



CORPORATE RESEARCH AND DEVELOPMENT • SCHENECTADY, NEW YORK

## CHEMICAL DESTRUCTION OF PCBs IN TRANSFORMER OIL

by

J.F. Brown, Jr., M.E. Lynch,  
J.C. Carnahan\*, and J. Singleton\*\*  
Physical Chemistry Laboratory

TECHNICAL INFORMATION SERIES

1

CLASS

Report No. 81CRD257

November 1981

\* Inorganic Materials and Structures Laboratory

\*\* General Electric Apparatus Service Shop, 1040 East Erie Ave.,  
Philadelphia, PA 19124

---

GENERAL  ELECTRIC

# TECHNICAL INFORMATION SERIES

AUTHOR <b>Brown, JF, Jr., Lynch, ME Carnahan*, JC, and Singleton**, J</b>		SUBJECT <b>PCBs</b>	NO. <b>81CRD257</b>
			DATE <b>November 1981</b>
TITLE <b>Chemical Destruction of PCBs in Transformer Oil</b>		GE CLASS <b>1</b>	NO. PAGES <b>8</b>
ORIGINATING COMPONENT <b>Physical Chemistry Laboratory</b>	CORPORATE RESEARCH AND DEVELOPMENT SCHENECTADY, N.Y.		
SUMMARY <p>One consequence of the restrictions on the use of polychlorinated biphenyls (PCBs) enacted into law by the U.S. Congress in 1976 and subsequently promulgated into regulation by the U.S. Environmental Protection Agency (EPA) has been to create a need for the near total removal of trace level PCBs from some still uncertain fraction of the 1.5 billion gallons of specially refined mineral oil (10C oil) currently in use in U.S. transformers. A known generic approach to the selective destruction of aromatic chlorides like PCB in hydrocarbon-like media at low temperatures consists of treatment with reactive anion radicals, formed either by interaction of sodium metal with an electron carrier in an aprotic cation-complexing solvent or as an intermediate in a free radical chain reaction. Experimental evaluation of the interactions of a number of sodium/electron carrier/solvent systems with 10C oils containing 125-800 ppm Aroclor 1254 or 1260 showed that most of the sodium adduct was consumed by reaction with the 10C oil rather than with the PCB, particularly when only low levels of ion-complexing solvent were present. Marked reductions in solvent requirements could be achieved, however, by forming the presumed adduct <i>in situ</i>, e.g., by simply stirring together the PCB-containing oil, finely dispersed sodium, catalytic quantities of an electron carrier, such as benzophenone or naphthalene, and an ion-complexing solvent, such as diglyme. Using various specimens of PCB-containing 10C oil that had been used in transformers, removal of PCBs to gas chromatographically undetectable levels (<math>0 \pm 2</math> ppm) could be thus effected in simple process equipment within a few minutes at room temperature.</p>			
* Inorganic Materials and Structures Laboratory			
** General Electric Apparatus Service Shop, 1040 East Erie Ave., Philadelphia, PA 19124			
KEY WORDS <b>10C oil, dielectric fluid, transformer oil, decontamination, sodium process</b>			

INFORMATION PREPARED FOR \_\_\_\_\_

# CHEMICAL DESTRUCTION OF PCBs IN TRANSFORMER OIL

J.F. Brown, Jr., M.E. Lynch, J.C. Carnahan\*, and J. Singleton\*\*

## ORIGIN OF NEED FOR REMOVING TRACE PCB FROM 10C OIL

Between the mid-1930s and 1977, two generic types of dielectric fluids were used in the manufacture of ordinary, liquid-filled, industrial, utility, and distribution transformers.

The more widely used of these was 10C oil. This is a specially refined mineral oil derived from naphthenic base crudes from certain wellfields. It was selected for its arc-quenching ability (i.e., ability to consume hydrogen atoms generated by corona via addition reactions rather than H<sub>2</sub>-producing H-abstraction reactions) and its resistance to autoxidation in use. Chemically, it consists of the same sort of complex mixture of hydrocarbons as found in a low viscosity lube oil, but with an aromatic content of 15-30% (depending upon source) provided mainly by alkyl benzenes and naphthalenes, and a sulfur content of 0.03-0.24%.

The less commonly used type bore the generic name "askarel" (which denotes any nonflammable dielectric fluid) and a variety of manufacturers' trade names, such as General Electric's "Pyranol" and Westinghouse's "Inerteen." Askarels, being more expensive than 10C oil, were used only where the fire hazard was considered sufficient to warrant the extra cost, as in transformers for indoor commercial or industrial use, or those used on railroads. Virtually all of the askarels used consisted of mixtures of PCBs (usually, Aroclors 1254 or 1260, which were themselves complex mixtures of polychlorinated biphenyl homologs and isomers averaging five or six chlorines per biphenyl residue, respectively) and polychlorinated benzenes (mixed isomers of tri- and/or tetrachlorobenzene).

Generally speaking, both oil- and PCB-filled transformers were manufactured and repaired in common facilities. As a result, trace levels of each type of dielectric often found their way into transformers of the other type. For many years such contamination attracted no attention, since it did not affect the performance of the dielectric in its designed use.

Beginning in 1966, however, it was discovered that PCBs were highly persistent in the environment and were accumulating to ppm levels in fish and fish-eating wildlife around the world. As a result, in the early 1970s there were voluntary restrictions by manufacturers to the sale of PCBs only for totally enclosed uses, such as in capacitors and transformers; provision of incineration facilities for destroying returned scrap PCBs; and development of biodegradable types of PCB for capacitor use.

Subsequently, however, investigation of an outbreak of "Yusho disease" in Japan traced it to the consumption of rice oil that had been accidentally contaminated with heat exchanger fluid that consisted of a PCB that had been pyrolysed to a mixture of polychlorinated quaterphenyls and dibenzofurans. This resulted in transient accumulations of undecomposed PCBs in the victims' adipose tissues, chronic accumulation of some toxic penta- and hexachlorodibenzofuran isomers in their livers, and chronic manifestation of chloracne symptoms. This evidence of human hazard led to widespread demands for tight controls on PCB use in Japan, Sweden, Canada, and the U.S.

In response, the U.S. Congress enacted the Toxic Substances Control Act of 1976 (TSCA), which generally banned PCB manufacture, import, distribution, processing, or use, and directed the U.S. Environmental Protection Agency (EPA) to define procedures for the marking and disposal of residual stocks. In regulations promulgated in 1979, EPA set forth such procedures, but excluded applicability of the disposal requirements to those PCBs contained in intact, nonleaking capacitors or transformers, or to mixtures containing PCBs at concentrations less than 50 ppm. As a result of a court challenge by the Environmental Defense Fund, however, EPA is currently reexamining these exclusions.

The 1979 regulations themselves, however, already mandate special ultimate disposal procedures for somewhere between 300 and 600 million gallons of the 10C oil that is currently in service in transformers or transformer systems, because of contamination with more than 50 ppm of PCBs. Since 10C oil is a valuable commodity, for which

\* Inorganic Materials and Structures Laboratory

\*\* General Electric Apparatus Service Shop, 1040 East Erie Ave., Philadelphia, PA 19124

production capacity is only about 100 million gallons per year, it would seem desirable to develop methods for decontamination and reuse of this oil rather than simply to dispose of it.

In principle, the removal of PCB from mineral oil could be effected by either a PCB separation or a PCB destruction process. The former would separate the oil into two fractions: a PCB mixture for separate disposal and a PCB-depleted oil for reuse. The latter would solve the PCB disposal problem and give a reusable oil in a single step; therefore it would presumably be preferable. However, current EPA regulations have been interpreted to require that a PCB destruction method that is an alternative to disposal by incineration must achieve an equivalent level of performance, or >> 99% destruction. Thus, reusable oil prepared by a PCB separation process may contain up to 50 ppm PCB, the lower limit for legally defined "PCB contamination," but that prepared by a PCB destruction process must contain no PCB, within the limits of analytical uncertainty, currently defined as about 2 ppm.

In summary, while it is impossible to predict future regulatory developments in this area, current requirements create an immediate need for small-scale, decentralized facilities for processing batches of oil provided by transformer repair and servicing operations. The challenge facing the chemist is to devise treatment processes that will consistently remove PCBs down to levels below 50 ppm, if done by separation, or to 0-2 ppm, if done by PCB destruction.

#### PRIOR USE OF SODIUM OR ANION RADICALS TO DESTROY PCBs

The PCBs are generally unreactive materials. Many of their past applications were, in fact, based upon their great thermal and chemical inertness. About the only class of chemical reactions they are known to undergo at low temperatures are electron transfer processes effected by anion radicals, such as the sodium adducts of certain aromatic hydrocarbons.

