATERIAL WAS ALSO OBSERVED. NO EVIDENCE WAS FOUND FOR THE PRESENCE OF CHLORINATED QUATERPHENYLS IN EITHER SAMPLE.

A SAMPLE OF OLD TRANS. FL. WAS BASE-EXTRACTED (J. CORBETT FOR DETAILS) IN ORDER TO CONCENTRATE ANY PHENOLICS PRESENT. THIS FRACTION WAS ANALYZED BY DR. C.E. PARKER BY GC-MS FOR THE PRESENCE OF CHLORO-PHENOLS. IONS CORRESPONDING TO EITHER BIPHENYLOLS OR DIPHENYL ETHERS WERE PRESENT, AND BECAUSE THEY FAILED TO SILYLATE , THEY WERE ASSIGNED TO BE CHLORO-BIPHENYL ETHERS.

Donald Harvan

DONALD HARVAN

9/18/1978

GENP 010462

783273

Xerox 3 copies to [illegible] G

NUCLEAR ENERGY SERVICES

ACTIVATION ANALYSIS REPORT

CLIENT

Dr. John McKinney
National Institute Environmental Health Sciences
Box 12233
Research Triangle Park, North Carolina 27709

P. O. No. PR-499683-8
Report No. 155091
Date of Report 4/04/78
Phone

EXPERIMENTAL PARAMETERS

1 min. and 4 hr. irrad. - $1.5 \times 10^{13} n/cm^2$-sec.

Monitored decay

100 to 2000 sec. count on an Ortec 24% Ge(Li) detector coupled to a computerize ND2200 MCA System

ANALYSIS RESULTS

TABLE 1 Attached

GENP 010463

783274

Issued by: Jack N. Weaver
Jack N. Weaver
Head, Nuclear Services Laboratory

LOCATED AT:
NUCLEAR ENGINEERING DEPARTMENT / N. C. STATE UNIVERSITY / RALEIGH, N. C. 27607 / PHONE: (919) 737-2443

TABLE 1

NAA Scan of Trace Elements

Transformer Fluid*

(ugrams element/gram sample)

Spl wt(g) 1.05 1.02 1.00 1.02

Element	NIEHS 1	NIEHS 2	NIEHS 3	NIEHS 4
Chlorine	644,523	573,383	623,205	576,373
Bromine	58.03	57.82	100.31	108.24
Zinc	2.09	1.63	1.68	1.30
Tin	<5	<5	<5	<5
Arsenic	<1	<1	<1	<1
Cobalt	<1	<1	<1	<1
Iron	<25	<25	<25	<25
Mercury	<1	<1	<1	<1
Selenium	<1	<1	<1	<1
Vanadium	<10	<10	<10	<10
Aluminum	<10	<10	<10	<10
Antimony	<1	<1	<1	<1
Chromium	0.12	<0.05	<0.05	<0.05
Manganese	<0.5	<0.5	<0.5	<0.5
Titanium	<5	<5	<5	<5

* Comments:

1. An organic sample containing very high concentrations of chlorine can not be analyzed for trace quantities of such elements as V, Al, Mn, Ti because the half-life of the isotopes of these elements are short as is the Cl-38 isotope. The high Cl-38 activity masks the much smaller activities of V-52, Al-28, Mn-56, Ti-51.
2. In a similar fashion, our high sensitivity to bromine and its 35 hr. half-life for Br-82 will mask such isotopes as As-76, Hg-197, Se-75, Sb-124, Co-60, etc.
3. In approximately 10 more days the Br-82 activity will be decreased sufficiently to provide real values for Se, Sb, Co, and ~~Sb~~ M.

NIEHS-1 and 2 = G.E. Pyranol – unused

NIEHS-3 and 4 = G E. Pyranol – used

783275

GENP 010464

NUCLEAR ENERGY SERVICES

ACTIVATION ANALYSIS REPORT

CLIENT Dr. James D. McKinney
National Institute Environmental Health Sciences
Box 12233
Research Triangle Park, North Carolina 27709

P. O. No. PR-499633-8
Report No. 155091-1
Date of Report 7/28/78
Phone

EXPERIMENTAL PARAMETERS

4 hr. irradiation - $1.5 \times 10^{13} n/cm^2$-sec.

Monitored decay

8000 sec. ct. on an Ortec 24% Ge(Li) detector coupled to a computerized ND 6:00 MCA

ANALYSIS RESULTS

TABLE 1
Transformer Fluids
(ugrams element/gram sample)

Element	NIEHS 1	NIEHS 2	NIEHS 3	NIEHS 4
Selenium	<0.001	0.019	0.015	0.030
Iron	<2.0	<2.0	20.4	<4.5
Cobalt	.014	0.024	<0.002	.007

783276

GENP 010465

Issued by: Jack N. Weaver
Jack N. Weaver
Head, Nuclear Services Laboratory

LOCATED AT: