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Carl L. Blesch

Polychlorinated Biphenyls: History of a Problem Chemical

INTRODUCTION

Polychlorinated Biphenyls (PCBs) are a group of stable chemicals composed of two directly-linked benzene rings with one to ten chlorine atoms attached to remaining ring positions. There are 210 possible PCB isomers. PCBs are known for their stability under high temperatures, their inertness, and their high dielectric constants. Presently, they are used mainly as a filler in transformers, large power capacitors, and smaller appliance capacitors (the sealed "aluminum can" type). PCBs have also been used as heat transfer fluids, hydraulic fluids, plasticizers, paint and varnish additives, casting wax components, Xerox toner, printing ink and carbonless copy paper additives, and adhesive material. (PCBs have been restricted or banned for many of these latter uses because of environmental concerns.)

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Inertness and stability--the properties that make PCBs ideal for many applications--also make them an environmental problem. PCBs are so stable (they are essentially unalterable by microbial or physical chemical reactions) that their chemical cousin DDT--which degrades in 15 years--looks innocuous in comparison.[1] Like other stable elements or compounds discharged into the environment, PCBs are concentrated in the food chain. PCBs tend to bioaccumulate in aquatic environments by factors of a few thousand to several hundred-thousand fold.[2] As a result, final feeders such as fish and predatory birds often have high PCB concentrations in their fat tissue. Because PCBs are fat-soluble, they are held in the body for a long time, rather than excreted.

PCBs in varying concentrations can interfere with reproduction--birds that have ingested PCBs show eggshell thinning and reduction of egg production.[3] In laboratory experiments, between 12 and 40 per cent of the female monkeys fed low doses of PCBs (at or below levels the FDA allows in human food), became pregnant, whereas 90 per cent of the female monkeys fed a PCB-free diet became pregnant.[4]

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[1]Robert H. Boyle, "Of PCB ppms from GE and a SNAFU from EPA and DEC," *Audobon*, 77/6:129, November, 1975.

[2]A. Karim Ahmed, "Statement of Dr. A. Karim Ahmed Before the House Subcommittee on Fisheries and Wildlife Conservation and the Environment," National Resources Defense Council, January 29, 1976, p. 3. (Hereafter cited as "Testimony").

[3]Ibid.

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[4]James R. Allen, "Response of the Nonhuman Primate to Polychlorinated Biphenly Exposure," *Federation Proceedings*, 34:1677, July, 1975.

The monkeys that ingested PCBs also had skin lesions and hair loss. PCBs have also been implicated for producing skin lesions and tumors in rats.[5]

The properties, manufacture, uses and problems of PCBs will be further discussed in following sections of this paper.

PCB HISTORY

Early Research

The chemical structures of mono- and dichlorinated diphenyls--the forerunners of PCBs--have been known for over 100 years. In 1874, Gustav Schultz of the Chemical Institute at the University of Strassburg prepared two monochlorinated diphenyl isomers using separate methods--the ortho isomer by oxidizing diphenyl in the presence of phosphorous pentachloride, and the para isomer by oxidizing diphenyl with glacial acetic acid and chromic acid (CrO_3).[6] He also describes preparation of the meta isomer by a method using lime and potassium phenol.[7] Schultz had also done considerable work with bromo-, nitro-, and amino-substituted diphenyls.

In 1877, Kramer of the Polytechnical School at Delft directly synthesized chlorinated diphenyls by passing

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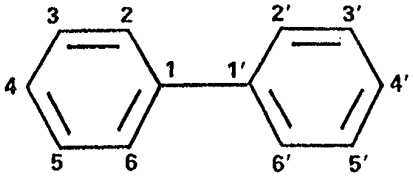
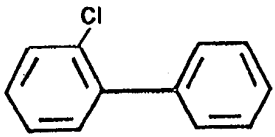
[5] A. Karim Ahmed, "PCBs in the Environment," *Environment*, 18/2:9, March, 1976.

[6] Gustav Schultz, "Ueber Diphenyl," *Annalen der Chemie*, 174:209, 1874.

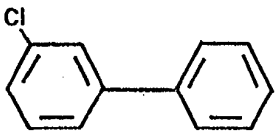
[7] Schultz attributes this method to Pfannkuch, citing a reference in the *Journal für Praktischen Chemie* which I could not find.



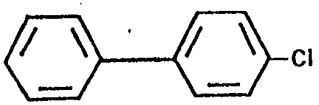
BIPHENYL



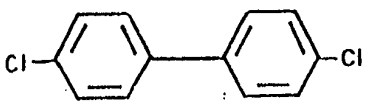
ortho monochlorodiphenyl



Meta monochlorodiphenyl



para monochlorodiphenyl



diparachlorodiphenyl

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chlorobenzene through a red-hot iron tube.[8] He obtained a mixture of ortho and para isomers, plus a small amount of dichlorodiphenyl.[9] He described the white crystals as insoluble in water, but highly soluble in benzene and petroleum either.[10] "In benzene, it melted like sugar in warm water," he said.

In an 1881 paper, Schultz and H. Schmidt describe a diparachlorodiphenyl synthesis by Grief from a chloride of tetrazodiphenyl with platinum tetrachloride:[11]

$$\begin{matrix} C_6H_4N{=}NCl \\ | \\ C_6H_4N{=}NCl \end{matrix} + PtCl_4 \rightarrow \begin{matrix} C_6H_4Cl \\ | \\ C_6H_4Cl \end{matrix}$$

They give no journal references to Grief's work, however.

Schultz and Schmidt also attribute to Kramer (but give no reference) the production of diparachlorodiphenyl by direct chlorination of diphenyl in the presence of antimony pentachloride.[12]

Another dichlorodiphenyl synthesis described by Schultz and Schmidt involves chlorinating diphenyl with a combination of hydrochloric acid, iodine monochloride, and iodine.[13]

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[8] J. G. Kramer, "Ueber die Producte der directen Chlorirung des Diphenyls," *Annalen der Chemie*, 189:142, 1877.

[9] Ibid., pp. 144-145. [10] Ibid., p. 144.

[11] H. Schmidt and Gustav Schultz, "Ueber Diphenylbasen," *Annalen der Chemie*, 207:338, 1881.

[12] Ibid. [13] Ibid., p. 339.

Production History

Chlorinated diphenyls were no more than a laboratory curiousity until 1929, when they suddenly became chemicals of great industrial interest. Jenkins, an industrial chemist with Swan Chemical Company, attributes the belated industrial production of these chemicals to the previously high cost of diphenyl synthesis. "Recently, a commercial process has been developed which makes possible the sale of diphenyl at 40 to 50 cents per pound, or approximately one per cent of its former price. This development has made diphenyl easily available to investigators and has stimulated research to find new uses for this hydrocarbon."[14] Jenkins never mentions what the new industrial process is, but it could be the synthesis described by Whitmore--mixing benzene vapor with melted lead and various catalysts.[15]

Jenkins also notes that chlorination of diphenyl had been tested on a semiplant scale, and "the commercial production . . . awaits only the development of sufficient demand."[16]

The industrial method Jenkins describes for making mono- and dichlorodiphenyls is direct chlorination using heat and an iron catalyst.[17] The products are a mixture of monochloro-

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[14]Russell L. Jenkins, Rogers McCullough, and C. F. Booth, "Synthesis in the Diphenyl Series," *Industrial and Engineering Chemistry*, 22/1:31, January, 1930.

[15]Frank C. Whitmore, *Organic Chemistry* (New York: D. Van Nostrand and Co., 1937), p. 700.

[16]Jenkins, p. 31.

[17]Ibid., p. 32.

diphenyl isomers and diparachlorodiphenyl. More chlorine and higher temperatures give more dichlorodiphenyl, and the chemicals can be separated by fractional distillation.[18]

The process described by Jenkins is the forerunner of polychlorination--adding more than two chlorines to the diphenyl structures. The first polychlorinated diphenyls were industrially produced by Swan Chemical Company in 1929 "in response to the electrical industry's need for an improved dielectric insulating fluid which would also provide increased fire resistant benefits when used in transformers and capacitors."[19] Monsanto, the only United States manufacturer of PCBs, took over Swan in the early 1930's. Swan assigned the trade name "Aroclor" to their PCBs, and used a four number suffix code to indicate the product's percentage of chlorination (e.g. in Aroclor 1242, the 12 refers to the parent biphenyl molecule and the 42 indicates that the molecule is 42 per cent chlorinated).[20]

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[18]Ibid.

[19]Monsanto Company, *Polychlorinated Biphenyls: A Risk/Benefit Dilemma*, (Report Submitted to the House Subcommittee on Fisheries and Wildlife Conservation and the Environment), January, 1976.

[20]Unlike the mono- and dichlorodiphenyls, which were separated into individual isomers, each PCB product is a mixture of isomers, all with approximately the same number of chlorines. The individual mono- and dichlorodiphenyl isomers are crystalline solids at room temperatures, but the low-chlorinated PCBs, being mixtures of several isomers, are liquids.

Although Monsanto today says that the Aroclors were developed mainly as a dielectric for the electrical industry, Swan industrial chemist Chester Penning reported in 1929 that "the Aroclors are being considered for use in a large number of greatly varied industries. . . . No attempt will be made to complete the list of multitudinous projects on which work is being done with the Aroclors."[21] PCBs were proposed for use in printing inks, artificial leather, leather finishing, textile finishing, varnishes, lacquers, plasticizers, and as a waterproofing and flameproofing additive to wood, paper, textiles, wallboard, stone, cement, stucco, and other materials.[22] Aroclor 1262 was suggested for use in adhesive tape, rubber cement, sealing wax, and glass-laminating cement because of its tackiness and nondrying properties. "It has even been considered for chewing gum as a substitute for chicle," Penning added.[23]

Describing some characteristics of PCBs, Penning said "Aroclor 1219 has a very distinctive, though not unpleasant, odor; the other [Aroclors] are practically odorless, and tasteless as well. They have no noticeable action upon the skin; the concentrated vapors are irritating to the nasal passages, and cause violent headaches to certain persons, but aside from this, no toxic effects have been noted."[24]

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[21]Chester H. Penning, "Physical Characteristics and Commercial Possibilities of Chlorinated Diphenyl," *Industrial and Engineering Chemistry*, 22/11;1181-1182, November, 1930.

[22]Ibid., p. 1181 [23]Ibid., p. 1182 [24]Ibid., p. 1180.

In spite of Penning's observations, no one suspected that PCBs would become an environmental problem.

CONTEMPORARY PCB PRODUCTION AND USE

Production

Since 1929, 1.4 billion pounds of PCBs have been produced in the United States.[25] Although Monsanto is the only domestic manufacturer of PCBs, other domestic companies marketing the chemicals have included Allis-Chalmers Manufacturing Co., Westinghouse, and General Electric.[26] Out of the roughly one and one-half billion pounds of PCBs produced in this country since 1929, 1.5 million have been exported, 750 million are still in service, and 500 million have entered the environment. And of these 500 million pounds, 300 million are in landfills, 150 million are in the air, water, soil, and bottom sediments of water bodies, and 50 million have been degraded or incinerated.[27] In the United States, a peak production of 72 million pounds occurred in 1970.[28]

The PCB manufacturers worldwide include Bayer (Germany), Prodelec (France), Kanegafuchi and Mitsubish (Japan), and

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[25]Russel Train, (Report presented to the Wisconsin Legislative Council), Environmental Protection Agency, February 13, 1976, p. 1.

[26]H.L. Hubbard, "Chlorinated Biphenyl and Related Compounds," *Chlorocarbons and Chlorohydrocarbons*, Vol. 5, *Encyclopedia of Chemical Technology* (New York: John Wiley and Sons, 1966) p. 289.

[27]Train, p. 1.

[28]Ahmed, Testimony, p. 1.

Cafforo (Italy).[29] In 1971, the United States led PCB production with about 40 million pounds, followed by Germany with about 18 million pounds, and France with about 17 million pounds.[30]

Manufacturing Processes

Polychlorinated biphenyls are produced by batch chlorination of diphenyl in cylindrical steel towers, often three feet in diameter and 18 feet high.[31] Anhydrous chlorine gas is pumped in at the bottom, where it passes up through a series of short iron tubes (which act as catalysts) at the cylinder bottom. German manufacturers substitute a ferric chloride catalyst for iron tubes.[32] Throughout the chlorination, the temperature is kept well above the melting point of the mixture. Samples are periodically withdrawn and analyzed for specific gravity to determine when the desired level of chlorination has been achieved. The time required for chlorination is 12 to 36 hours, depending on the percentage of chlorination desired. The crude product of batch chlorination is then distilled under reduced pressure to remove such by-product impurities as hydrogen chloride and ferric chloride.[33]

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[29] Train, p. 9.

[30] Organization for Economic Cooperation and Development, *Polychlorinated Biphenyls, Their Use and Control* (Paris: 1973), p. 20. Hereafter cited as "OECD."

[31] Hubbard, p. 292.

[32] Ibid.

[33] Ibid., p. 293.

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Properties

PCBs are colorless, mobile oils at chlorination levels up to 42 per cent, light yellow viscous oils around 50 per cent, sticky yellow resins around 60 per cent, and white crystalline powders around 70 per cent. Above this, PCBs are hard brittle resins ranging from yellow to amber to black.

Contemporary Uses

To date, about one billion pounds of the PCBs made in the United States have been used in transformers and capacitors, whereas 103 million pounds have been used in paper products, sealants, lubricants, paints, hydraulic oils, inks, and casting waxes.[34]

Nonflammibility, high dielectric constant, thermal stability, and chemical stability make PCBs well-suited for use in transformers and capacitors. Alternative fillers, such as mineral oil or air, have disadvantages. Power surges in large transformers cause arcing, which can sometimes decompose and even ignite mineral oil. The risk of explosion is low, so mineral oils are still used in more than 85 per cent of electrical insulating applications.[35] But for those places where the risk of explosion must be absolutely zero (e.g. transformers in subway trains, public buildings, substations located in the middle of densely-populated areas or expensive industrial equipment), there is still no reasonably-

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[34]Train, p. 2.

[35]"Pollution Cop's Lot Not 'Appy," *Chemical Week*, April 21, 1971, p. 19.

priced and proven alternative to PCBs.[36] Air-filled transformers or capacitors must be huge and bulky in comparison to mineral oil or PCB-filled equipment. Because of their high dielectric constants, PCBs are also used in the small "aluminum can" type capacitors found in such appliances as air conditioners, refrigerators, and fluorescent light fixtures.

PCBs are used on a limited basis in hydraulic fluids, mainly in such situations as mining and aviation, where flammibility must be avoided at all costs.[37]

In situations where PCB substitutes are readily available and equally effective, however, PCBs have largely been phased out because of environmental considerations. But prior to 1970, the uses for PCBs were numerous. PCBs were widely used as plasticizers, imparting increased hardness to plastic films[38] and rendering many plastic resins fireproof and resistant to acids and alkalis.[39]

PCBs also found wide use in carbonless copy paper as an ink encapsulator,[40] and in Xerox toner as an ink transfer additive.[41] Other uses for PCBs have included lubricant additives, adhesives, heat transfer media, and casting wax additives.

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[36] In Japan, where PCB manufacture is now banned, railway electrical equipment contains a silicon dielectric described later in this report.

[37] OECD, pp. 30-31.

[38] Hubbard, P. 295.

[39] OECD, pp. 34-35.

[40] Hubbard, p. 296.

[41] Boyle, p. 128.

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PCBs AS AN ENVIRONMENTAL PROBLEM

Up until 1966, when PCBs were first detected in the environment, "nobody had suggested or even suspected that these compounds may be a possible source of environmental pollution.[42] But their non-degradibility coupled with previously unperceived toxic effects have made them a chemical of public concern.

Environmental History

PCBs were first detected in 1966 by Sören Jensen, who found the chemical in fish and wildlife.[43] At the time, Jensen was measuring DDT and other organochlorane insecticide concentrations in animals. But he found the PCBs when he used mass spectrometry to identify unknown peaks in earlier gas chromatographic analyses.[44]

The toxic effects of PCBs were first demonstrated as the result of a Japanese food industry accident. PCBs being used as a heat transfer fluid leaked into a vat of rice oil. About 1000 people became ill after eating the contaminated oil, showing such symptoms as dizziness, nausea, headaches, loss of appetite, and temporary loss of vision.[45, 46] In

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[42]United Kingdom, *Control of Polychlorinated Biphenyl Pollution in the United Kingdom*, (Paper submitted to the OECD), October, 1971, p. 8.

[43]Sören Jensen, "Report of a New Chemical Hazard," *New Scientist*, 32:612, 1966.

[44]R. Edwards, "The Polychlorobiphenyls, Their Occurrence and Significance: A Review," *Chemistry and Industry*, 1971:1340 November 20, 1971.