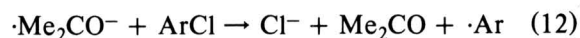
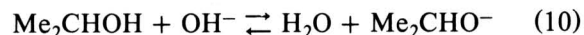
The use of metallic sodium itself is apparently effective only at elevated temperatures. A Japanese patent<sup>(1)</sup> reports that 6 hours at 120° was required for the removal of PCB from kerosene, or 2 hours if catalytic quantities of isopropanol were added. A Goodyear report<sup>(2)</sup> indicates that heating with molten sodium to 300° for 6 hours was required for the removal of PCB from a heat transfer oil.

Conversely, the intensely colored solutions prepared by dissolving sodium metal in solutions of certain aromatic hydrocarbons in aprotic, cation-complexing solvents such as tetrahydrofuran (THF)

or diglyme (DGM) are known to react readily with organic halides. The deep blue adduct of sodium and biphenyl is frequently used as an analytical reagent for quantitatively converting organic to inorganic chlorides, and the deep green adduct of sodium and naphthalene has been reported to do likewise to the PCBs.<sup>(3)</sup>

Two reports<sup>(2,4)</sup> have described the reaction between this 1:1 sodium/naphthalene adduct (naphthalenide anion radical) and PCB in the THF solution at 60° in some detail. From these and the prior literature<sup>(5)</sup> it is evident that a number of types of chemical reactions can occur in such systems. These generic types of interactions, summarized in Table 1, include the reversible formation of 1:1 (Equation 1) and sometimes 2:1 (not shown) adducts between the sodium and electron carrier; a variety of forms of attack on the solvent system, including hydrogen abstraction, alkoxide elimination, and metallation processes (Equation 2); reductive dechlorination of the aromatic halide, presumably via electron transfer followed by fragmentation, which produces inorganic chloride and aryl radicals (Equation 3); occasional reduction of the aryl radical by hydrogen abstraction or metallation (Equations 4 and 5); and a variety of radical recombination processes (Equations 6-9). The reported data<sup>(4)</sup> on the interaction between preformed sodium naphthalenide and various Aroclors in THF solution indicate a net consumption of PCB, naphthalene, and THF in roughly comparable molecular proportions and the formation of chlorine-free, soluble resinous products, which we may presume to have been complex mixtures of species derived from various recombination processes (Equations 6-9).

Several papers have described the light-,<sup>(6)</sup> radiation-,<sup>(7)</sup> or peroxide-initiated<sup>(8)</sup> free radical chain reactions between alkali, isopropanol, and PCB to give inorganic chloride, acetone, and biphenyl. These processes have been presumed to proceed by a pathway analogous to that of the Sherman Mechanism;<sup>(9)</sup> that is, via the reversible formation of isopropoxide (Equation 10), its conversion to the anion radical (Equation 11), and attack of the latter on PCB (Equation 12). The

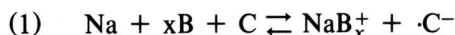


process of Equation 11 is obviously analogous to that of Equation 4, and that of Equation 12 to Equation 3; from the latter we may conclude that

**Table 1**  
**GENERIC TYPES OF REACTIONS**  
**KNOWN TO OCCUR DURING INTERACTIONS**  
**AMONG SODIUM METAL (Na), CATION CARRIERS (B),**  
**ELECTRON CARRIERS (C), AND AROMATIC CHLORIDES (ArCl)**  
**IN ORGANIC MEDIA**

---

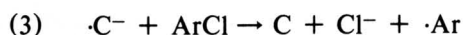
Adduct formation:



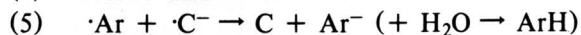
Solvent attack; metallation:



Dechlorination:



Aryl radical reduction:



Aryl radical recombination:



Mixed radical recombinations:



ketone as well as hydrocarbon anion-radicals are capable of attacking PCB molecules at low temperatures.

Not resolved by either of these bodies of prior literature is the question of how well an anion-radical-mediated PCB destruction process might perform in a medium that was predominantly 10C oil rather than a cation-complexing solvent. In such a medium one might expect the adduct formation equilibrium (Equation 1) to be shifted to the left; solvent attack processes (Equation 2) to be favored over PCB attack (Equation 4); and possible complications from radical reduction processes (Equations 4 and 5), which would mean the incompletely dechlorinated PCB molecules would still appear in the gas chromatogram as PCBs, albeit of lower degrees of chlorination, rather than as constituents of a nonvolatile resin.

