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EPRI EL-4503
Project 2028-12
Final Report
March 1986

State-of-the-Art Review: Pyrolysis and Combustion of PCB Substitutes

Prepared by
SCS Engineers, Inc.
Long Beach, California

REPORT SUMMARY

SUBJECTS: Hazardous/toxic substances / T&D: Substations

TOPICS: PCB; Transformers; Chemical analysis; Capacitors; Fires; Electrical insulation

AUDIENCE: Environmental managers / Distribution engineers

State-of-the-Art Review: Pyrolysis and Combustion of PCB Substitutes

Utilities are concerned about the possible long-term toxic effects of trace combustion products of potential PCB substitutes. This literature review turned up much information on the bulk combustion products of replacement compounds that are already in wide use but few data on either the trace or bulk products of relatively new materials.

BACKGROUND

Several compounds are under consideration as substitutes for polychlorinated biphenyls (PCBs) in transformers and capacitors. To ensure that these insulating materials do not pose problems similar to those encountered with PCBs, utilities need to determine not only their electrical, thermal, and physical characteristics but also the bulk and trace materials they produce when pyrolyzed or combusted.

OBJECTIVE

To review the literature on the materials produced during the pyrolysis and combustion of several solid, liquid, and gaseous substitutes for PCBs.

APPROACH

Researchers focused their review on 18 potential PCB replacement materials—2 solids (epoxy resins and polyvinyl chloride), 2 gases (Freon 113 and sulfur hexafluoride), and 12 liquids, including phthalate esters, benzyl-neocaprate, silicone, chlorobenzenes, methylated diphenylethane, and perchlorethylene. In particular, project workers sought information on trace products related to those found during PCB thermal decomposition—for example, polyaromatic hydrocarbons, polychlorinated dibenzofuran, and polychlorinated dibenzodioxin.

RESULTS

The literature contains a great deal of information on the bulk pyrolysis and combustion products of PCB substitutes that have had wide use in the electricity industry and other industries. Examples of such substitutes are epoxies, sulfur hexafluoride, silicone, phthalate esters, methylated diphenylethane, perchlorethylene, and polyvinyl chloride. However, there is little information on the trace products of concern. Literature on both the bulk and trace combustion products of some of the less familiar replacement compounds is sparse and, in some cases, nonexistent. For example, researchers found no information on the materials generated during thermal

decomposition of benzylneocaprate and alkylbiphenyls. The study concluded that further laboratory work is needed to identify additional trace meteriels of the better known PCB substitutes and both bulk and trace products of the newer compounds.

EPRI PERSPECTIVE

Concern over the toxicity of PCBs has focused on both its bulk and trace combustion products. To build a database as sophisticated as that for PCBs, researchers must perform intensive analyses of all potential substitutes. EPRI is currently conducting laboratory studies to enlarge the present database. Four such studies are project RP2028-11, which is focusing on the bulk pyrolysis and combustion products of several liquid PCB substitutes, and projects RP2028-15, RP2028-16, and RP2028-17, which are analyzing the bulk and trace products of a group of liquid, solid, and gaseous PCB substitutes.

PROJECT

RP2028-12
EPRI Project Manager: Gil Addis
Electrical Systems Division
Contractor: SCS Engineers, Inc.

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EL-4503
Research Project 2028-12

Final Report, March 1986

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ABSTRACT

An extensive literature search was conducted to identify the combustion and pyrolysis by-products of several PCB substitutes. These compounds included phthalate esters, benzylneocaprate, siloxanes, chlorinated benzenes, dixylylethane, alkylbiphenyls, paraffinic hydrocarbons, perchloroethylene, chlorofluorocarbons, sulfur hexafluoride, epoxy resins, and polyvinyl chloride. No information was found on the thermal decomposition of benzylneocaprate or the alkylbiphenyls. Siloxanes decompose to silica, cyclic siloxanes, and hydrocarbons of relatively low toxicity. Paraffinic hydrocarbons decompose into a series of shorter hydrocarbon compounds. Epoxies yield both alkyl and aryl hydrocarbons. Sulfur hexafluoride yields a series of sulfur and thionyl fluoride compounds and unidentified toxic PICs. The phthalate esters produce phthalic anhydride, naphthalene, and biphenyl. Methylated diphenylethane and phenylxylylethane decompose into a series of polynuclear aromatic hydrocarbons. Perchloroethylene produces predominantly hydrogen chloride and chlorine and sometimes phosgene. Chlorofluorocarbons yield these compounds and their fluoride analogs. Polyvinyl chloride decomposes into phosgene, naphthalene, benzene, and chlorinated benzenes. Chlorinated benzenes and possibly butylated monochlorodiphenylether can produce PCDDs and PCDFs.

ACKNOWLEDGMENTS

It is impossible to do an adequate state-of-the-art review without consulting those individuals and organizations currently engaged in research. Published information is often months to years out of date, and only contacts with researchers can produce a timely review. Consequently, it was necessary to request assistance from many organizations. There is no way to list every company or individual talked to during the course of this effort, but several, because of the extent of their cooperation, deserve special mention.

Among the organizations and companies which provided extensive assistance and/or material were EPRI, Westinghouse Electric Corporation, General Electric Corporation, Dow Chemical, Monsanto, RTE Corporation, ISC Chemicals Limited, and Ciba-Geigy. Individuals deserving special thanks include R. Crespi and B. Kueng (Ciba-Geigy); E. Walsh, C. C. Claiborne, and D. L. Mandelcorn (Westinghouse); N. Burns and S. J. Parkinson (ISC Chemicals Limited); D. Duvall, F. Hileman, M. Hughes, and L. Parts (Monsanto); R. Ristow, E. Feuerstein, and T. L. Mayes (General Electric Corporation); K. Kinnebrew (General Electric Transformer Service Group); J. Hearse (National Industrial Transformers, Inc.); P. Gervason (Prodelec); T. Lovkvist (ASEA Kobel); H. M. Wortnington (The Micanite and Insulators Company, Ltd.); C. P. McShane (RTE Corporation); H. W. Stacy (Southwest Research Institute); D. C. Wilson (Harwell Laboratory); G. A. Gauger (Thomas A. Edison Technical Center, McGraw-Edison Company); H. L. C. Meuzelaar (University of Utah); W. Rubey (University of Dayton Research Institute); C. T. Olsen (Air Force Aeronautical Medicine Research Laboratory, Wright Patterson Air Force Base); M. Saperstein (Southern California Edison); and C. Milado. Thanks also to the EPRI Project Manager, G. Addis, for constructive guidance and assistance in formulating and executing the project.

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EXECUTIVE SUMMARY

Since 1976, the manufacture and commercial use of polychlorinated biphenyls (PCBs) have been restricted by law. Proposals have been made to remove existing PCB-containing transformers and capacitors from service. A number of chemicals have been and are being considered for use as PCB substitutes in electrical applications. Although all have been tested for acceptable dielectric, heat transfer, and flammability properties, few have been extensively analyzed for combustion by-products.

PCBs were not restricted for problems with their dielectric properties or heat transfer capabilities, but rather for suspected toxicological properties that were not considered when PCBs were first commercially produced. These toxicological properties are attributed not only to the PCBs themselves, but also to the presence of various toxic chlorinated aromatics in the by-products of PCB/askarel fires. It is thus necessary to examine the chemical behavior of proposed PCB substitutes to identify the potential for similar problems. The purpose of this report was to conduct a state-of-the-art literature review to determine what is known regarding the chemical and toxicological nature of the combustion by-products of various PCB substitutes.

DATA ASSESSMENT

Until very recently, the major concern in any fire or explosion episode was firefighter safety. As a result, tests have focused almost exclusively on major gaseous combustion products such as carbon monoxide, hydrogen cyanide, oxides of nitrogen and sulfur, hydrogen chloride, and so forth. These are the immediate life-threatening combustion products with which one must deal, and they are generally the simplest to detect and measure.

However, it has become evident in the aftermath of several PCB incidents that the toxic trace combustion product problem is concerned more about soot deposits than the vapors formed. Trace products of incomplete combustion (PICs) are produced

in such low levels that vapor emissions dispersing in the atmosphere rapidly reach inconsequential levels. These same PICs may concentrate in soot, however, and soot provides a reservoir for continued emissions or exposure long after a fire has been extinguished and the gases dispersed.

Furthermore, analysis of soot or even gas samples for trace PICs at the levels typically produced requires very sophisticated analytical instrumentation and highly trained specialists. Even then, complete identification of PICs in a particular sample may take years of work. As the level of sensitivity of analytical instruments increases, even more toxic PICs may become evident. For instance, continued research on PCB combustion by-products has identified not only chlorinated dioxins and dibenzofurans, but also polychlorinated chrysenes, pyrenes, xanthenes, terphenyls, quaterphenyls, and others.

This level of research has been directed at PCB because of its negative publicity and the perceived crises in regards to several PCB incidents. No such crises exist for the proposed PCB substitutes. As a result, with a very few exceptions, comparable research has not been conducted into their PICs. As noted above, existing data tend to focus on the macro combustion products present in the vapor state rather than trace PICs in the soot. Consequently, there is relatively little data on trace PICs comparable to that on dioxins or dibenzofurans. These types of by-products simply have not been identified and studied in most cases.

PROPOSED PCB SUBSTITUTES: LIQUIDS

Two types of esters, phthalate esters and benzylneocaprate, have been considered as PCB substitutes. In general, pyrolysis of esters will produce gases similar to and no more toxic than those obtained from hydrocarbons. One major decomposition product is phthalic anhydride which can react further to form naphthalene and biphenyl. In the presence of chlorobenzenes, PCB and chlorinated naphthalene may be produced.

Polydimethyl siloxane has been widely used as a retrofill fluid. During thermal decomposition, amorphous silica, several cyclic siloxanes, and a variety of simple hydrocarbons are produced. Most of these compounds are not highly toxic, and animal inhalation tests on pyrolyzed siloxanes have generally indicated a low toxicity.

Chlorobenzenes have generally not been considered PCB substitutes as much as additives to PCBs and other dielectrics. Decomposition of chlorobenzenes can produce a variety of highly toxic compounds. Pyrolysis of monochlorobenzene can yield mono- and dichlorobiphenyls, chloronaphthalene, and vinyl chloride. In the presence of air, chlorobenzenes can produce chlorophenols which can, in turn, dimerize to PCDFs and PCDDs. Many of these combustion/pyrolysis products are very highly toxic.

Methylated diphenylethane and phenylxylylethane are used as components in dielectric fluid mixtures. No information was found on the combustion/pyrolysis products of either compound, but pyrolysis of chemically similar diphenylmethane and 1,2-diphenylethane produces a number of polynuclear aromatic hydrocarbons. Few of these are considered to be highly toxic, but several are known or suspected carcinogens.

There is no information available on the thermal decomposition products of butylated monochlorodiphenylether, another PCB substitute. However, both the unsubstituted diphenylether and polychlorinated diphenylethers have been studied. Diphenylether can break down into phenol, benzene, and dibenzofuran. Polychlorinated diphenylether can produce PCDFs and PCDDs.

There is also no information available on the thermal decomposition products of the alkyl biphenyls, specifically isopropylbiphenyl and n-propylbiphenyl.

Paraffinic hydrocarbons, such as polyalphaolefin and RTEmp, tend to decompose into a variety of short-, medium-, and long-chain saturated and unsaturated hydrocarbons. In the presence of air, organic acids, alcohols, and aldehydes are formed.

Perchloroethylene is being promoted as a transformer fluid neat, mixed with mineral oil, or mixed with fluorocarbons. Chlorine or hydrogen chloride are the principal decomposition products to be expected. Under certain conditions, phosgene or trichloroacetic acid may be produced.

DIELECTRIC GASES

Chlorofluorocarbons are used as dielectrics both neat and mixed with perchloroethylene. Although generally thermally stable, at high temperatures or during

arcing, decomposition is possible. Chlorine, hydrogen chloride, hydrogen fluoride, phosgene, and carbonyl fluoride are among the by-products which can be expected. Phosgene and carbonyl fluoride, in particular, are highly toxic.

Sulfur hexafluoride can be used alone as a dielectric or in a mixture of gases. It produces a number of long-lived by-products under fire and arcing conditions. The principal by-product is thionyl fluoride; other products include sulfuryl fluoride, thionyl tetrafluoride, and sulfur dioxide. Toxicity tests on sparking gases have yielded a higher toxicity than the above compounds would indicate. Thus, there are one or more unidentified trace decomposition products which contribute significantly to the toxicity of the decomposition gases.

PROPOSED PCB SUBSTITUTES: SOLIDS

Two solids were reviewed: epoxy resins and polyvinyl chloride (PVC). Complicating an assessment of their decomposition is the fact that neither is a pure compound or even a mixture of a few discrete compounds. Rather, each is a mixture of resin, hardener, filler, and various other materials, many of which may have a variable composition. Thus, the decomposition products of these solids can vary extensively, depending on the nature of the additives.

Pyrolysis of epoxy resins can produce a variety of organic compounds including benzene, methyl chloride, ethyl chloride, acetone, propylene, ethane, pentane, toluene, cresol, phenol, and others. Several of these are known or suspected carcinogens.

Decomposition of PVC can yield benzene, toluene, xylene, aliphatic hydrocarbons, β-methylnaphthalene, several chlorinated benzenes, and phosgene. Because of the production of chlorinated benzenes, the formation of PCDDs and PCDFs is a distinct possibility, although none have been identified in PVC pyrolysis gases to date.

Section 1

INTRODUCTION

BACKGROUND

The U.S. Congress passed the Toxic Suostances Control Act in 1976. Under requirements of the Act, the EPA issued restrictions on the manufacture and commercial use of polychlorinated bipnenyls (PCBs). PCB production in tne United States was halted in 1977, and tne production of PCB-containing transformers and capacitors nas been limited since then; however, there was no order to take such units out of service. The service life of these units is measured in tens of years, so that the replacement rate is low (about 0.2% per year) (117). However, should the EPA order PCB-containing units removed from service (FR 49(198):39966-39989, 11 October 1984, Proposed Rules), the need to find acceptable PCB substitutes will become critical.

Several possible substitutes for PCBs are readily available (92, 97). PCBs were not restricted for problems with their dielectric properties or heat transfer capabilities, rather for suspected toxicological properties not considered in 1929 when PCBs were first commercially produced (117). These toxicological properties are attributed not only to the PCBs themselves, but also to the presence of polycnlorinated dibenzodioxins (PCODs), polychlorinated dibenzofurans (PCDFs), and otner cnlorinated aromatics in utility PCB fluids and in the by-products of PCB/askarel fires. It is thus necessary to examine the chemical and toxicological benavior of proposed PCB substitutes and to identify potential problems for each alternative cnemical option for transformers and capacitors before its use becomes widespread.

OBJECTIVES

The available PCB substitutes are of widely variant chemical composition. The toxicology and environmental hazard evaluation of most of these compounds has been reported (97). The objective of this study is to review the state of the art regarding the thermal degradation cnemistry of PCB substitutes, the formation

of hazardous products of incomplete combustion (PICs) from these compounds, and the toxicity and environmental hazard of those PICs.

The liquid, gaseous, and solid dielectrics examined in this study are described below.

Liquids

- Phthalic esters di-(2-ethylhexyl)-phthalate and dioctylphthalate.
- Benzyl neocaprate.
- Polydimethylsiloxane.
- Chlorobenzenes.
- Butylated monochlorodiphenylether.
- Methylated diphenylethane.
- Phenylxylylethane.
- Isopropylbiphenyl.
- Propylbiphenyl.
- Poly(1-octene).
- RTEmp.
- Perchloroethylene.

Gases

- Freon 113.
- Sulfur hexafluoride.

Solids

- Epoxy resins.
- Polyvinyl chloride.

The risk from exposure to these compounds is modified in this study by the assumption that the hazard from the compounds studied occurs only when the compound is in a transformer or capacitor which has failed catastrophically (ruptured) due to internal arcing, which involves temperatures of up to 6000 °C for periods of less than a second, or due to short-circuits which cause internal "hot

spots," involving temperatures of up to 250 °C for a few minutes before evolution of gas from the fluid ruptures the transformer case, or which has suffered fluid loss as a result of an external fire (15, 71). Any unit which completes its service life without losing fluid to the environment is considered to pose no hazard in the context of this study. Such units may pose a disposal problem; this difficulty is not considered here.

REPORT ORGANIZATION

Section 2 of this report discusses proper assessment of the data. Sections 3, 4, and 5 cover the thermal degradation of the liquid, gaseous, and solid dielectrics, respectively, and the toxicology of their PICs.

Section 2

DATA ASSESSMENT

INTRODUCTION

If comparative toxicologic action of the combustion products of several materials is to be used, even in part, as a method of preferential selection, available information must include:

- The nature and amount of the toxicologic agents generated when the materials undergo combustion or pyrolysis under specified decomposition conditions.
- The dose-response characteristics of these agents.
- The additive, antagonistic, or synergistic stress from the products generated by the degradation (72).

The available data for each of the above criteria are highly variable, in terms of both quantity and quality. Some chemicals have been studied extensively, some not at all. Before addressing the specific data for each PCB substitute, it is necessary to examine the types of data available and their limitations.

COMBUSTION/PYROLYSIS CHEMISTRY

The ideal way to identify the expected thermal degradation products of a given substance is to combust or pyrolyze it under conditions nearly identical to those which might be encountered in the field, yet in a tightly controlled environment, followed by a full-spectrum analysis of the vapors and soot produced. This is virtually impossible to do for a variety of reasons, not the least of which is the cost of such experiments. In general, available data are based on laboratory tests and incomplete analyses.

Part of the problem is that, until very recently, the major concern in any fire or explosion episode was firefighter safety. As a result, tests have focused almost exclusively on major gaseous combustion products such as carbon monoxide, hydrogen cyanide, oxides of nitrogen and sulfur, hyorogen chloride, and se forth.

These are the immediate life-threatening combustion products with which one must deal, and they are generally the simplest to detect and measure.

However, it has become evident in the aftermath of several PCB incidents that the toxic trace combustion product problem is concerned more about soot deposits than the vapors formed. This is not to suggest that a compound like a dioxin is less toxic in the vapor state. However, trace PICs are produced in such low levels that vapor emissions dispersing in the atmosphere rapidly reach inconsequential levels. These same PICs may concentrate in soot, however, and soot provides a reservoir for continued emissions or exposure long after a fire has been extinguished and the gases dispersed.

Furthermore, analysis of soot or even gas samples for trace PICs at the levels typically produced requires very sophisticated analytical instrumentation and highly trained specialists. Even then, complete identification of PICs in a particular sample may take years of work. As the level of sensitivity of analytical instruments increases, even more toxic PICs may become evident. For instance, continued research on PCB combustion by-products has identified not only chlorinated dioxins and dibenzofurans, but also polychlorinated chrysenes, pyrenes, xanthenes, terphenyls, quaterphenyls, and others (113).

This level of research has been directed at PCB because of its negative publicity and the perceived crises in regards to several PCB incidents. No such crises exist for the proposed PCB substitutes. As a result, with a very few exceptions, comparable research has not been conducted into their PICs. As noted above, existing data tend to focus on the macro combustion products present in the vapor state rather than trace PICs in the soot. Consequently, there is relatively little data on trace PICs comparable to that on dioxins or dibenzofurans. These types of by-products simply have not been identified and studied in most cases.

A major fraction of the available data was not generated with a view toward utility dielectric applications. Experimental conditions were not designed to match a transformer failure or similar occurrence. The fact that a particular dielectric can, in a laboratory, pyrolyze or combust to a dioxin or dibenzofuran does not, in itself, indicate that a similar reaction will occur in an actual incident. The experimental temperatures to which the dielectric was exposed and the residence time at those temperatures, must be compared to the conditions expected to occur during normal operation of a transformer or capacitor and during catastrophic failure of such a unit.

It is not the purpose of this report to speculate on potential PICs. Rather, the objective is to report the state-of-the-art. In some cases, where there is little combustion data on a particular compound, there are more data on a structurally analogous compound. Such data are included as guidelines for any future research, although even very closely analogous compounds may not behave identically.

TOXICITY AND EXPOSURE LIMITS

There is no single, universally accepted standard for expressing chemical toxicities; rather, there is a series of terms depending on the nature of the data and how it was obtained. Lethal dose, lethal concentration, toxic dose, and threshold limit value are examples of the types of toxicity data available. Furthermore, within each type there may be variations to describe the lowest recorded value or the value at which a certain percent of a test population died or showed adverse reactions. The data may be expressed in terms of liquid concentration, atmospheric concentration, or concentration per unit body weight, often with a time factor included. Finally, the data are generally identified by the types of organism from which they were obtained, either human, rat, mouse, guinea pig, or other animal.

These different types of data are frequently unrelatable. High oral toxicity, for instance, may or may not accompany an equally high inhalation or dermal toxicity. Toxic dose, letnal dose, and threshold limit value express three different types of data which, even within the same animal species, may be unrelated for a particular chemical. Finally, due to morphological differences, extrapolation from animal toxicities to human may not be possible (22, 68).

Unfortunately, every particular type of data is not available for every chemical. This can make toxicity assessment and comparison a difficult task. There is no way to take an oral TC_{LO} for rats and a dermal LD_{50} for guinea pigs, and project an inhalation TLV for humans. Consequently, it is necessary to establish a few guidelines to the application of the data to be presented later in this report.

In general, this report tries to present inhalation or dermal toxicity data for humans, wherever such were available. As they frequently are not available, inhalation data for rats, oral date for humans or rats, or inhalation or oral data for other animals were used, in the above order of preference. Some attempt was made to qualitatively assess the data.

It is also recognized that discrete toxicity data values presented in isolation probably mean little to most readers. Sax (95) attempted to describe toxicity data as follows:

- High toxicity: LD_{50} < 500 mg/kg.
- Moderate toxicity: LD_{50} 500 to 7,500 mg/kg.
- Low toxicity: LD_{50} 7,500 to 15,000 mg/kg.
- No toxicity: LD_{50} > 15,000 mg/kg.

These are general descriptions and are not to be relied upon dogmatically. For instance, synergistic effects (to be discussed below) are overlooked entirely.

Table 2-1 presents toxicity data for several common or well-known toxicants. Data comparable to that presented elsewhere in this report are presented in order to provide a general basis for comparison with PCB substitute by-products.

SYNERGISM

The toxicity data, as presented in this report, are specific for individual compounds. In a fire or catastrophic failure situation, a variety of compounds will be produced. Depending on the nature of the toxic effects, a mixture of two equally toxic compounds may be twice as toxic as either compound alone. On the other hand, if the action of the two compounds is sufficiently different, there may be little evidence of this "additive" effect. Furthermore, there is a potential for synergistic effects whereby a mixture of two toxic chemicals is far more toxic than the sum of the individual toxicities. These questions generally have not been studied in regard to PCB substitute thermal by-products; consequently, little data relating to combined toxicities or synergisms are presented. The potential for such should not be overlooked, however.

Table 2-1

TOXICITY AND EXPOSURE LIMITS DATA OF COMMON TOXICANTS (83)

	LC_{50} (inh-rat)	LD_{50} (orl-rat)	LD_{50} (orl-mus)	TD_{LU} (orl-hum)	LD_{LO} (orl-hum)	TC_{LO} (inh-hum)	LC_{LO} (inh-hum)	TLV-TWA	STEL
Ethanol	20,000 ppm/10H*		7800 ug/kg	1430 ug/kg	2000 mg/kg			1000 ppm	
Hydrogen Cyanide	484 ppm/ 5H				570 ug/kg		120 mg/m^3 1H	10 ppm (TLV-CL)	
DDT		113 mg/kg	135 mg/kg					1 mg/m^3	3 mg/m^3
Hydrogen Sulfide	444 ppm						600 ppm/ 30M*	20 ppm	
Carbon Monoxide	1807 ppm/ 4H					650 ppm/ 45M	4000 ppm/ 30M	50 ppm	400 ppm
2,3,7,8-tetra-chlorodibenzo-p-dioxin		22.5 ug/kg	114 ug/kg						
Benzene	10,000 ppm/7H	4894 mg/kg		130 mg/kg		100 ppm	20,000 ppm/5M	10 ppm	25 ppm

See Glossary for definitions of abbreviations (Appendix A).

*H - Hours.
M = Minutes.

Section 3

PROPOSED PCB SUBSTITUTES: LIQUIDS

INTRODUCTION

The liquid PCB suostitutes can be divided into the following groups based on their chemical structures:

- Esters:
  - --Phthalic acid esters (di-2-ethylhexyl phthalate and dioctyl-phthalate).
  - --Benzylneocaprate.
- Siloxanes:
  - --Polydimethylsiloxane.
- Aromatics:
  - --Chlorobenzenes (mono-, tri-, and tetra-chlorobenzene).
  - --Butylated monochlorodiphenylether.
  - --Methylated diphenylethane and dixylylethane.
  - --Isopropylbiphenyl.
  - --Propylbipnenyl.
- Paraffinic hydrocarbons:
  - --Poly (1-octene).
  - --RTEmp.
- Perchloroethylene.

ESTERS

In general, pyrolysis of esters under high thermal and disruptive charge conditions will produce gases similar to those obtained from the hydrocarbons. The presence of oxygen in the molecule results in the formation of higher levels of carbon oxide gases. The products of disruptive discharge and the volume of gas

produced per joule of energy dissipated are reported to be less than those produced from mineral oils, askarels, and silicones. The deposit formed is also less carbonaceous, and thus causes less switch contact fouling. The products of decomposition are reported to be no more toxic than those produced by hydrocarbons (119). The structure of the ester molecule greatly influences thermal stability. The stability is greatly improved by the absence of hydrogen atoms on the carbon in the B-position to the hydroxyl and carbonyl group of the alcohol and acid components, respectively.

Phthalic Acid Esters

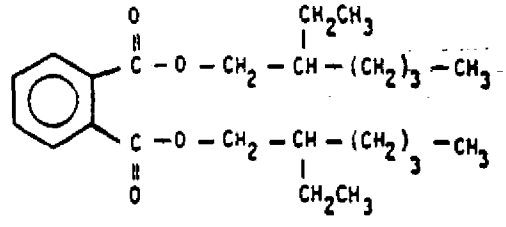
General. Di-(2-ethylhexyl)-phthalate (Figure 3-1) was marketed in the United States by General Electric under the trade name of Dielektrol II, which is a mixture of di-(2-ethylhexyl)-phthalate, 1,2,4-trichlorobenzene, and small amounts of 1,2,3-trichlorobenzene. It is also sold in Japan under the trade name Selectrol I. Trichlorobenzene was added to raise the corona extinction voltage (35). Chemical and physical properties of these two compounds are shown in Table 3-1.

Table 3-1

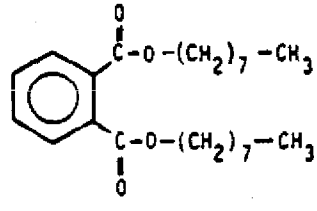
CHEMICAL AND PHYSICAL CHARACTERISTICS OF SELECTED PHTHALATE ESTERS (97)

	Di-(2-ethylhexyl)-phthalate	dioctylphthalate
Molecular Weight	390.6	390.6
Melting Point	-55 °C (-67 °F)	-25 °C (-13 °F)
Boiling Point	231 °C (448 °F) at 5 mm Hg	220 °C (428 °F) at 4 mm Hg
Flash Point	215 °C (420 °F)	
Ignition Temperature	390 °C (735 °F)	
Specific Gravity		0.978
Vapor Pressure	1.32 mm Hg (200 °C)	<0.2 mm Hg
Viscosity	81 cps (20 °C)	

Thermal Decomposition of Phthalic Esters. Phthalate esters are most widely used as plasticizers in various plastics such as polyvinyl chloride. Consequently, most of the detailed decomposition data relates to decomposition in plastics under high-temperature processing conditions with a view toward the impact on the stability of the plastic. The degree to which these data apply to neat phthalate esters or phthalate ester/chlorobenzene mixtures is unknown.



di-(2-ethylhexyl)-phthalate

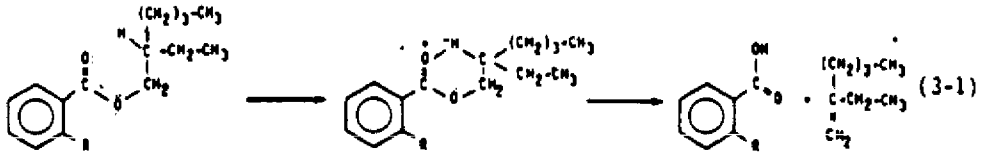


dioctylphthalate

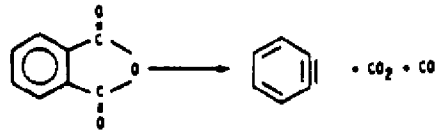
Figure 3-1. Phthalate Esters

Table 3-2 presents some of the degradation products of di-(2-ethylhexyl)-phthalate and dioctylphthalate and the effects of temperature on the thermal decomposition of these esters. It should be noted that these are not trace PICs. The smallest weight percent shown is 0.1, which is equivalent to 1000 ppm. No attempt was made to identify any PICs present in the ppb to few-ppm range. This same type of analytical procedure, used on askarels, would fail to detect dioxins or dibenzofurans. No data were found on the decomposition of either ester at higher temperatures.

The thermal decomposition of these compounds is believed to proceed via a cis-elimination that takes place according to a two-step mechanism. In the first step, a six-member intermediate is formed from the abstraction of the β-carbon in the side chain by the carbonyl oxygen. The second step, which is regarded as therate-determining step, involves carbon-oxygen cleavage from the intermediate with a β-carbon radical (47).


(3-1)

Phthalic anhydride, a major decomposition product of both di-(2-ethylhexyl)-phthalate and o-dioctylphthalate, can pyrolyze to produce the highly reactive intermediate benzyne (or dehydrobenzene).


(3-2)

Phthalic Anhydride Benzyne

In the presence of an excess of benzene, phthalic anhydride reacts to form naphthalene and biphenyl (8). The major pathway to biphenyl is probably by overall insertion of benzyne into a C-H bond of benzene; and naphthalene is formed by either 2+2 or 2+4 cyclo addition of benzyne to benzene, followed by elimination of acetylene.

Table 3-2

EFFECT OF REACTION TEMPERATURE ON THE THERMAL DECOMPOSITION OF SELECTED PHTHALATE ESTERS (87, 88)

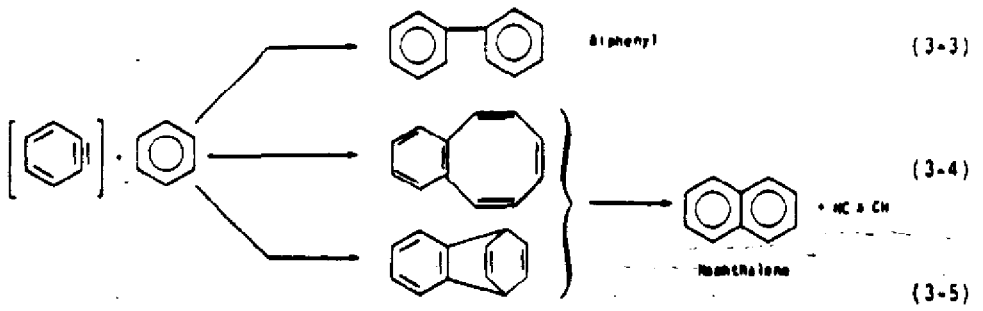
DI-(2-ETHYLHEXYL)-PHTHALATE

Component	Composition of Decomposition Products, wt%, at:									
	250°C	280°C	300°C	360°C	380°C	400°C	420°C	450°C	480°C	500°C
2-ethyl-1-hexene	0.1	0.1	0.2	1.5	3.3	8.9	19.5	41.9	51.0	52.0
2-ethylhexanal	0.4	0.3	0.6	0.7	0.9	0.3	0.2	0.1	0.2	0.1
2-ethyl-1-hexanol	-	-	0.1	0.4	0.6	3.2	2.2	18.5	35.5	31.4
Phthalic anhydride	0.5	0.2	0.2	0.2	0.8	4.2	7.5	7.4	10.5	18.1
Methyl, 2-ethylhexylphthalate*	0.3	0.1	0.1	1.7	4.2	7.1	8.1	7.2	9.6	0.2
Di-(2-ethylhexyl)-phthalate	98.7	99.3	99.2	95.8	90.2	76.3	55.5	24.8	6.7	0.1

DIOCTYL PHTHALATE

Component	Composition of Decomposition Products, wt%, at:												
	250°C	280°C	300°C	320°C	340°C	350°C	360°C	380°C	400°C	420°C	450°C	480°C	500°C
1-octene	0.4	0.3	0.2	0.5	1.7	2.1	2.0	5.2	8.4	20.3	43.9	0.4	5/.2
Octanal	-	-	-	0.1	0.4	-	0.4	0.1	0.1	-	-	-	-
1-octanol	0.4	0.5	0.4	0.4	0.5	0.5	0.6	1.0	3.4	10.0	22.1	24.5	22.6
Phthalic anhydride	0.1	0.1	0.1	-	-	0.2	-	0.5	3.0	6.3	4.3	4.5	8.8
Methyl, octylphthalate*	0.3	0.3	0.5	0.4	2.5	1.3	3.2	4.0	5.0	9.4	8.8	8.9	9.8
Dimethylphthalate*	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.6	0.2	0.1
Dioctylphthalate	99.8	98.7	98.6	98.4	94.7	95.7	93.7	89.1	79.9	53.6	20.4	1.4	1.6

*Components of low heat stability were converted to methyl esters for analysis. The actual decomposition products were 2-ethylhexylphthalate (methyl, 2-ethylhexylphthalate), octyl phthalate (methyl, octylphthalate), and phthalic acid (dimethyl phthalate).



Since the dielectric fluids Dielectrol II and Selectrol I also contain substantial amounts of chlorobenzenes, it is conceivable that these reactions may occur, possibly producing PCB and chlorinated naphthalene.

Decomposition tests on PVC plastics containing phthalic acid esters have yielded basically the same products, although some are chlorinated. Apparently HCl, produced from the PVC, reacts with some of the ester decomposition products to give chlorinated species (88). The same type of Cl- addition reaction is conceivable in the presence of chlorobenzenes.

Toxicity and Exposure Limits of Decomposition Products. Toxicity and exposure limits data for di-(2-ethylhexyl)-pnthalate, dioctylphthalate, and their identified PICs are shown in Table 3-3. This table does not include the chlorinated compounds mentioned above, as none of these PICs has actually been identified.

In general, the identified PICs appear to have the same degree of low to moderate toxicity as their precursors. However, an assessment of the toxicities is difficult, as all of the available data relate to animals, and, in most cases, inhalation data are not provided. It is still worth noting the low TLV for phthalic anhydride (TLV-TWA = 1 ppm). Phthalic annydride is a pyrolysis product of both 2-(diethylhexyl)-phthalate and dioctylphthalate, and is formed in considerable quantities at the higher temperatures.

Table 3-3

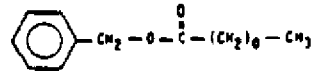
TOXICITY AND EXPOSURE LIMITS OF DI-(2-ETHYLHEXYL)-PHTHALATE, D-DIOCTYLPHTHALATE, AND THEIR PICs (83)*

	LC_{LO} (inl-rat)	LD_{50} (inl-mus)	LC_{50} (inl-mus)	TD_{LO} (orl-man)	LD_{50} (orl-rat)	LD_{50} (orl-mus)	TLV-TWA	STEL
di-(2-ethylhexyl-phthalate				143 mg/kg	31 mg/kg		5 mg/m^3	10 mg/m^3
dioctylphthalate			5000 mg/m^3			6513 mg/kg		
phthalic anhydride					4020 mg/kg	2 gm/kg	1 ppm	4 ppm
2-ethyl-1-hexene	4000 ppm/4H	100 mg/kg						
2-ethyl-1-hexanol					2460 mg/kg			
1-octanol						1790 mg/kg		
phthalic acid					7900 mg/kg			

*No data were available for 1-ethylhexyl phthalate, benzyne, octyl phthalate, or 1-octene.

Benzylneocaprate

General. There is little published information available on benzylneocaprate. It has been marketed by Asea of Sweden as Faradol 100, but the manufacturers have recently discontinued production. The only data found on the chemical and physical characteristics of this compound are its molecular weight (262) and vapor pressure (0.0003 mm Hg at 25 °C).



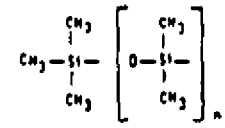
Benzylneocaprate

Thermal Decomposition of Benzylneocaprate. No information was available on the thermal degradation of benzylneocaprate. Benzylneocaprate would be expected to be thermally very stable. The cis-elimination reaction with the six-membered transition ring, by which the phthalic esters decompose, would not be expected to occur. The lack of hydrogen atoms available for abstraction from the β-carbon results in a "hindered" β-carbon. The degradation of such esters presumably follows a free radical mechanism which requires high energy levels, and therefore high thermal degradation temperatures (11g).

SILOXANES

General

The principal siloxane used as a transformer insulating liquid is polydimethylsiloxane (PDMS).



Polydimethylsiloxane

PDMS is produced commercially by Dow Corning as DC561 and DC200, General Electric as SF97, Union Carbide as L305, and SWS Silicone as F101 and F190. Table 3-4 lists the important properties of a typical PDMS transformer fluid.

Table 3-4

CHEMICAL AND PHYSICAL CHARACTERISTICS
OF A TYPICAL PDMS TRANSFORMER FLUID (119)

Molecular Weight	2826
Boiling Point	250 °C
Fire Point	360 °C
Flash Point	300 °C
Specific Gravity	0.961 at 25 °C

Thermal Decomposition of PDMS

PDMS begins to thermally decompose at 200 °C. The thermal degradation occurs rapidly at 300 °C with a breaking of the Si-O bond and formation of lower molecular weight compounds such as tri- and tetracyclic siloxanes (D_3 and D_4, respectively) (Figure 3-2) (119). These are volatile, low flash point materials that boil at 150 to 170 °C. Their presence in excess of 2.5% reduces the flash point of the silicone liquid to that of a similar viscosity mineral oil. In addition to the cross-linked volatiles, both gaseous and solid (i.e., amorphous silica) decomposition products are found.

Silicone transformer liquids, after being aged for 4 hours at 350 °C, have been found to generate several cyclic siloxanes, notably D_3, D_4, D_5, and D_6 (in that order, quantitatively) (110). These same compounds can be produced at lower temperatures if the thermal aging process is extended, for instance, 5 months at 240 °C. With increasing time, the rate of formation of D_4 begins to exceed that of D_3 at the lower temperatures.

In one experiment, PDMS was pyrolyzed over the temperature range of 600 to 1200 °C; a rapid temperature rise (60 °C/msec) and a residence time of 20 sec were used (61). The following decomposition products and tendencies were observed:

- 600 to 800 °C - Predominantly cyclic siloxanes arising from siloxane rearrangement. The relative amount of cyclic siloxanes decreased regularly with increasing molecular weight, with the exception of a greater abundance of D_6 compared to D_5 at temperatures below 800 °C.
- 800 to 900 °C - Compared to the lowest temperature range tested, total volatiles increased and the relative fraction of high-volatility material increased. Methane and hydrogen were the major components of the high-volatility fraction; C_2 hydrocarbons (C_2H_2, C_2H_4, C_2H_6) have also been identified.

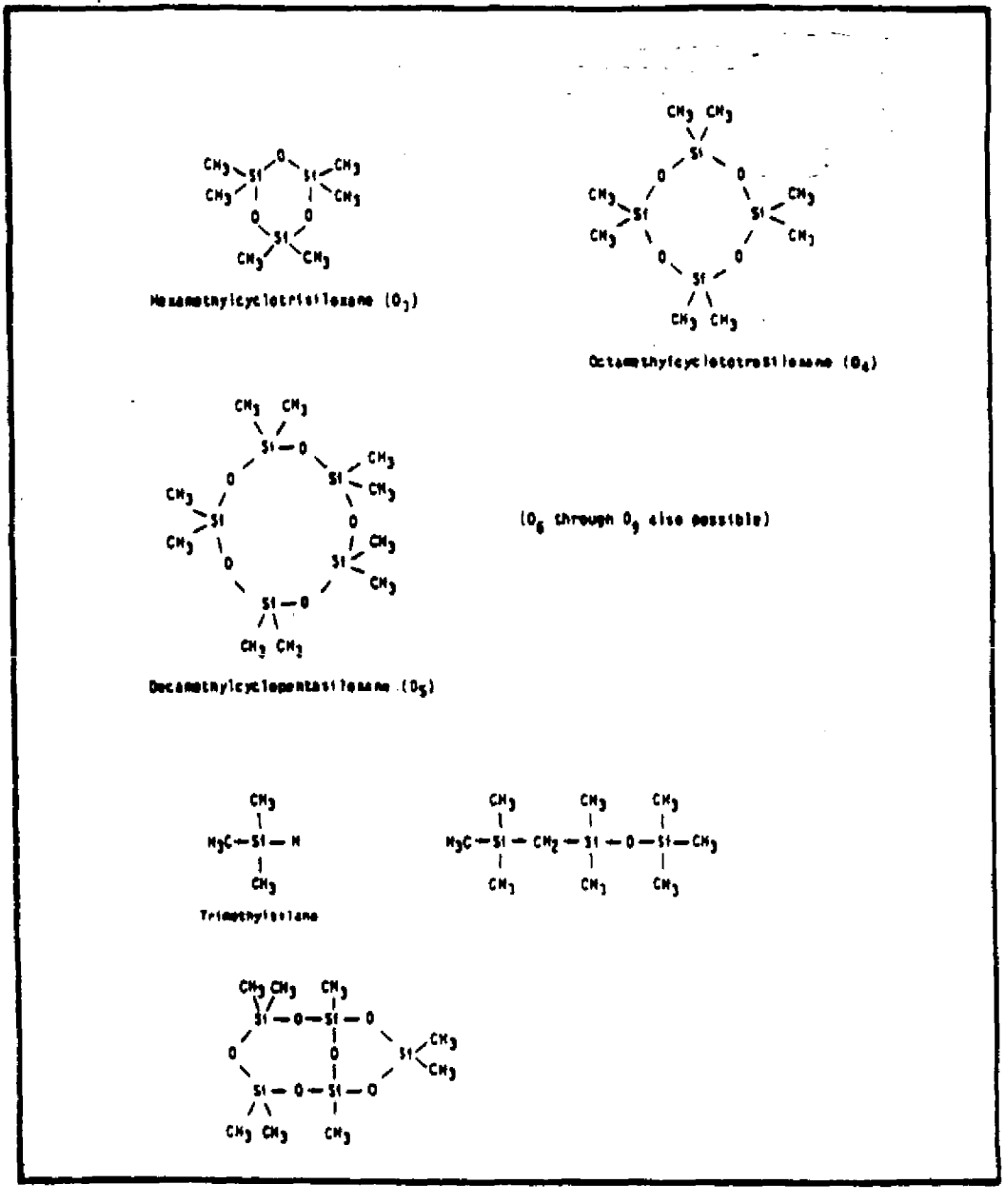


Figure 3-2. Typical PDMS Pyrolysis Products

MDNS 216014

- 900 to 1200 °C - A number of trace components appear at 900 °C and become more abundant at higher temperatures. The identified trace compounds include those shown in Figure 3-2. They appeared to arise via C-H and Si-C bond cleavage, and contain silylhydride, silmethylene, and monomethyl siloxane structures.
- 1200 °C - At this temperature, the high-volatility fraction accounted for the majority of the volatiles.

In the absence of oxygen and under arcing conditions, a variety of hydrocarbons can be produced, including methane, acetylene, ethylene, ethane, and propylene (21, 61, 112). Thermal oxidation of PDMS leads to the formation of paraformaldehyde and formic acid, as well as carbon oxides (77).

Thermal degradation is catalyzed by trace impurities of materials such as water, metals, and ionic compounds. The manufacture of the siloxanes, via an organic chloride with the production of hydrogen chloride, introduces the possibility of chlorine contamination, although chlorine concentrations probably do not exceed 1 ppm (119).

Toxicity and Exposure Limits of PDMS Decomposition Products

There are no available data on the toxicities of the various cyclic and cross-linked organosiloxanes (Figure 3-2) formed during PDMS decomposition. Of the organic compounds produced, only formaldehyde and formic acid are particularly toxic, and neither is considered highly toxic (formaldehyde LD_{50} (rat-orl) - 800 mg/kg; formic acid LD_{50} (rat-orl) - 1100 mg/kg). Both are irritants, and formic acid can be dangerously caustic to the skin (69). Both are liquids at ambient temperatures, and may therefore be found in the soot as contaminants on surfaces following a fire.

The silica produced is amorphous. Crystalline silica is a known cause of silicosis, and is considered to be far more toxic than the amorphous form. The TLV for crystalline silica (cristobalite, 0.05 mg/m^3) is several orders of magnitude lower than that of amorphous silica (precipitated silica, 5 mg/m^3) for respirable dust. Silicon carbide, formed under arcing conditions, is considered to be a mild irritant when inhaled.

The toxicity of the pyrolysis gas of PDMS (Dow Corning 561 silicone transformer liquid) was evaluated using a method developed by Hilado, where rats are subjected to inhalation of the pyrolyzed compound (44). The toxicity of PDMS was

Table 3-5

CHEMICAL AND PHYSICAL PROPERTIES OF SELECTED CHLORINATED BENZENES (97)

	Mono-Chloro	Trichloro			Tetrachloro		
		1,2,3	1,2,4	1,3,5	1,2,3,4	1,2,3,5	1,2,4,5
Molecular Weight	112.56	181.45	181.45	181.45	215.9	215.9	215.9
Melting Point	-45.2 °C	16.95 °C	63.5 °C	52.6 °C	47.5 °C	54.5 °C	140 °C
Boiling Point	132 °C	213 °C	208.5 °C	221 °C	254 °C	246 °C	243 °C
Flash Point	29 °C	110 °C	107 °C	113 °C	NI*	NI	155 °C
Vapor Pressure	8.8 mm Hg @ 20 °C	1 mm Hg @ 38.4 °C	10 mm Hg @ 78 °C	1 mm Hg @ 40 °C	NI	NI	<0.1 mm Hg @ 25 °C
Specific Gravity	1.1	1.446	NI	1.69	NI	NI	1.858

*NI = No information.

compared to that of another transformer liquid, a paraffinic hydrocarbon. Under the specific test conditions, the toxicity of the pyrolysis gas from PDMS was found to be less than that of the paraffinic hydrocarbon. The silicone transformer liquid was among the least toxic of over 270 substances tested by Hilado under the same conditions.

AROMATICS

Chlorobenzenes

General. Chlorobenzenes generally were not used independently as dielectric fluids. Rather, they were mixed with other fluids (e.g., di-(2-ethylhexyl)-phthalate or PCBs) to lower pour points. The principal chlorobenzenes used are the tri- and tetra- congeners. These compounds typically make up about 30% of a dielectric fluid mixture. Figure 3-3 shows the different tri- and tetrachlorobenzene isomers possible. Monochlorobenzene has also been considered for use in dielectric fluids. Table 3-5 lists some of the chemical and physical properties of these chlorinated benzene compounds.

Thermal Decomposition of Chlorobenzenes. The chlorobenzenes are relatively thermally stable compounds. Table 3-6 lists the temperatures for the onset of thermal decomposition and 99% decomposition for some of the compounds.

Table 3-6

CHLOROBENZENE DECOMPOSITION TEMPERATURES

	Onset °C	99% Decomposition °C
Monochlorobenzene	540	710
1,2,3-trichlorobenzene	645	780
1,2,4-trichlorobenzene	640	750
1,2,3,4-tetrachlorobenzene	660	800
1,2,3,5-tetrachlorobenzene	655	760

As with other chlorinated organic compounds, the major combustion/pyrolysis products are HCl, hydrogen and methane (no air), and carbon oxides (in air). However, considerable research has been focused on the trace PICs produced.

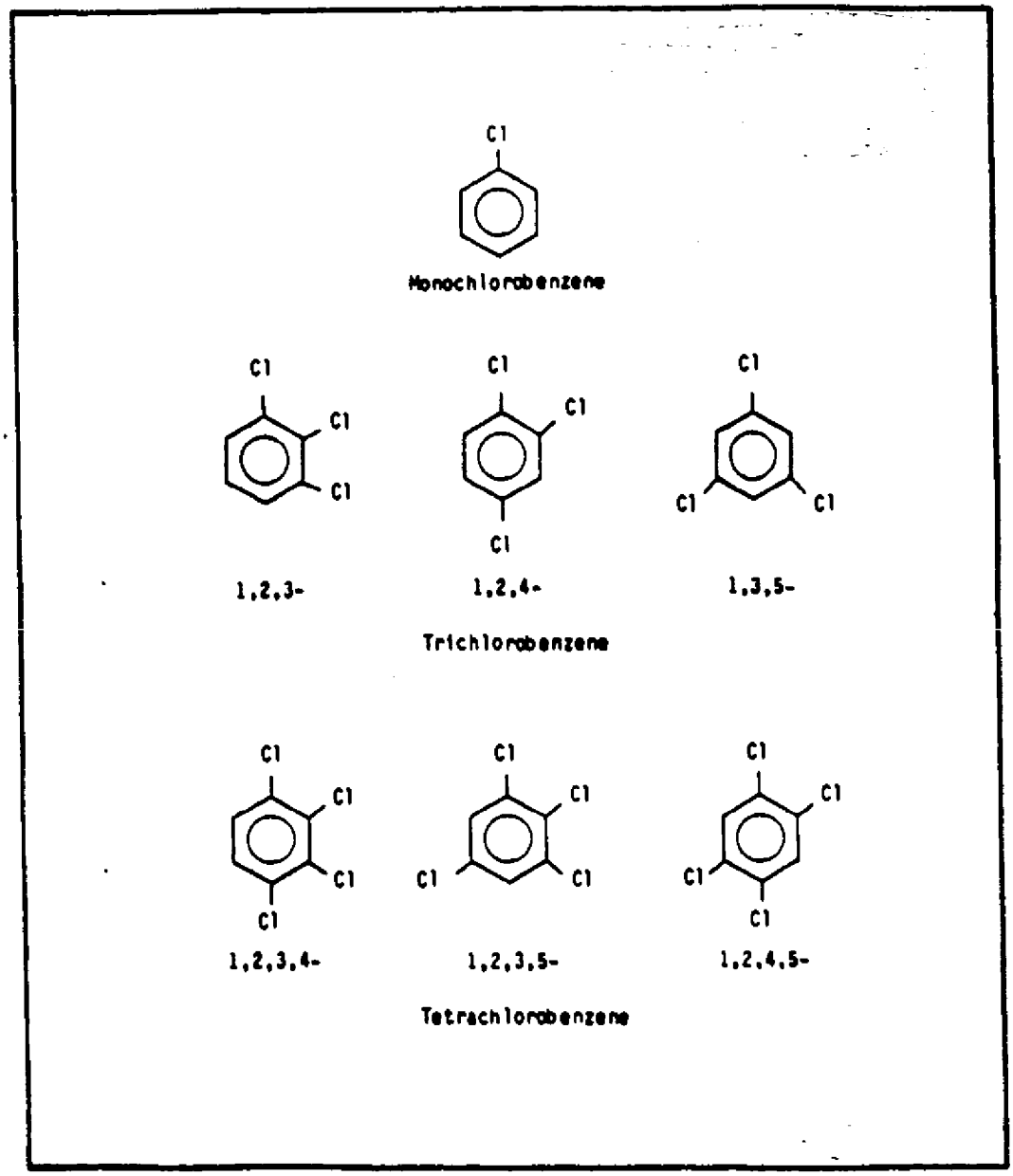
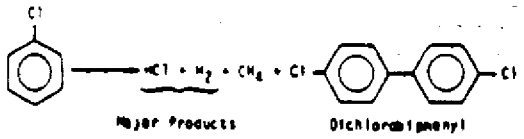


Figure 3-3. Chlorinated Benzene Compounds Used in Dielectric Fluids

MONS 216018

Monochlorobenzene, pyrolyzed at 690 °C for 24 sec, can produce chlorobiphenyls, dichlorobiphenyls, naphthalene, and chloronapnthalenes (19). At 770 to 800 °C and 850 to 880 °C, the following reaction has been observed:



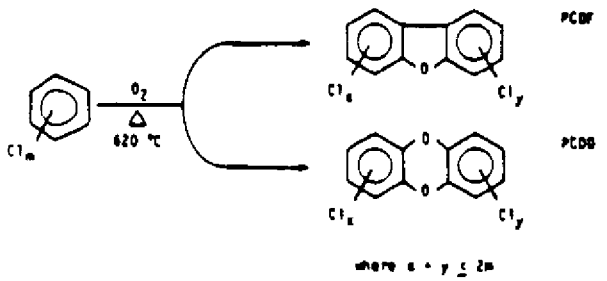
(3-6)

Between 850 and 880 °C, yields of HCl, hydrogen, methane, and chlorinated diphenyl decrease, but considerable quantities of vinyl chloride (CH_2 = CHCl) are produced.

Pyrolysis of chlorobenzenes in the presence of air yields chlorophenols which can, in turn, dimerize to PCDFs and PCDDs (17, 27, 113). The degree of chlorination in the chlorophenols tends to be the same or higher than that of the parent chlorobenzene (16). In other words, monochlorobenzene will produce mono-, di-, or trichloropnenols; trichlorobenzene will produce tri-, tetra-, and pentachlorophenols.

Buser (16) pyrolyzed tri-, tetra-, and pentachlorobenzenes at 620 °C in sealed quartz mini-ampules in the presence of air. The pyrolysis gases included higher chlorinated benzenes, chlorophenols, PCDFs, PCDDs, and, in some cases, polychlorinated naphthalenes, polychlorinated styrenes, and small quantities of PCBs. Polychlorinated diphenyl ethers and polychlorinated biphenylenes were identified in other experiments (17, 113).

Table 3-7 lists the quantities of PCDFs and PCDDs produced. The known toxic compounds (those with chlorine atoms in the 2, 3, 7, and 8 positions) were identified, but these were not major components. In general, the degree of chlorination in the PCDD/PCDF product seems to follow the pattern below,



(3-7)

(3-8)

where x + y ≤ 2m

MONS 216019

Following this pattern, a monochlorobenzene would not generally produce higher than a dichlorodibenzodioxin or dichlorodibenzofuran. Tri- or tetrachlorobenzenes could produce up to hexa- and octa- isomers, respectively (see Table 3-7). Figure 3-8 summarizes the various chlorobenzene reactions discussed above.

Table 3-7

FORMATION OF PCDFs AND PCDDs FROM THE PYROLYSIS OF CHLOROBENZENES AT 620 °C (16)

	PCDFs (ppm)				
Parent Compound	Tetra-	Penta-	Hexa-	Hepta-	Octa-
Trichlorobenzene	2000	5500	2750	250	<25
Tetrachlorobenzene	<10	25	800	2250	1000
	PCDDs (ppm)				
Trichlorobenzene	150	100	<25	<25	<25
Tetrachlorobenzene	<10	25	700	800	150

Toxicity of Chlorobenzene Decomposition Products. Many of the combustion/pyrolysis products of the chlorobenzenes are very highly toxic (Table 3-8). It is generally believed that, on a molecular basis, 2,3,7,8-tetrachlorodibenzodioxin is the most toxic synthetic molecule known to man. Although an identified chlorobenzene PIC, 2,3,7,8-TCDD has not been found except in trace quantities. However, the other PICs, while less toxic than 2,3,7,8-TCDD, are also very toxic.

In general, toxicity seems to be related to chlorine content and position. Chlorinated aromatics with three or fewer chlorine atoms tend to be significantly less toxic than higher chlorinated congeners. Thus, PICs from monochlorobenzene would probably be less toxic than those from tri- or tetrachlorobenzene. However, they are still moderately to highly toxic as discrete compounds. The combined toxic effects could be synergistic and greater, or possibly antagonistic and less. A further problem with these PICs is that, with the exception of vinyl chloride, all are solids or liquids at normal ambient temperatures. Thus, they tend to be found as surficial contaminants with soot in the aftermath of a fire. The soot provides a reservoir for continued exposure unless completely removed.

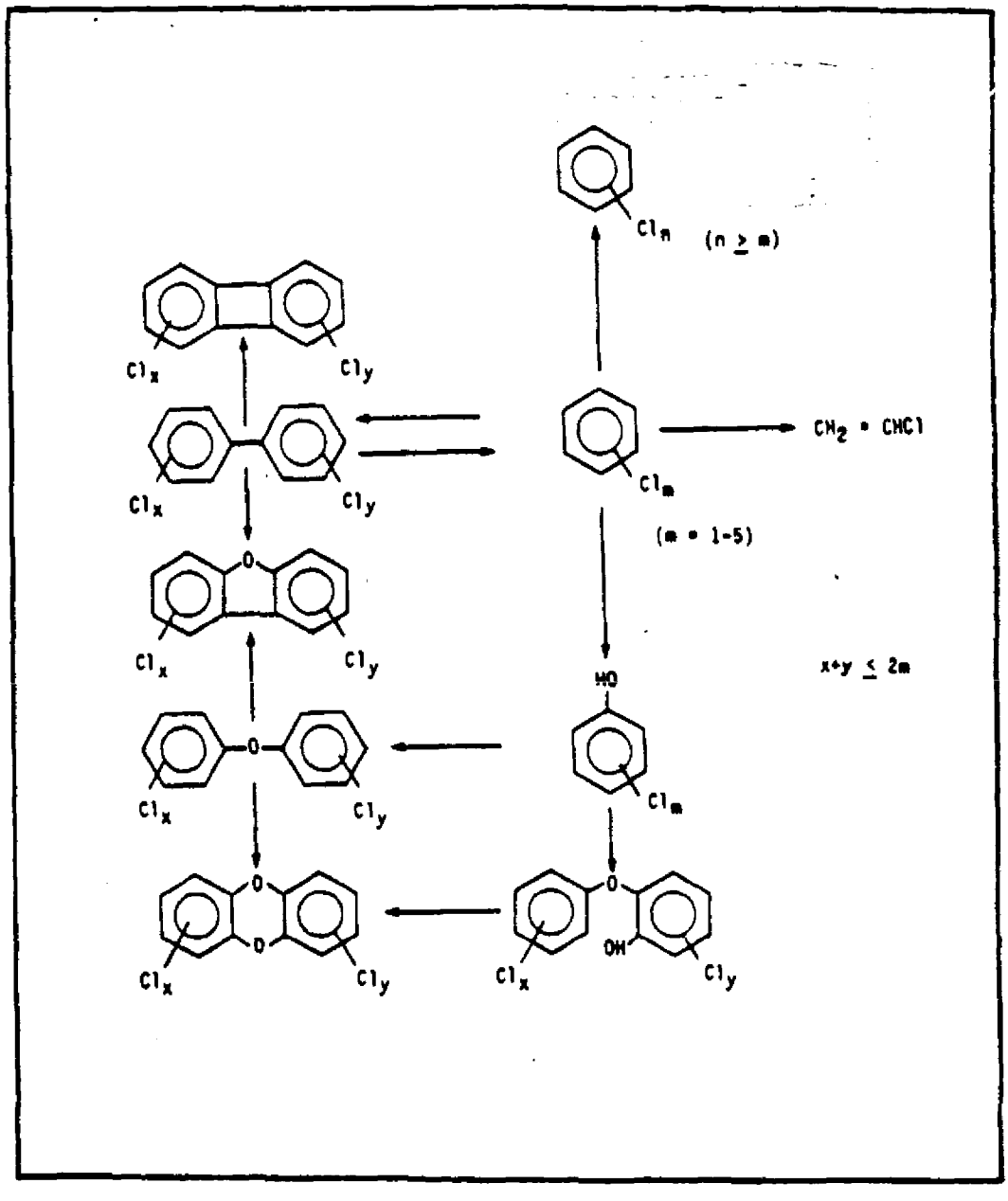


Figure 3-4. Typical Chlorobenzene Thermal Reactions

MONS 216021

Table 3-8

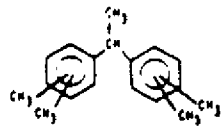
TOXICITIES AND EXPOSURE LIMITS OF CHLOROBENZENE COMBUSTION/PYROLYSIS PRODUCTS (83)

Chlorophenols	LO_{50}, orl-rat		
m-chlorophenol	570 mg/kg		
o-chlorophenol	670 mg/kg		
p-chlorophenol	261 mg/kg		
2,4-dichlorophenol	580 mg/kg		
2,6-dichlorophenol	2940 mg/kg		
2,4,5-trichlorophenol	820 mg/kg		
2,4,6-trichlorophenol	820 mg/kg		
2,3,4,6-tetrachlorophenol	140 mg/kg		
Naphthalenes			
Naphthalene	1780 mg/kg	TLV-TWA	10 ppm
1-chloronaphthalene	1540 mg/kg		
2-chloronaphthalene	2078 mg/kg		
trichloronaphthalene		TLV-TWA	5 mg/m^3
tetrachloronaphthalene		TLV-TWA	2 mg/m^3
pentachloronaphthalene		TLV-TWA	500 ug/m^3
octachloronapnthalene		TLV-TWA	100 ug/m^3
Dioxins			
2,3,7-trichlorodibenzodioxin	29.4 mg/kg (LD_{50}, orl-gpg)		
2,3,7,8-tetrachlorodibenzodioxin	22.5 ug/kg 0.5 ug/kg (LO_{50}, orl-gpg)		
1,2,3,6,7,8-hexachlorodibenzodioxin	1250 ug/kg (LD_{50}, orl-mus)		
1,2,3,4,7,8-hexachlorodibenzodioxin	825 ug/kg (LO_{50}, orl-mus)		
Mixture of 1,2,3,7,8,9- and 1,2,3,6,7,8-hexachlorodibenzodioxins	800 ug/kg		
2,3,7,8-tetrachlorodibenzofuran	5 ug/kg (LO_{50}, orl-gpg)		
Vinyl chloride	500 mg/kg	TLV-TWA	5 ppm

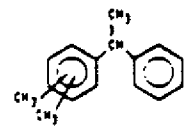
MONS 216022

Methylated Diphenylethane and Phenylxylylethane

General. The chemically similar methylated diphenylethane (1,1-dixylylethane) and phenylxylylethane (see below) are used as components in dielectric fluid mixtures. Edisol II, manufactured by McGraw Edison, is a mixture of the 1,1-bis (3,4-dimethylphenyl) ethane and propyldiphenyl. Phenylxylylethane is found in Dielektrol III (General Electric), Selectrol II (Sangamo), and SAS-295 and SAS-296 (Nisseki Company; mainly the 1-phenyl-1-(3,4-xylyl)- and 1-phenyl-1-(2,4-xylyl)- isomers).



Methylated Diphenylethane (1,1-dixylylethane)



Phenylxylylethane

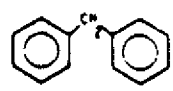
Very little information is available on the physical and chemical properties of these compounds (see Table 3-9).

Table 3-9

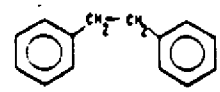
PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED DIARYL ALKANES

	Methylated Diphenylethane	Phenylxylylethane
Molecular Weight	238	210
Boiling Point	315 °C	
Flash Point	162 °C	
Specific Gravity	0.97	
Vapor Pressure		0.0008 mm Hg at 25 °C

Thermal Decomposition Products of Dixylylethane and Phenylxylylethane. No information was found on the combustion/pyrolysis products of either of these compounds. The thermal decomposition of chemically similar compounds, diphenylmethane and diphenylethane (bibenzyl), has been studied, however (7).



Diphenylmethane



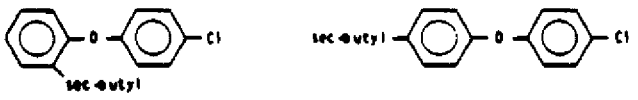
1,2-Diphenylethane

Pyrolysis of these compounds at 700 °C has yielded benzene, toluene, ethylbenzene, styrene, stilbene, phenanthrene, and fluorene. If dixylylethane and phenylxylylethane follow the same general decomposition mechanisms, then products could include benzene, toluene, xylene, trimethylbenzene, ethylbenzene, ethylxylene, methylated fluorene, methylated phenanthrene, methylated styrene, and so forth. Combustion in the presence of air may produce phenols, cresols, and other oxygen-containing species. It is possible that methylated dioxins or dibenzofurans could be formed. All of this is supposition, however. Without further study, it is impossible to determine with certainty what trace PICs might be formed.

Toxicity of Dixylylethane and Phenylxylylethane Decomposition Products. Since the specific products cannot be identified with certainty, toxicities cannot be determined. None of the possible PICs discussed above is considered to be highly toxic, although several are known or suspected carcinogens. Most are liquids or solids at normal ambient temperatures, and could be expected to deposit on nearby surfaces with soot and other conventional fire by-products.

Butylated Monochlorodiphenylether

General. Butylated monochlorodiphenylether is marketed by Dow Chemical Company under the trade name of Dielectric Fluid C-4 (formerly XFS-4169L). The name specifies neither the extent of butylation nor the isomeric form of the compound. Among the isomeric forms which have been found in dielectric fluids are:



2-sec-butyl-4'-chlorodiphenylether 4-sec-butyl-4'-chlorodiphenylether

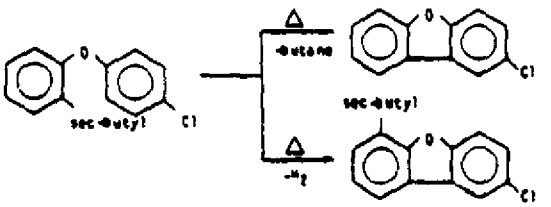
The major components of one sample of XFS-4169L were (wt %): 4-chlorodiphenylether (19.6); 2-sec-butyl-4'-chlorodiphenylether (27.2); 4-sec-butyl-4'-chlorodiphenylether (24.0); and small amounts of di- and tri-butylated chlorodiphenylethers (2). Physical and chemical property data were not available on individual isomers.

Thermal Decomposition of Butylated Monochlorodiphenylether. There is no information available on the thermal decomposition products of butylated monochlorodiphenylether. However, both the unsubstituted diphenylether and polychlorinated diphenylethers (PCDPEs) have been studied.

Vapors of diphenylether passed through a glass tube at red heat have been shown to break down into phenol, benzene, and dibenzofuran (46).

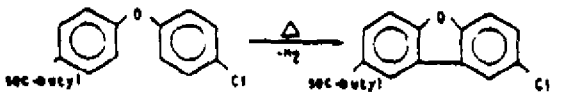
At 600 °C, the thermal conversion of PCDPEs into PCDFs is of the same order of magnitude as that from PCBs (17). Lindahl et al. (59) conducted a series of tests with tri- to octachlorodiphenylethers at 600 °C, and concluded that PCDFs form primarily via loss of ortho-H_2 or ortho-HCl with a minor fraction formed by loss of ortho-Cl_2. A few PCDDs were also observed, formed presumably via loss of ortho-Cl_2. The PCDDs formed showed lower chlorination than the PCDPEs. Figure 3-5 shows these reactions.

If butylated monochlorodiphenylethers follow the same mechanisms, the following reactions could result.



(3-9)

(3-10)



(3-11)

Assuming that the chlorine is always in the 4' position, no reaction will occur via Cl_2 loss. This is important as Lindahl et al. (59) observed dioxin formation only via Cl_2 loss. Thus, butylated-4'-chlorodiphenylethers would not be expected to degrade to dioxins.

Also important is the fact that the PCDPE to PCDF reaction is monomolecular. In contrast, the PCB to PCDF reaction is bimolecular, requiring PCB and oxygen molecules, while the chlorobenzene to PCDF reaction is trimolecular, requiring two chlorobenzenes and oxygen. These multimolecular reactions can be significantly less frequent in oxygen-starved or dilute systems. Being monomolecular, neither oxygen content nor PCDPE concentration will affect the rate of PCDPE conversion to PCDF.

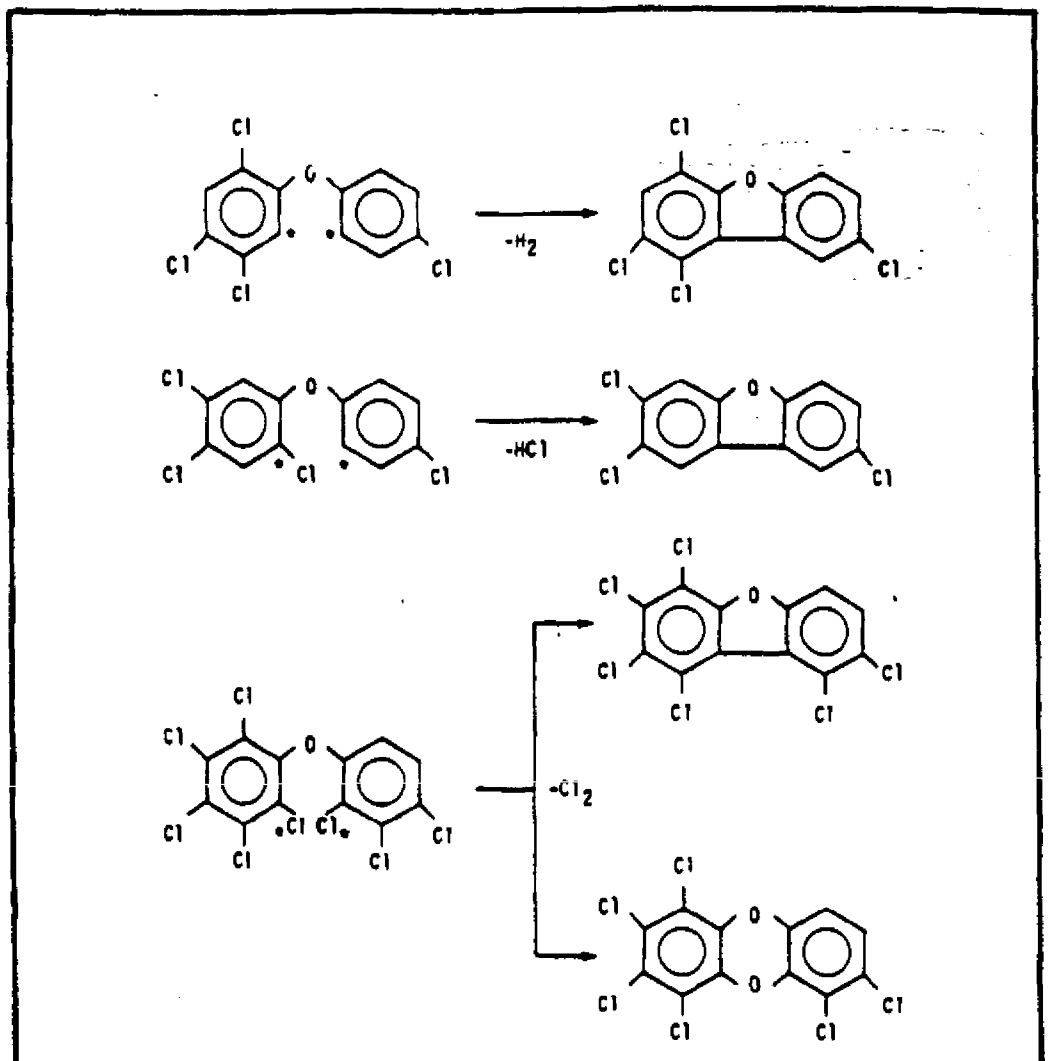


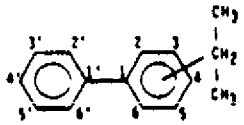
Figure 3-5. Formation of PCDFs/PCDDs from PCDPEs (31B)

No other PICs have been identified or suggested for butylated monochlorodipnenylether.

Toxicity of Butylated Monochlorodiphenylether Decomposition Products. As noted above, there is no definite information on the combustion/pyrolysis products of butylated monochlorodiphenylether. Thus, no toxicity information is available. Assuming that the reactions discussed above are possible, then reaction products could include monochlorodibenzofuran (from the 4-chlorodiphenylether) and butylated (mono-, di-, and tri-) monochlorodibenzofuran. There is no information available on the toxicities of these compounds.

Alkyl Biphenyls

General. Isopropylbiphenyl is manufactured by Westinghouse under the trade name of Wemcol. Wemcol is described by the manufacturer as being predominantly 4-isopropylbiphenyl with considerable amounts of the 3- isomer and traces of more highly substituted biphenyls. However, an independent analysis (107) revealed the following composition (wt %): 3-isopropylbiphenyl (60.3%); 4-isopropylbiphenyl (38.4%); 3,5-diisopropylbiphenyl (0.3%); 3,3'-diisopropylbiphenyl (0.4%); 3,4'-diisopropylbiphenyl (0.2%); and 4,4'-diisopropylbiphenyl (0.1%).



Isopropylbiphenyl

n-propylbiphenyl is mixed with dixylylethane in Edisol II, manufactured by McGraw Edison. Several mono- and dipropyl isomers are possible, but there is no information available on which isomers are found in Edisol II. Table 3-10 presents physical and chemical properties for these compounds.

n-propylbiphenyl

Table 3-10

PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED ALKYL BIPHENYLS (97)

	Isopropylbiphenyl	n-propylbiphenyl
Molecular Weight	196	196
Boiling Point	270 °C	280 °C
Flash Point	141 °C	>100 °C
Ignition Temperature	435 °C	445 °C
Specific Gravity	1.0	

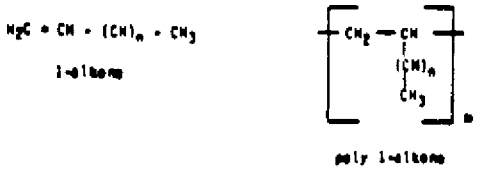
Thermal Decomposition of Isopropylbiphenyl and n-propylbiphenyl. No information was found in the literature on the combustion/pyrolysis products of either of these compounds. Assuming that they degrade by C-C bond fission like other alkyl aromatic compounds, the pyrolysis products could include biphenyl, propylbenzene, propene, and similar compounds. In the presence of air, phenols, alkyl alcohols, unsubstituted and alkyl substituted dibenzofurans, and so forth might be possible. All of this is conjecture, however.

Toxicity of Isopropylbiphenyl and n-propylbiphenyl Decomposition Products. No information is available on the combustion toxicology of these compounds.

PARAFFINIC HYDROCARBONS

Polyalphaolefins

General. A polyalphaolefin (PAO), or poly 1-alkene, is a polymeric chain of alkene monomers with a single double bond in the 1-position.



Among the polyalphaolefins marketed for use as transformer oils are PAO 13CE and PR, manufactured by Uniroyal Chemical and Gulf Oil Chemicals, respectively. PAO 13CE is derived from 1-octene, and has an average molecular weight of 600 (1).

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No mention of the degree of cross-linking was found. Table 3-11 presents the chemical and physical properties of PAO 13CE.

Table 3-11

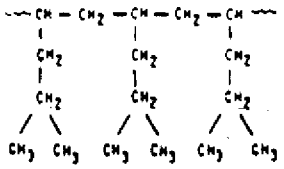
CHEMICAL AND PHYSICAL CHARACTERISTICS OF PAO 13CE (117)

Molecular Weight	600
Flash Point	290 °C
Fire Point	307 °C
Specific Gravity	0.84
Viscosity (Centistokes)	14 at 100 °C

Thermal Decomposition of Polyalphaolefin. Information on the thermal decomposition products of poly (1-octene) is very limited; no specific PICs are named. PAO is reported to undergo practically no thickening or sludge formation when exposed to temperatures of 175 °C for 100 hours (101).

Random chain scission along the backbone chain is the dominant mechanism in the pyrolysis of polyolefins. As the term implies, scission is a random event, and polymer molecules are first broken into large macroradicals. There is a rapid decrease in molecular weight, and almost no monomer is formed in the early stages (39). The expected decomposition products would include a variety of short-, medium-, and long-chain saturated and unsaturated hydrocarbons, mainly olefins, paraffins, and cyclic hydrocarbons (106). In the presence of air, various oxy-species could also be expected.

For instance, pyrolysis (approximately 300 to 350 °C) tests on poly (4-methyl-1-pentene) in vacuum yielded isobutene, propane, isobutane, 4-methyl-1-pentene, isopentane, 2,3-dimethylbutane, n-pentane, propene, and a series of C_{11} to C_{18} branched saturated and unsaturated hydrocarbons (4). In the presence of air, peroxides and hydroperoxides are formed initially, leading to the formation of such products as isobutyraldehyde, acrolein, acetic acid, acetaldehyde, acetone, isobutyric acid, isovaleric acid, isopropanol, ethanol, crotonalydehyde, methanol, isobutanol, propionic acid, oxalic acid, propionaldehyde, butyric acid, butyraldehyde, and n-propanol.



Poly(4-methyl-1-pentene)

Toxicity of Poly 1-Octene Decomposition Products. No information was available on the combustion toxicology of poly 1-octene. The types of hydrocarbons mentioned above are generally of low to moderate toxicity, but the presence of more highly toxic compounds cannot be ruled out without further testing.

RTEmp

General. RTEmp is a high molecular weight, purified paraffin manufactured by RTE Corporation. It is refined from crude oil and solvent extracted so that there are no aromatic or polyaromatic compounds present.

RTEmp is also characterized by its lack of halogens and inorganic compounds. The exact composition is difficult to ascertain. According to material supplied by the manufacturers to the Occupational Safety and Health Administration, it is listed as having a boiling point above 427 °C, corresponding to an n-alkane of chain length C_{26}. Table 3-12 presents chemical and physical properties of RTEmp.

Table 3-12

CHEMICAL AND PHYSICAL CHARACTERISTICS OF RTEmp (117, 121)

Boiling Point	427 °C
Flash Point	284 °C
Ignition Temperature	312 °C
Specific Gravity	0.87
Viscosity (Centistokes)	120-140 at 40 °C; 12-14 at 100 °C

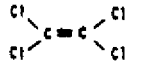
Thermal Decomposition of RTEmp. The lack of knowledge of the exact chemical nature of the compound has made it impossible to describe the thermal degradation

products of pyrolysis/combustion. The "fire hazard properties" of RTEmp have been studied under simulation of a "worst case" scenario for a catastrophic transformer failure. The major arcing product reported was hydrogen, with lesser amounts of acetylene, methane, ethylene, and other gaseous hydrocarbons not specifically named (62). All of the above gases are flammable and are believed to contribute to the fireball observed in catastrophic electrical failure tests.

Toxicity of RTEmp Decomposition Products. Since combustion products, and particularly PICs, have not been identified, it is impossible to assess their individual toxicities. However, the toxicities of the gross pyrolysis gases were evaluated using a method developed by Hilado where rats are subjected to inhalation of the actual pyrolysis gases (15). Exact toxicities were not given, but the toxicity of the pyrolysis gases from RTEmp was compared to that of another transformer liquid, a polydimethylsiloxane (Dow Corning 561 silicone transformer liquid). Under the specific test conditions, the toxicity of the RTEmp pyrolysis gases was greater than that of the silicone transformer liquid.

Perchloroethylene

General. Perchloroethylene (tetrachloroethylene; C_2Cl_4) is a nonreactive, nonflammable liquid which has generally been used as a solvent. Table 3-13 lists its chemical and physical properties. It is manufactured as Wecosol® transformer fluid by Westinghouse, and may be used neat or mixed with mineral oils. Perchloroethylene is also a major component in a relatively new British import, Formel NF (98). This fluid is a mixture of perchloroethylene and three fluorocarbons (112, 112a, and 113).



Perchloroethylene

Table 3-13

CHEMICAL AND PHYSICAL CHARACTERISTICS OF PERCHLOROETHYLENE

Molecular Weight	165.83
Melting Point	-22.4 °C
Boiling Point	121.2 C at 1 atm
Flash Point	None
Fire Point	None
Vapor Pressure	14 mm Hg at 20 °C
Specific Gravity	1.62

Thermal Decomposition of Perchloroethylene. The amount of data available on the thermal decomposition of perchloroetnylene is quite limited. It is a very stable compound due to high molecular bond dissociation energies and a lack of hydrogen atoms available for abstraction or formation of hydroxy radicals. As a result, few decomposition products would be expected.

Claiborne (21) heated perchloroethylene in varying levels of air in a stainless steel tube to 1000 °C. The principal products were CO_2 and chlorine. A small amount of HCl was found. Phosgene was not detectable either by gas chromatography or mass spectrometry.

Low energy (30 kW-sec input energy for 30 min) arcing experiments generated small quantities of CO, CO_2, chlorine, and HCl (60). No other products were reported.

Decomposition tests on Formel NF-filled transformers produced only traces of chlorine and several chlorofluorocarbons, other than the fluid constituents (98). No HCl or phosgene were detected. The halocarbons were probably produced from the halocarbon components of the fluid mix (see Section 4, Freon 113).

There are reports that perchloroethylene may decompose to phosgene or trichloroacetic acid in the presence of arc welding (25). The tests cited above do not confirm this, but the experimental conditions did not simulate arc welding. It does not appear that these highly toxic compounds are generated under simple pyrolysis or low-energy arcing conditions.

Toxicity and Exposure Limits of Perchloroethylene Decomposition Products. Table 3-14 lists the toxicities for various known and suspected perchloroethylene decomposition products. The most toxic of the PICs formed are chlorine, phosgene, and trichloroacetic acid, which appear to be clearly more toxic than the parent compound. However, with the exception of chlorine, these PICs seem to be formed in trace quantities, if at all. Furthermore, of the PICs listed, only trichloroacetic acid is likely to be found on surfaces in the aftermath of a fire. The others are gaseous and would readily disperse.

Table 3-14

TOXICITY AND EXPOSURE LIMITS OF PERCHLOROETHYLENE AND DECOMPOSITION PRODUCTS (83)

	inh-hum			inh-rat		ori-rat	unk-man		
	LC_{50}	LC_{LO}	TC_{LO}	LC_{50}	LC_{LO}	LD_{50}	LD_{LO}	TLV-TWA	STEL
Perchloro-ethylene		4000 ppm/ 4H	96 ppm/ 7H					50 ppm	200 ppm
Chlorine		873 ppm/ 30 min		293 ppm/ 1H					
Carbon Dioxide		10%/1 min			65%/ 15 min			0.5%	1.5%
Phosgene (Carbonyl Chloride)	3200 mg/ m^3		25 ppm/ 30 min		50 ppm/ 30 min				
Trichloro-acetic Acid						5000 mg/kg		1 ppm	
Hydrochloric Acid		1300 ppm/ 30 min		3124 ppm/ 1H			81 mg/kg	5 ppm	
Hydrogen Chloride (Gas)		1000 ppm/ 1 min	4701 ppm/ 30 min						

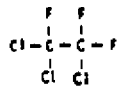
Section 4

DIELECTRIC GASES

CHLOROFLUOROCARBONS

General

Freon is DuPont's registered trademark for carbon compounds containing fluorine, and is used only for fluorocarbons that are nonflammable and low in toxicity. Freon 113, used as a dielectric gas, refers to 1,1,2-trichloro-1,2,2-trifluoroethane.



Freon 113

In addition to being used individually as a dielectric gas, chlorofluorocarbon 113 is a component of the Formel NF mixture. This fluid contains two other fluorocarbons, 1,1,2,2-tetrachloro-1,2-difluoroethane (chlorofluorocarbon 112) and 1,1,1,2-tetrachloro-2,2-difluoroethane (chlorofluorocarbon 112a). These two fluorocarbons are not discussed elsewhere in this report, but many of the following comments on Freon 113 decomposition apply to them generally.

Thermal Decomposition of Freon 113

The chlorofluoroalkanes, of which Freon 113 is a member, are thermally stable up to 250 °C (119). At higher temperatures or during arcing, the fluorocarbons can decompose.

Sparking tests on 1,1,1- and 1,1,2-trichlorotrifluoroethane produced the negative ions Cl^-, F^-, Cl_2^-, and CCl_3^- (93). All of these could continue to react with the parent compound. In this test, analyses were not carried forward to identify the final decomposition products.

Partial combustion of $C_2Cl_3F_3$ at 1000 °C in air produced six trace compounds tentatively identified as CF_4, Cl_2, COF_2, CO, $CClF_3$, and $COCl_2$ (phosgene) (21). In addition, the quartz reaction chamber was noticeably etched, suggesting the possibility of HF formation.

Tests on Formel NF (which contains perchloroethylene as well as the fluorocarbons mentioned above) yielded only Cl_2 and several unidentified halocarbons (98). No phosgene or HCl were detected. Hydrogen chloride would not generally be expected from these compounds because of the lack of hydrogen.

Many fluorocarbon decomposition reactions depend on the presence of at least one hydrogen atom on the molecule. At high temperatures, a hydrogen halide can form, resulting in an unsaturated halocarbon or a halocarbon radical leading to the formation of longer chain molecules and even polymerization. These are fairly common reactions, but would not be expected with Freon 113 or Formel NF.

Toxicity and Exposure Limits of Freon 113 Decomposition Products

Table 4-1 lists the toxicities of the identified Freon 113 decomposition products. Most of these products are more toxic than the parent molecule, and several (phosgene, carbonyl fluoride) are highly toxic. All are generated as vapors, however, and would be expected to disperse with adequate ventilation. Carbonyl fluoride decomposes in the presence of water. Thus, there would be few, if any, highly toxic residues (of the identified PICs) remaining after an incident. There is a potential for highly corrosive and irritating residues of hydrogen chloride and hydrogen fluoride on surfaces, but these present a low toxicity hazard.

SULFUR HEXAFLUORIDE

General

Sulfur hexafluoride (SF_6) can be used alone as a dielectric or in a mixture of gases such as perfluorocarbons. Its physical and chemical properties are listed in Table 4-2.

Table 4-1

TOXICITY AND EXPOSURE LIMITS OF FREON 113 DECOMPOSITION PRODUCTS (83)

	inh-hum			inh-rat		inh-mus		
	LC_{LO}	LC_{50}	TC_{LO}	LC_{LO}	LC_{50}	LO_{LO}	TLV-TWA	STEL
Freon 113				87,000 ppm/ 6 min		25 pph/ 1.5 min	1,000 ppm	1,250 ppm
Carbon Monoxide	4,000 ppm/ 30 min (man)		650 ppm/ 45 min (man)				50 ppm	400 ppm
Phosgene ($COCl_2$)		3,200 mg/m^3	25 ppm/ 30 min	50 ppm/ 30 min			0.1 ppm	
Hydrogen Chloride (Gas)	1,000 ppm/ 1 min				4,701 ppm/ 30 min		5 ppm	
Hydrogen Fluoride			110 ppm/ 1 min	50 ppm/ 30 min			3 ppm	6 ppm
Carbonyl Fluoride (COF_2)					360 ppm/ 1 hr		2 ppm	5 ppm
Tetrafluoro-methane (CF_4)				895,000 ppm/15 min				

Table 4-2

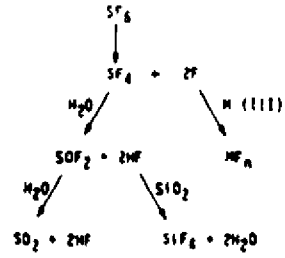
CHEMICAL AND PHYSICAL CHARACTERISTICS OF SULFUR HEXAFLUORIDE (97)

Molecular Weight	146.07
Melting Point	-50.8 °C
Boiling Point	-63.5 °C
Specific Gravity	1.79 (-39 °C) (liquid) 5.11 (20 °C) (vapor)
Vapor Pressure	21 mm Hg @ 20 °C

Thermal Decomposition of Sulfur Hexafluoride

The thermal decomposition of sulfur hexafluoride has been studied under conditions simulating arcing, arc welding, and fires (20, 35, 45, 111). A number of long-lived by-products have been identified.

The principal by-product in most tests was thionyl fluoride (SOF_2). Under sparking at 36 kJ, the typical concentration of SOF_2 deposited into the test cell following 24-hour storage was 1.2% (36). Other identified products (and their concentrations at the conditions above) include sulfuryl fluoride (SO_2F_2 - 0.15%), thionyl tetrafluoride (SOF_4 - 0.22%), silicon tetrafluoride (SiF_4 - 0.03%), and sulfur dioxide (SO_2 - 0.002%). A suggested generalized reaction sequence is (94):



This reaction sequence indicates that sulfur tetrafluoride (SF_4) and hydrogen fluoride (HF) are also decomposition by-products. Both are highly reactive, however, and were not found during analysis.

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Silicon tetrafluoride is not really an SF_6 decomposition by-product. Rather, it is a product of the reaction between HF (a probable decomposition by-product) and silica-containing components of the test cell (or, by inference, the transformer) such as ceramic insulators (36).

The presence of impurities influences the types and quantities of decomposition products formed (35, 111). These impurities can include production impurities in commercial grades of gases, volatilized electrode material, and volatile fractions of other equipment components (e.g., greases). It has been found that the addition of only a few percent of a hydrocarbon impurity can increase SOF_2 production by two orders of magnitude (35). In the presence of hydrocarbons, additional by-products formed can include C_2F_6, CF_4, and $Si(CH_3)_2F_2$ (111).

Finally, as will be noted below, the compounds identified above may not account for all of the toxicity noted in SF_6 decomposition gases (37). It has been suggested that there is a potentially large array of PICs at trace concentrations which have not been identified. For instance, several researchers have hypothesized the production of S_2F_{10}, although it has not been found (36, 37). However, the analyses to date have concentrated on the major PICs; sulfur dioxide at 0.002% (20 ppm) was the lowest PIC concentration.

Toxicity and Exposure Limits of Sulfur Hexafluoride Decomposition Products

Table 4-3 lists toxicity data for sulfur hexafluoride decomposition products. The major products formed during arcing (SOF_2, SO_2F_2, SiF_4, SO_2) are all more toxic than the parent compound, SF_6.

The sparking decomposition products have been found to exhibit strong cytotoxic effects on mammalian cells. The cytotoxicity of the sparking gases was tested using an in vitro cell culture system (Chinese hamster lung cells) (87). The cytotoxicities of the individual decomposition products were tested to identify the most potent cytotoxicant. There were, however, no conclusive results. The sum of the toxicities of the individual products could not account for the toxicity of the sparking gas. The toxicity of a synthetic mixture with a composition similar to that of the identified sparking decomposition products exhibited a toxicity of a lower degree than that of the sparking gas.

Thus, it is reasonable to assume that there are perhaps several as-yet-unidentified decomposition products which, although present in trace amounts, contribute

Table 4-3

TOXICITY AND EXPOSURE LIMITS OF SULFUR HEXAFLUORIDE DECOMPOSITION PRODUCTS (83)

	inh-hmn	inh-rat		orl-rat	inh-mus		
	LC_{LO}	LC_{LO}	LC_{50}	LD_{50}	LC_{LO}	TLV-TWA	STEL
SF_6						1000 ppm	1250 ppm
SOF_2					260 ppm/ 1H	2.5 mg (F)/ m^3	
SO_2F_2			3020 ppm/ 1H	100 mg/kg		5 ppm	10 ppm
SiF_4						2.5 mg (F)/ m^3	
SO_2	1000 ppm/ 10M	1000 ppm				2 ppm	5 ppm
S_2F_{10}					1780 ppm/ 1H	25 ppb	75 ppb

significantly to the cytotoxicity of the decomposition gases. One compound that has been suggested is S_2F_{10}, a highly toxic compound with a TLV in the several ppb range.

The identified decomposition products are all gases at normal ambient temperatures, and would present a problem only in the absence of proper ventilation. Hydrogen fluoride may be found on surfaces, but the amount generated does not seem to be significant. The physical state, and thus the persistence and long-term hazard, of the unidentified decomposition products are unknown.

Section 5

PROPOSED PCB SUBSTITUTES: SOLIDS

INTRODUCTION

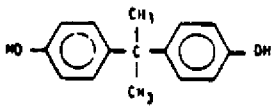
Solid dielectrics can be cast or impregnated into the coils of a transformer, used as films in capacitors, or used as insulation for various parts of transformers, capacitors, or other electrical equipment. There are several types of solid materials which have been considered, including silicone resins, epoxy resins, and a variety of polymers. The two solids to be considered within the context of this review will be epoxy resins and polyvinyl chloride (PVC).

EPOXY RESINS

General

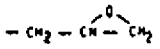
Epoxy resins are those polymers whose monomeric units are linked or cross-linked through an epoxide-hydroxyl dehydration reaction. Cured "epoxy" resins contain few epoxide moieties.

The monomeric units may be simple or complex. The most commonly used resin is based on bisphenol A.



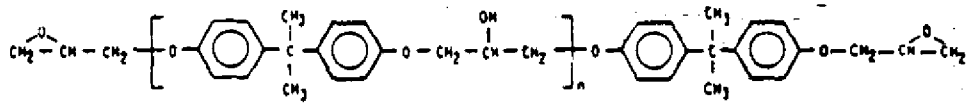
Bisphenol A

This molecule is linked into long chains by a chlorine-containing epoxide compound, epichlorhydrin.



Epichlorhydrin

The result is a long chain polyether which terminates with epoxides.



Most commonly, this compound is then "cured" with a cycloaliphatic anhydride or amine as a "hardener" to effect cross-linking (96). The largest producer of resins for use in casting transformer coils used in the United States reports that roughly 80% of their production for transformer coils may be approximated by the above generalities. The remainder use cycloaliphatic compounds in place of bisphenol A. The principal constituent of the material used to impregnate transformer coils is not the resin (typically 25% of the mixture) or the hardener (up to 25% of the mixture) but the filler material, a fine siliceous material (usually SiO_2, 50% to 75% of the mixture).

Thermal Decomposition of Epoxy Resins

All epoxy links are etheric, of weaker bond energy than the adjacent carbon-carbon bonds. One might then expect to find the monomer (e.g., bisphenol A) as an initial degradation product. This is not the case. The extensive cross-linking and the presence of the filler, both specifically improve heat resistance and prevent any degradation below temperatures at which the monomers are stable. Pyrolysis of a Novolac epoxy (based on a chain of phenol-methyl moieties rather than bisphenol A) yielded no detectable monomer, but did yield significant amounts of benzene at temperatures above 500 °C (71) (Table 5-1). The major portions of the volatilized fraction of the epoxy is designated Vpyr, an otherwise unidentified material that is volatile at pyrolysis temperatures but liquid at room temperatures. The only data available for the 800 °C material is an average molecular weight of 350.

Lum and Feinstein (63, 64) studied the thermal degradation of Novolac epoxies at relatively low temperatures (0 to 500 °C). Release of significant amounts of benzene, phenol, and cresol was detected in the 300 to 500 °C range.

Table 5-1

VOLATILE PRODUCTS FROM PYROLYSIS OF EPOXY RESIN (66)*

Component†	360 °C	500 °C	800 °C	1200 °C
	(%)			
Hydrogen	--	--	0.8	2.1
CO	4.7	3.1	11.2	25.9
CO_2	16.2	6.0	3.7	1.8
Methane	1.0	0.8	1.6	4.3
Acetylene	0.3	--	--	2.5
Ethylene	--	--	3.0	3.0
Acetone	0.9	2.2	--	--
Propane	--	1.1	--	--
Propylene	6.5	2.3	2.2	--
Ethane	--	--	1.6	--
Cyclopentadienes	--	--	--	0.6
Pentanes	--	0.5	--	--
Benzene	--	1.3	2.8	8.1
Methyl Chloride	5.1	--	--	--
Ethyl Chloride	1.7	--	--	--
Others	--	0.7	--	0.8
Vpyr#	63.6	82.0	73.1	50.9
Volatilized Part of Sample, %	38	75	86	87

*Percentages are based on weight of total volatilized fraction.

†Components in amounts of less than 0.5% are not shown.

#A heavy fraction, volatile at pyrolysis temperature, but not room temperature.

Oxidative degradation of a complete 800 kVA GEAFOL cast resin transformer was carried out by the Trafo-Union Corporation of the Federal Republic of Germany (5). The experiment consisted of sequentially (not simultaneously) burning a wood fire (1000 °C) under one coil of a transformer, and a propane fire (1200 °C) under the other coil. The filtered combustion gases were fed continuously to a GC/MS apparatus, which accepted a 10-microliter sample each 20 seconds for the duration of the fire. Mass spectra in the range of m/e = 12 to m/e = 650 were recorded each second. The results are shown in Table 5-2. No peaks above m/e > 92 were found. Nowhere are the carbon dioxide concentrations in the smoke reported, so there is no way to exactly convert the peak intensities to absolute concentrations. A further problem with these tests was the failure to separate the wood and propane combustion gases from the resin combustion gases. Consequently, it is impossible to say with certainty which of the product gases are attributable to the epoxy resin.

Table 5-2

PICs FOUND IN FIRE GASES
FROM TWO CAST RESIN TRANSFORMER FIRES (5)

PIC	Wood Fire	Propane Fire
Acetylene	3.6 ppm	3.4 ppm
Aromatic Fragment	0.4 ppm	0.4 ppm
Benzol	1.2 ppm	1.2 ppm
Toluene	1.6 ppm	1.2 ppm

As part of this same series of tests, a sample of resin was burned at 600 °C, and the product gases were analyzed for 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzofuran. Neither was detected down to 50 ppb. No other dioxin or dibenzofuran was analyzed for.

Toxicity and Exposure Limits of Epoxy Resin Decomposition Products

Table 5-3 presents toxicity data for most of the decomposition by-products mentioned above. Few are highly toxic. Several of the oy-products, however, are known or suspected carcinogens. These compounds are generally solids or liquids

Table 5-3

TOXICITY AND EXPOSURE LIMITS OF EPOXY DECOMPOSITION BY-PRODUCTS (83)

	TC_{LO} (inl-hmn)	LD_{LO} (orl-hmn)	LC_{LO} (inl-rat)	LC_{50} (inl-rat)	LD_{50} (orl-rat)	LC_{50} (inl-mus)	LC_{50} (inl-mam)	TLV-TWA
Acetone	500 ppm		16,000 ppm/4H					
Acetylene							500,000 ppm/5M	
Benzene	100 ppm			10,000 ppm/7H				
Cresol								5 ppm (skin)
m-cresol					242 mg/kg			
o-cresol					121 mg/kg			
p-cresol					207 mg/kg			
Cyclopentadiene, 1,3-								75 ppm
Ethylene						95 pph		
Phenol		140 mg/kg		316 mg/m^3				5 ppm

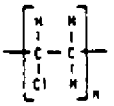
at normal ambient temperatures, and are a risk via dermal exposure as well as oral or inhalation.

The toxicity of the unidentified Vpyr fraction has not been assessed. Finally, few of the tests conducted to date have been concerned with identifying by-products at trace levels.

POLYVINYL CHLORIDE (PVC)

General

PVC is a synthetic thermoplastic polymer.



It is generally resistant to weathering and moisture, and to most acids, fats, petroleum hydrocarbons, and fungus. It is dimensionally stable with good dielectric properties. The first important use for plasticized PVC was as electrical cable insulation sheathing. The electrical industry is still a major consumer of PVC, with most being used as flexible cable insulation or rigid electrical conduit.

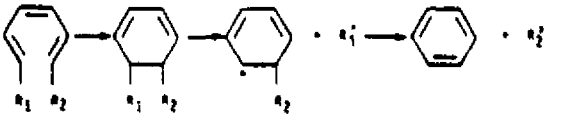
PVC resins are always compounded with a variety of additives. Stabilizers are added to act as scavengers for free radicals produced by heat or light. Metallic salts, oxides, and salts of fatty acids are common stabilizers. Fillers such as calcium or magnesium carbonate can be added to retard the catalytic chain dehydrochlorination effect of released hydrogen chloride. Plasticizers may be added to impart or improve flexibility. Plasticizers may be up to 30% by weight of the compounded plastic. Typical plasticizers include phosphates, dioctylphthalate, and low-molecular-weight propylene glycol polymers. To increase flexibility, vinyl chloride may be copolymerized with vinyl acetate. The vinyl acetate can constitute 3 to 15% of the copolymer. There is no single compound formula used ubiquitously in the electrical industry.

Thermal Decomposition Products of PVC

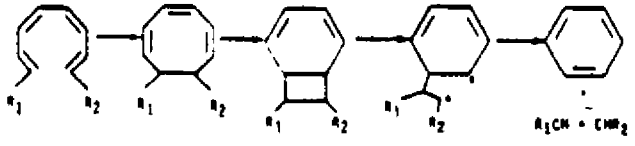
Data on the thermal degradation of PVC are fairly extensive. The major problem with using the data is the variety of PVC formulations available. A given test sample may be stabilized or unstabilized. There are several different stabilizers available. Other additives (plasticizers, fillers, dyes, etc.) can vary in composition as well. The extent to which these additives affect the thermal degradation of the polymer and the extent to which the additives themselves contribute to the final by-product mix are unresolved. Furthermore, most of the published research is not highly specific regarding the formulation or composition of the PVC being tested. Consequently, there is some question regarding the applicability of a particular test result to other PVCs. As a result, the following discussion must be taken as being only generally indicative and not necessarily specific for any particular PVC formulation.

In the absence of oxygen, PVC pyrolyzes by dehydrochlorination (loss of HCl), followed by cyclization of polyene (19, 39, 76). The reaction proceeds via 1,4-elimination of chlorine from cis double bonds, generally from groups at or near chain ends. The principal products formed are benzene and hydrogen chloride (19).

Benzene is believed to form probably by one of the two following mechanisms (76):



(5-1)



(5-2)

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The presence of HCl may catalyze the thermal degradation, but this has been disputed (19, 76).

Benzene is not the only decomposition product. Table 5-4 lists the decomposition yields of several more aromatic compounds at various temperatures from 300 to 800 °C. In addition to these compounds, aliphatic hydrocarbons, β-methylnaphthalene, monochlorobenzene, o-dichlorobenzene, p-dichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,4-trichlorobenzene were also identified in the pyrolysis gases (19).

Table 5-4

DECOMPOSITION YIELDS* OF SOME AROMATICS OBTAINED BY THE PYROLYSIS† OF PVC (GEON-103 EP) AT VARIOUS TEMPERATURES (19)

	Yield, wt %					
Product	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
Benzene	3.50	4.67	5.00	5.23	6.30	9.95
Toluene	--	0.21	0.67	0.82	1.55	2.10
Ethylbenzene	--	--	0.16	0.18	0.18	0.23
o-Xylene	--	--	0.16	0.18	0.23	0.25
Styrene	--	0.13	0.22	0.37	0.74	1.06
Naphthalene	--	0.47	0.52	0.73	1.50	3.00

*Calculated using gas chromatography with p-dichlorobenzene as an internal standard.

†Samples (powder), 1-3 mg, were pyrolyzed in helium gas; flow rate of helium being 25 ml/min.

Ahling et al. (3) combusted PVC over the range of 570 to 1130 °C. They found from di- to hexachlorinated benzenes, octachlorostyrene, and PCBs. During the combustion experiments, PVC was mixed with wood chips to help sustain combustion.

The combustion of PVC can also yield carbonyl chloride (phosgene) (13). Yields are on the order of 0.06 to 0.15 mg/g (or a concentration of 0.5 to 1.3 ppm from 4 to 7 g decomposed in a 200-l animal exposure chamber). Subjecting the PVC to an electric arc can increase yields of phosgene 10 to 20 times.

Because of the production of chlorinated benzenes, the formation of PCDDs and PCDFs is a distinct possibility (see Section 3, Chlorobenzenes) (19). The presence of other chlorinated polycyclic aromatics, such as chlorinated naphthalenes, is also feasible. To date, none of these have been identified in PVC pyrolysis gases, but PVC is suspected to be one of the potential sources of the PCDDs and PCDFs found in fly ash and flue gases from municipal and industrial incinerators (19).

Toxicity and Exposure Limits of PVC Thermal Degredation Products

Table 5-5 lists the toxicities for the identified PVC degredation products. Speculative by-products, such as PCDDs, PCDFs, PCNs, etc., are not included, although the circumstantial evidence for their production is good. Their toxicities are discussed elsewhere in this review.

The identified PVC by-products are of variable toxicity, but generally fall into the moderate to high toxicity range. In addition, several are known or suspected carcinogens. Most of these compounds are solids or liquids at normal ambient temperatures, and could be found in soot or on surfaces after a fire. Phosgene, a gas, is the notable exception.

Table 5-5

TOXICITIES AND EXPOSURE LIMITS OF PVC THERMAL DEGRADATION BY-PRODUCTS (83)

	LC_{50} (inh-hum)	TC_{LO} (inh-hum)	TD_{LO} (ori-hum)	LC_{LO} (inh-rat)	LC_{50} (inh-rat)	LD_{50} (ori-rat)	LD_{LO} (ori-rat)	TLV-TWA
Phosgene	3200 mg/m^3	25 ppm/30M		50 ppm/30M				100 ppb
Benzene		100 ppm			10,000 ppm/7H			10 ppm
Toluene		200 ppm		4000 ppm/4H				100 ppm
Ethylbenzene		100 ppm/8H		4000 ppm/4H				100 ppm
o-Xylene				6125 ppm/12H				
Styrene		600 ppm		5000 ppm/8H				50 ppm
Naphthalene						1780 mg/kg		10 ppm
Methylnaphthalene							5000 mg/kg	
Monochlorobenzene						2910 mg/kg		75 ppm
o-Dichlorobenzene				821 ppm/7H		500 mg/kg		
p-Dichlorobenzene			300 mg/kg			500 mg/kg		75 ppm
1,2,4-Trichloro-benzene						756 mg/kg		

Section 6

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Appendix A

GLOSSARY AND ABBREVIATIONS

Gpg	Guinea pig
Hum	Human
Inl	Inhalation
LC_{LO}	Lethal concentration low
LC_{50}	Lethal concentration fifty
LD_{LO}	Lethal dose low
LD_{50}	Lethal dose fifty
Letnal Concentration Fifty	A calculated concentration of a substance in air, exposure to which for a specified time (H - hours, M - minutes) is expected to cause the death of 50% of a defined animal population
Lethal Concentration Low	The lowest concentration of a substance in air which has been reported to have caused death in humans or animals
Letnal Dose Fifty	A calculated dose of a substance which is expected to cause the death of 50% of a defined animal population
Lethal Dose Low	The lowest dose of a substance reported to have caused death in humans or animals
Mus	Mouse
Orl	Oral
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
PCN	Polychlorinated naphthalenes
PIC	Product of incomplete combustion
ppn	Parts per hundred
ppm	Parts per million
STEL	Short-term exposure limit; maximum allowable exposure concentrations for 15-minute exposure

Appendix A (continued)

TCDD	Tetrachlorodibenzo-p-dioxin
TCDF	Tetrachlorodibenzofuran
TC_{LO}	Toxic concentration low
TD_{LO}	Toxic dose low
TD_{50}	Toxic dose fifty
Threshold Limit Value	The ACGIH-recommended concentration of a substance to which most workers can be exposed without adverse affect; may be expressed as time-weighted average (TWA), short-term exposure limit (STEL), or ceiling value (CL)
TLV	Threshold limit value
Toxic Concentration Low	The lowest concentration of a substance in air to which humans or animals have been exposed for any given period of time that has produced any toxic effect
Toxic Dose Fifty	A calculated dose of a substance reported to cause toxic effects in 50% of a defined population
Toxic Dose Low	The lowest dose of a substance reported to produce any toxic effect in humans or animals
TWA	Time-weighted average; average allowable exposure over an 8-hour workday or 40-hour work week

Appendix B

GENERIC AND TRADE NAMES

Benzylneocaprate	FARADOL 100 (Asea)
Butylated monochlorodiphenylether	DIELECTRIC FLUID C-4 (Dow), XFS-4169L (Dow)
DC 200 (Dow)	Polydimethylsiloxane
DC 561 (Dow)	Polydimethylsiloxane
Di-2-ethylhexyl phthalate	Component of DIELECTROL II (General Electric) and SELECTROL I (Sangamo)
DIELECTRIC FLUID C-4 (Dow)	Butylated monochlorodiphenylether
DIELECTROL II (General Electric)	Di-2-ethylhexyl phthalate
DIELECTROL III (General Electric)	Dixylylethane
Dixylylethane	DIELECTROL III (General Electric), SELECTROL II (Sangamo), SAS 295 Misseki), SAS 296 (Misseki)
EDISOL II (McGraw Edison)	Mixture of methylated diphenylethane and propyldiphenyl
Epoxy	GEAFOL (Trafo-Union)
F 101 (SWS Silicone)	Polydimethylsiloxane
F 190 (SWS Silicone)	Polydimethylsiloxane
FARADOL 100 (Asea)	Benzylneocaprate
FORMEL NF (ISC Chemicals)	Mixture of perchloroethylene and freons
Freon	Component of FORMEL NF (ISC Chemicals)
GEAFOL (Trafo-Union)	Epoxy
Isopropylbiphenyl	WEMCOL (Westinghouse)
L 305 (Union Carbide)	Polydimethylsiloxane
Methylated diphenylethane	Component of EDISOL II (McGraw Edison)
PAO 13CE (Uniroyal)	Poly 1-octene

Appendix B (continued)

Perchloroetnylene	WECOSOL (Westinghouse), component of FOKMEL NF (ISC Chemicals)
Poly 1-octene	PAO 13CE (Uniroyal), PR (Gulf Oil)
Polydimethylsiloxane	DC 200 and DC 561 (Dow Corning), F 101 and F 190 (SWS Silicone), L 305 (Union Carbide), SF 97 (General Electric)
PR (Gulf Oil)	Poly 1-octene
Propylbiphenyl	Component of EDISOL II (McGraw Edison)
SAS 295 (Nisseki)	Dixylylethane
SAS 296 (Nisseki)	Dixylylethane
SELECTKOL I (Sangamo)	Mixture of di-2-ethylhexyl phthalate and trichlorobenzene
SELECTROL II (Sangamo)	Dixylylethane
SF 97 (General Electric)	Polydimethylsiloxane
Trichlorobenzene	Component of DIELECTROL II (General Electric), SELECTROL I (Sangamo)
WECOSOL (Westinghouse)	Perchloroethylene
WEMCOL (Westinghouse)	Isopropylbiphenyl
XFS-4169L (Dow)	Butylated monochlorodiphenylether

MONS 216064

EPA Hearing on Proposed Regulations
on PCB Transformer Use

Statement of Dr. John Craddock, Chairman
Chemical Manufacturers Association
PCB Program Panel

January 15, 1985

Good afternoon. I am John Craddock, Chairman of the Chemical Manufacturers Association PCB Program Panel. CMA appreciates the opportunity to appear here today.

CMA has actively participated in many EPA proceedings concerning PCBs. Following remand from the Court of Appeals in 1980, CMA conducted surveys for the Agency of PCB use in electrical equipment in the chemical industry and of inadvertent generation of PCBs in chemical manufacture. CMA has filed extensive comments in each of EPA's many PCB rulemakings. We also worked jointly with the Environmental Defense Fund and Natural Resources Defense Council to develop the consensus proposal that EPA employed as the basis for its final rule on inadvertant PCB generation. Most recently, the Panel has submitted comments in response to both the ANPR and the current proposal concerning risks should PCB transformers be involved in fires.

As our comments detailed, CMA believes the incidence of fires involving PCB transformers has been greatly overestimated because a few unusual incidents in recent years focused

public attention on this issue. Indeed, CMA's survey of transformer use in the chemical industry over the past 40 years found no fires involving PCB transformers. Our comments thus conclude there is insufficient information to justify new regulations on PCB transformers, especially those in use under controlled conditions in the chemical industry.

This ~~morning~~ afternoon -- rather than restating CMA's previously detailed position -- I would like to address the issues in this proceeding by posing several questions to the Agency and to other interested parties. The fundamental question underlying this proceeding is whether any of us can conclude with confidence that any of the wide range of measures being proposed by EPA or other parties will in fact reduce the number of transformer fires or the risks associated with such fires. CMA suggests the answer is no, and, accordingly, concludes this regulatory initiative should be abandoned until considerably more information exists.

EPA believes that a health risk exists when a fire occurs in the vicinity of a PCB transformer. It is concerned that PCBs, dioxins and dibenzofurans will be released and spread through nearby buildings. It has thus proposed a variety of controls that EPA believes will make it less likely that fires will get out of control or that their combustion products will spread. As we have determined from talking to companies within the chemical industry, and as

EPA's economic consultants recognize, the expense involved in EPA's proposals may lead many operators to choose retro-fill or removal even if such actions are not mandated. Thus, CMA believes that the practical impact of the regulation will be a forced phaseout of many transformers currently in use.

Serious questions for which the record currently offers no firm answers are raised:

-- Will fires involving transformers be more, or less, likely should any of these controls be imposed?

-- Will the consequences of such fires be more, or less, dangerous?

-- Will combustion products should a fire occur be more, or less, dangerous?

-- What risks will be posed by the storage and disposal of PCBs forced out by regulation?

Without answers to these questions -- answers that are not at all clear today -- it is possible that the new EPA controls will create risks that are greater than any risks EPA hopes to reduce. I would like to review briefly each of these questions to explain why CMA believes EPA may be embarking on a potentially counter-productive rulemaking.

First, the record in this proceeding is woefully lacking in evidence that any particular EPA solution will make it less likely that fires will occur. As is well known, PCBs were initially chosen for transformer dielectric use

precisely because of their fire resistant characteristics. Further, electrical specialists have for many years been aware of the risk of fires with electrical equipment and have thus taken numerous precautions through the National Electric Code and other guidance to minimize fire risks.

For EPA, whose expertise in electrical matters is limited, to attempt to impose new regulations intended to reduce fire risks creates the distinct possibility that wise choices may not be made. As the many comments received by the Agency over the past two months demonstrate, EPA has in fact chosen electrical protective devices whose availability and efficacy are questioned by many experts in the field. At the same time, little data exist on the risks that alternative transformer fluids may contribute to the initiation or spread of fires. In other words, the best protection against fires involving transformers may well be continued use of PCB transformers as they are used today. At a minimum, the record does not indicate whether there will be fewer, or more, fires if new EPA controls are promulgated. Nor does the record indicate whether the isolation requirement will adequately contain the fire and combustion products for any period of time; nor whether there will be more, or possibly different, toxic combustion products as a result of EPA controls.

Furthermore, some of the control measures suggested by the Agency could increase other fire risks. For example,

many building emergency systems depend on continued flow of electricity to allow occupants to evacuate. Deenergization measures that might be useful in limiting fires might at the same time hinder building evacuation. Experts in electrical design and fire safety should be making decisions in this area.

Third, EPA has focused all its attention on the possibility of PCB, dioxin and dibenzofuran contamination. Even if the proposed regulations were to reduce spread of these chemicals -- either through controlling fires involving PCB transformers or removal of PCBs from transformers -- the possibility remains that other combustion products will be formed during fires and pose their own toxic risks -- risks that perhaps will be more significant than those presented by dioxins and by dibenzofurans. We do know that the record demonstrates PCBs are not the source of dioxins, but we do not know whether the regulations would reduce dibenzofuran combustion products while increasing production and dissemination of other toxic compounds. Until all such risks are assessed, no assurance will exist that removal of PCBs will be beneficial.

Finally, if the EPA regulations do in fact cause substantial PCB removal from transformers, we must be concerned with the fate of this fluid. As EPA's economic report recognizes, a three-year phaseout is not a practical alternative. Current approved PCB ininceration capacity in this

country is already overburdened. What risk will be created by the necessary handling and storage of PCBs until such incineration capacity exists is yet another unexplored issue.

In sum, the record reveals an alarming lack of data indicating whether the proposed controls will in effect reduce risks. We all can agree it is undesirable to have any transformers involved in fires and that it is desirable, should such incidents occur, that the fires be quickly controlled and their combustion products handled. But, we must also recognize that EPA should not impose new measures to prevent such fires unless it is sure that those measures will in fact reduce overall risks. If alternative wiring or isolation protection creates new risks, or if alternative fluids increase the risk of fire or the production of toxic combustion products, the nation will not be better off.

As in EPA's prior PCB proceedings, the focus should be on development of reasonable controls to limit human or environmental PCB exposure. In this proceeding EPA has ventured far afield into complex questions of electrical system design, building emergency procedures, relative risks of a wide variety of chemicals under unusual fire conditions, and, indeed, of fire itself. The resulting regulatory proposals thus raise more questions about potential new risks than they answer about the risks initially perceived.

CMA is concerned that the Agency may issue a regulation whose risks are greater than its benefits -- without even considering the costs imposed. We urge the Agency to reconsider and withdraw its proposal until it obtains a more substantial base of information upon which to compare the risks of various fire control alternatives.