#### ASSESSMENT OF SODIUM ADDUCT-PCB INTERACTIONS IN 10C OIL

In order to assess the pattern of interactions among sodium adducts, PCBs, and 10C oil, 0.5

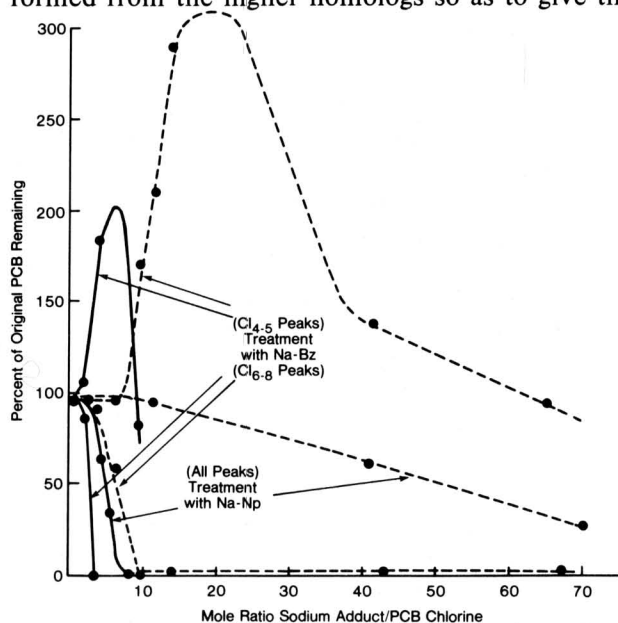
molar solutions of various 1:1 and 2:1 adducts were prepared by stirring together under nitrogen the appropriate quantities of sodium metal (40% dispersion in light mineral oil, from Matheson, Coleman, and Bell), the selected cation-complexing solvent (dried over Linde 4A molecular sieve), and the selected electron carrier. The resulting intensely colored solutions were then added, a few ml at a time, to 100 ml portions of askarel-contaminated 10C oil, with stirring under nitrogen at room temperature. After the disappearance of the color of each portion of the adduct, and before the addition of the next portion, a sample of the oil was removed for gas chromatographic determination of its PCB content. This was done by comparing eight of the more prominent peak heights with those in Aroclor 1254 or 1260 standards.

Generally speaking, it was observed that decolorization of the first few ml of added adduct occurred almost instantly in all cases, but with no change in PCB levels, indicating consumption of the adduct by traces of highly reactive non-PCB species such as H<sub>2</sub>O, O<sub>2</sub>, or carboxylic acids. The

colors of subsequent portions of the adducts generally persisted 1-5 minutes, except in the case of the 1:1 sodium-benzophenone adduct (sodium diphenylketyl), which reacted more slowly.

The titration curves obtained by plotting % PCB removed as a function of the relative amount of adduct added exhibited the general features shown in Figure 1.

In most cases, as illustrated in the lower part of Figure 1, the initial flat was followed by a pseudo-linear decline of PCB with added adduct until a rather sharply defined point of PCB disappearance was reached. In all such cases, there appeared to be little difference in the relative reactivities of the different PCB isomers; the individual peaks in the gas chromatogram maintained roughly the same relationship to each other as they declined. Conversely, during titrations with the 1:1 sodium-benzophenone adduct (upper curves, Figure 1), the disappearance of species in the Cl<sub>6</sub>-Cl<sub>8</sub> biphenyl range was accompanied by an initial sharp rise in concentration of those in the Cl<sub>4</sub>-Cl<sub>5</sub> range, and then followed by a slow and incomplete disappearance of the lower homologs. Evidently, this reagent was far more reactive with the higher than with the lower chlorinated biphenyl homologs, and some constituent of the reaction system, presumably benzhydrylate (by analogy to Equation 11), was capable of transferring hydrogen to the radicals formed from the higher homologs so as to give the



**Figure 1.** Changes in PCB levels resulting from titrations of 10C oils containing Aroclor 1254 (—), 120 ppm, or Aroclor 1260 (---), 800 ppm, with 0.5 M solutions of sodium adducts of benzophenone (Bz) or naphthalene (Np) in Diglyme or tetrahydrofuran, respectively, at room temperature.

reduced products observed.

Returning to the more usual case, where there were no complications arising from partial reduction of the PCBs, the first notable feature of the titration curves shown at the bottom of Figure 1 was their low slopes, which indicated that most of the sodium adduct was being consumed by reaction with species other than PCB. Similar behavior has also been reported for reactions of sodium naphthalenide/THF with PCBs in heat oil transfer oil.<sup>(2)</sup> The second significant feature was their roughly linear (rather than hyperbolic form), indicating that the *relative* rates of attack on PCB must have been increasing with increasing volumes of titrant solution in the medium. The latter point was also illustrated by the comparative titrations of 10C oil solutions containing 120 and 800 ppm of PCB; it generally required only 2-5 times as much titrant to destroy seven times as much PCB.

The approximate relative efficiencies of a number of different adduct-solvent combinations in the removal of Aroclor 1254 or 1260 from 10C oil are shown in Table 2. Generally speaking, the relative activities in attacking the less reactive PCB species (rather than unidentified components of the 10C oil), as indicated by the quantities of the adduct solutions that had to be added in order to achieve complete removal of the PCB, were roughly comparable for the 1:1 sodium-naphthalene adduct, the 2:1 sodium-biphenyl adduct, and the 2:1 sodium-naphthalene adduct, which formed a very slowly reacting black suspension in the system, decidedly higher for the removal of the more highly chlorinated PCB homologs by the 1:1 sodium-benzophenone adduct, and decidedly lower for the removal of the lower homologs (i.e., all PCBs) by that adduct.

Several rather poorly reproducible experiments using triglyme or tetraglyme (which are apparently harder to obtain in consistent purity) suggested higher  $\Delta\text{PCB}/\Delta\text{Na}$  ratios than exhibited in runs using diglyme as the ion-complexing solvent; conversely, somewhat lower ratios were shown by monodentate complexes such as THF or diethylether (Table 2).

The overall conclusion drawn from these experiments was that if one desired to destroy the PCB in 10C oil with reasonable speed and efficiency by adding to the oil a near-saturated solution of a reactive sodium adduct, roughly 20 volumes of adduct solution would be required per 100 volumes of oil, almost regardless of the choice of adduct or PCB level in the oil. Since the effective ion-complexing solvents are all about 10 times as costly as 10Coil, and since they would almost certainly alter its

**Table 2**  
**APPROXIMATE EFFECTIVENESS**  
**OF VARIOUS 0.5 M SODIUM ADDUCT SOLUTIONS**  
**IN DESTROYING PCBs<sup>a</sup> IN 10C OIL**  
**AT ROOM TEMPERATURE**

Adduct Former ( <i>b</i> )	Na-Adduct Ratio	Solvent ( <i>b</i> )	PCB Type ( <i>c</i> )	PCB Conc. (ppm)	$\frac{\Delta\text{PCB}}{\Delta\text{Na}}$ ( <i>d</i> )	% Soln. for 99% $\Delta$ PCB (v/v)
BZ	1:1	ETH	1260	800	0.06 <sup>e</sup>	(f)
BZ	1:1	THF	1260	800	0.04 <sup>e</sup>	(f)
BZ	1:1	DGM	1260	800	0.08 <sup>e</sup>	(f)
BZ	1:1	DGM	1254	120	0.4 <sup>e</sup>	(f)
BZ	1:1	TGMT	1260	800	0.9 <sup>e</sup>	(f)
BZ	2:1	TGMT	1260	800	0.7 <sup>e</sup>	> > 10
NP	1:1	THF	1260	800	0.03	20
NP	1:1	GLM	1260	800	0.02	> 20
NP	1:1	DGM	1254	120	0.003	> 25
NP	2:1 <sup>g</sup>	DGM	1260	800	0.05	8 <sup>g</sup>
BP	1:1	THF	1260	800	0.002	> > 20
BP	2:1	GLM	1260	800	0.02	15

a. As measured by disappearance of gas chromatographic peaks in range characteristic of Cl<sub>4</sub>-Cl<sub>8</sub> biphenyls. Unless noted (e), all such peaks disappeared at approximately the same rate. b. Key: BZ, benzophenone; NP, naphthalene; BP, biphenyl; ETH, ether; THF, tetrahydrofuran; DGM, diglyme; TGMT, 1:2 tetraglyme-toulene; GLM, glyme. c. Aroclor 1260, mainly mixture of Cl<sub>5</sub>-Cl<sub>7</sub> biphenyls; Aroclor 1254, mainly mixture of Cl<sub>4</sub>-Cl<sub>6</sub> biphenyls. d. Ratio of moles PCB lost per mole adduct sodium added determined from approximate slope near middle of titration curve. e. Data for peaks in Cl<sub>6</sub>-Cl<sub>8</sub> biphenyl range only. f. Not yet demonstrated that any quantity of the 1:1 Na-BZ adduct solution sufficient to remove the less highly chlorinated PCB homologs. g. Presumed adduct formed by dispersing solid Na-in-naphthalene dispersion (Coronet Chemical Co.) in diglyme; formed black suspension rather than solution; reactions with PCB/10C required several hours rather than minutes.

dielectric properties and thermal stability if appreciable amounts were left in oil destined for reuse, it was evident that any practical use of preformed adduct solutions for PCB removal would have to be followed by some reasonably efficient recovery of the ion-complexing solvent.

#### CATALYSED SODIUM PROCESS FOR DESTROYING PCBs IN 10C OIL

In order to determine whether such substantial needs for ion-complexing solvents in the reaction system could be reduced, we conducted a number of experiments in which the prior formation of the adduct was eliminated. In these experiments, various types and levels of electron carriers, cation-complexing solvents, and commercial sodium dispersions were added to Aroclor 1260-containing 10C oil with stirring under nitrogen at room tem-

peratures, and the mixture periodically checked for disappearance of both sodium and PCB.

It was observed that there was considerably more batch-to-batch variation in the reactivity of the sodium dispersions than was encountered during the preparation of the sodium adducts in ion-complexing media. Most freshly opened commercial samples appeared to react completely with the 10C/PCB/electron carrier/ion carrier mixtures within an hour, leaving only a fine gray haze of suspended sodium chloride particles. However, in a few cases, reaction was found to be complete within a few minutes, and some older dispersion specimens did not react at all. Evidently, in media consisting of 10C oil containing only 1-5% of ion-complexing solvent the reaction with electron carrier was more sensitive to inhibition by oxide films

on the dispersed sodium particles than in those composed by solvent alone. The rate of sodium disappearance did appear to be related to the quantity of cation-complexer present, but this proportionality was difficult to quantitate because of the variability in the dispersion reactivity. The disappearance of the sodium was accompanied by that of the PCB in roughly the same proportions as observed using solutions of the preformed adducts; i.e., most of the sodium was consumed by reactions with constituents of the 10C oil rather than with PCBs, and hence large excesses of sodium were still required for complete PCB removal.

Reaction of the sodium with PCB and 10C oil was found to depend not only on the presence of the cation-carrier, but also on that of the electron carrier. In parallel experiments using 10C oil containing 800 ppm Aroclor 1260, 5% diglyme, and 0.23% sodium with or without 0.32% naphthalene, elimination of the PCB required an hour in the first case and a week in the second. Even in that latter case, an electron carrier may have been involved: most 10C oils are known to contain some alkyl naphthalenes, and the reaction medium in this case did exhibit the typical deep green color of a 1:1 naphthalene adduct by the end of the week. We have also learned, from another laboratory where this process was being checked, that some Texaco 10C oils, which are particularly high in alkyl naphthalene, do not require naphthalene addition for successful dechlorination.<sup>(10)</sup>

A number of parallel runs were made using either benzophenone or naphthalene as the electron carrier, without revealing any significant differences in performance between them as regards either reaction rates or efficiency of PCB removal. In both cases, the Cl<sub>4</sub>-Cl<sub>7</sub> biphenyl isomers all disappeared at roughly the same rate without evidence for stepwise reduction, and the reactions proceeded without ever developing more than traces of the intensely colored 1:1 adducts. From this, we concluded that the reactive intermediate was some species other than the 1:1 adduct present in the preformed solutions used earlier, and instead was probably either a soluble 2:1 adduct or else some sort of a surface complex.

The performance of the sodium-naphthalene-diglyme system on a number of different specimens of PCB-containing 10C oil, all taken from transformers returned for service work, is summarized in Table 3. From this, it was concluded that contaminants arising during transformer use would not seriously interfere with use of this system for PCB removal.

This table also points out that in some runs,

which were examined by electron-capture gas chromatography just after the disappearance of the dominant Cl<sub>4</sub>-Cl<sub>7</sub> biphenyl peaks of the Aroclor 1254 or 1260, there remained some weak peaks in the retention range covered by the Cl<sub>2</sub>-Cl<sub>4</sub> biphenyl peaks of Aroclor 1016. A few of the peaks had retention times similar to those of 1016, and we could not exclude the possibility that such mixtures contained traces of the lower chlorinated biphenyls, in addition to other electron-capturing species, such as sulfur compounds or autoxidation products. Fortunately, upon continuation of the sodium treatment, these enigmatic peaks disappeared in all cases.

In order to examine the feasibility of scaling up the process, a 55-gallon drum was equipped with a lid, stirrer, and provision for flushing with nitrogen. In a typical experiment, this was charged with 40 gallons of PCB-containing 10C oil (which was pumped in through a 30 in. column of 1/16 in. pellets of Linde 4A Molecular Sieve, #87956, to remove any water present), 4 lb of a 20% dispersion of sodium in mineral oil (Coronet Chemical Co., Newark, New Jersey) and a solution of 1 lb naphthalene in 2 gallons of diglyme (diethylene glycol dimethyl ether; Ansul Chemical Co., Marietta, Wisconsin). Gas chromatographic analysis showed the level of Aroclor 1260 to be initially 852 ppm; after 15 min, 17.6 ppm; after 60 min, 1 ppm.

A portion of the resulting Na-treated, but unwashed, oil, which was initially almost clear except for the NaCl haze, and no more colored than the original 10C oil, was allowed to stand with exposure to air for several weeks. As a result, the oil developed a purple color and deposited most of its sodium salts as a black precipitate that appeared reddish-purple in thin layers. This deposit, after filtration and washing with hexane, was found to react with water without gas evolution to produce sodium hydroxide and a light yellow, water-insoluble, hydrocarbon-soluble resin.

Examination of this resin by gel permeation chromatography showed a broad, weakly bifurcated peak, with the two maxima at positions corresponding to those of linear polymers with molecular weights of 310 and 620, respectively. (On the same columns, 10C oil itself gave an asymmetrical peak, having a centroid and a maximum at points corresponding to polymers of molecular weights 242 and 161, respectively; the actual average molecular weight of 10C oil is about 250.) Examination by gas chromatography showed the lower molecular weight population to be a very complex mixture, and field desorption mass spectrometry indicated a detectable peak at almost every mass



**Table 3**  
**REDUCTIONS IN PCB LEVELS**  
**RESULTING FROM STIRRING RANDOMLY SELECTED SPECIMENS**  
**OF USED, PCB-CONTAINING 10C OIL**  
**WITH DIGLYME, NAPHTHALENE AND DISPERSIONS**  
**OF SODIUM METAL (0.24% w/v; 0.10 M)**  
**UNDER NITROGEN AT 24 °C**

Initial Aroclor 1260 (ppm)	% (v/v) diglyme solution added <sup>a</sup>	Initial naphthalene in 10C Oil <sup>a</sup> (M)	Reaction time (min)	% Reduction in PCBs	
				Lower peaks <sup>b</sup> (1% of initial 1260)	Higher peaks <sup>c</sup> (99% of initial 1260)
930	5	0.025	30	92	100
434	3	0.015	30	98	100
434	3	0.015	30	98	100
410	3	0.015	40	98	100
410	3	0.015	40	92	100
180	3	0.030	30	98	100
180	3	0.030	30	100	100
180	5	0.025	30	100	100
180	5	0.025	30	99	100
372	3	0.030	30	98	100
372	3	0.030	30	100	100
372	5	0.025	30	98	100
372	5	0.025	30	98	100
336	2	0.010	30	99	100
336	2	0.010	60	96	100
336	3	0.015	10	99	100
333	1	0.010	15	92	91
333	1	0.010	30	99	100
333	2	0.020	15	100	100

a. Naphthalene introduced into 10C oil by adding 1-5% (as indicated) of 0.5 or 1.0 M solution in diglyme. b. Electron capture gas chromatographic peaks mainly in range characteristic of trichlorobiphenyls; some, but not all, corresponding to positions of peaks in Aroclor 1016. c. Peaks mainly in range characteristic of penta-, hexa-, and heptachlorobiphenyls.

number between 150 and 350. The UV spectrum of the resin resembled that of an alkyl benzene, with a sharp maximum near 272 m $\mu$ , but with some broadening on either side. The NMR spectrum indicated an aromatic/aliphatic proton ratio of 0.43. The infrared spectrum revealed prominent carbonyl and hydroxyl (i.e., carboxylic acid?) bands in a specimen that had been aged a year; however, these were less evident earlier. It was concluded that the precipitated purple salt was probably an autoxidation product derived mostly from metallation and coupling products of various constituents of the 10C oil (e.g., via processes like Equations 2 and 9), rather than from those of the PCBs.

However, the available data do permit certain

conclusions to be drawn regarding the nature of the PCB conversion products. First, it is evident from the absence of stepwise reduction products (which were easily detected in the case of treatments with preformed sodium diphenylketyl) that aryl radical reduction reactions (Equations 4 and 5) must be rather unimportant in these heterogeneous systems. Second, the absence of any high molecular weight polycondensates or insoluble poly(biphenyl) gels indicates that aryl radical recombination reactions (Equation 6) must also be unimportant. According to classical polymer gelation theory, gelation in a polycondensation of hexafunctional monomers should occur when the reaction is only 20% complete. In addition, we might note that no gelation

has been reported even in systems using high concentrations of PCBs,<sup>(2,4)</sup> which would favor aryl-aryl coupling; hence such coupling would appear particularly unimportant in systems where the PCB levels are only 100-1000 ppm. Accordingly, we conclude that most of the radicals generated by the removal of the chlorines from the PCB molecules must be consumed via mixed radical recombination processes (Equations 7 and 8), and hence that the PCB conversion product must consist of an extremely complex mixture of molecular species, each of which contains a single biphenyl nucleus linked to 4-7 aralkyl hydrocarbon, dihydronaphthalene, or glycol ether residues. Such a product would be similar to asphalt in its chemical and environmental properties.

It is this apparent that catalyzed sodium processes of the types just described are capable of removing PCBs from transformer oil down to the levels sought by the EPA without the formation of objectionable products. Moreover, such processes are capable of being carried out in a single step at room temperature in simple process equipment, and hence are suitable for small-scale, decentralized operations. A minimal objective of such operations would be to render scrap transformer oil acceptable for sale as fuel. Still undetermined is whether the 10C oil treated by this or any of the alternative PCB-removal processes, all of which tend to alter the levels of multicyclic hydrocarbons and/or sulfur compounds, as well as those of the PCBs and chlorobenzenes, still possesses the long-term oxida-

tive and dielectric stability required for reuse in transformers; however, active research on this question is currently in progress.<sup>(10)</sup>

## REFERENCES

1. Hiraoka, M., T. Takase, and J. Matsuno, *Japan Kokai* 74 82520, 08 Aug. 1974 (*Chem. Abstr.*, 82:89831k (1975)).
2. Goodyear Tire and Rubber Co. "A Safe, Efficient Chemical Disposal Method for Polychlorinated Biphenyls—PCB's," Research Laboratories Report, March, 1980.
3. Oku, A., K. Yasufuku, and H. Kataoka, *Chem. and Ind.*, (1978), p. 841.
4. Smith, J.F. and G.L. Bubar, "The Chemical Destruction of Polychlorinated Biphenyls by Sodium Naphthalenide," Report from the Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L3G1, November, 1979.
5. Holy, N.L., *Chem. Rev.*, 74:243 (1974).
6. Nishiwaki, T., A. Ninomiya, S. Yamanaka, and K. Anda, *Nippon Kagaku Kaisho*, (1972), p. 2225 (*Chem. Abstr.*, 78:29339p (1973)).
7. Sawai, T., and Y. Shinozaki, *Chem. Lett.*, (1972), p. 865.
8. Sawai, T., *Kogai*, 8:234 (1973) (*Chem. Abstr.*, 85:166160g (1976)).
9. Sherman, W.V., *J. Am. Chem. Soc.*, 90:6773 (1968).
10. Rouse, T.O., Private Communication.

H81CRD257  
CAMPBELL VC 6065102090  
GENERAL ELECTRIC CO.  
TB DEPT 6-183 EP  
SYRACUSE NY 13221

J.F. Brown, Jr.  
Marie E. Lynch  
J.C. Carnahan  
J. Singleton

CHEMICAL DESTRUCTION  
OF PCBs IN TRANSFORMER OIL

Report No. 81CRD257  
November 1981

---

GENERAL ELECTRIC COMPANY  
CORPORATE RESEARCH AND DEVELOPMENT  
P.O. BOX 8, SCHENECTADY, N.Y. 12301

---

GENERAL  ELECTRIC