[45]Monsanto, pp. 2-3. [46]Ahmed, *Environment*, p. 8.

addition, many infants born to mothers who had eaten the rice oil during pregnancy were underweight and had darkened skin.[47]

Since then, scientists around the world have found PCBs in many fish and bird species. EPA sampling of fish in the Hudson River north of Albany, New York, and in the Housatonic River below Pittsfield, Massachusetts (both sites are downriver from General Electric transformer and capacitor manufacturing plants) showed that some fish species have PCB levels up to 500 ppm.[48] This is far above the FDA's maximum allowable level of five ppm for human food.

Wisconsin Department of Natural Resources studies in 1974 showed several species of salmon, trout, whitefish, and carp to have PCB levels well above five ppm, with lake trout (up to 43.8 ppm) and carp (up to 51.6 ppm) showing the highest concentrations.[49] Fish sampled in the Fox and Mississippi Rivers also showed similar high PCB concentrations.[50]

PCB Entry Into the Environment

The products in which PCBs are used are generally classified into two classes--open systems or closed systems. Open systems include such products as carbonless copy paper, plasticizers, and lubricating oil, from which the PCBs are inevitably discharged to the environment upon product disposal. Closed systems include electrical transformers and capacitors,

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[47]Ibid.

[48]Ahmed, Testimony, p. 2.

[49]Ahmed, *Environment*, p. 7.

[50]Ibid.

where the PCB is sealed inside the component, and is often recoverable (as in the case of transformers and large capacitors, where the PCB can be drained before the units are scrapped).

PCBs therefore enter the environment mainly upon disposal of open system products, but closed system products have also contributed to the PCB problem. PCBs can easily be recovered from some closed systems uses, but there are other closed systems uses where recovery is virtually impossible. While PCBs can be easily be drained from large transformers when they are taken out of service, it would be impossible to collect every capacitor from every discarded household appliance. While the PCBs are theoretically sealed in these capacitors, the capacitors could crack when the appliance is disposed, and PCBs could leach from the disposal site.

Prior to 1972, hydraulic fluid leaks and spills accounted for 30 per cent of all PCBs in the environment; plasticizers in paints, adhesives, inks, and other products accounted for another 30 per cent. Fifteen per cent of the PCBs discharged to the environment before 1972 came from the wastewater effluent of paper recyclers who recycled carbonless copy paper; and another 15 per cent came from transformer and capacitor manufacturers. The metal recycling industry discharged five per cent upon reclaiming metal from electrical equipment, and the casting industry discharged five per cent when they disposed of PCB-containing wax.[51]

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[51]Bruce P. Boller, "The PCB Controversy" (Milwaukee: R.W. Baird Research Report), January 19, 1976, p. 1.

Currently, hydraulic fluid leaks and spills account for 50 per cent of the PCBs being discharged; metal scrap dealers--25 per cent; transformer and capacitor maunfacturers--15 per cent; wastepaper recyclers--five per cent; wax and plasticizers--five per cent.[52]

Accidents also account for some PCB discharge. The Japanese rice-oil incident, for example, was one such accident. Another serious accident occurred on March 5, 1973, when a General Electric transformer being trucked through Tennessee began to leak PCB oil. A local policeman refused to let the truck proceed while it was leaking, so the driver's dispatcher instructed the driver to drain the transformer and drive it to a repair facility. Only after the incident had occurred was GE notified, and GE had to remove all contaminated soil from the area.[53]

PCBs that escape into the environment, by landfill leaching, accidental spill, transformer manufacturer's effluent, etc., end up settling in river, lake, or ocean bottoms. In rivers, PCBs tend to settle where the current slows--such as in Lake Pepin on the Mississippi River.[54]

A researcher for the Minnesota Pollution Control Agency's Division of Water Quality notes that industrial and muni-

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[52]Ibid.

[53]"GE Digs Its Way Out After Costly PCB Spill," *Electrical World*, June 15, 1973, p. 155.

[54]Marvin E. Hora (Paper prepared by the Minnesota Pollution Control Agency, Division of Water Quality), November 12, 1975, p. 1.

cipal effluents cannot be considered to be significant sources of PCBs in Mississippi River water. The source appears to be dredging operations that resuspend PCBs settled over the years.[55] He also notes that PCB concentrations in fish seem to correspond to PCB concentrations in the river sediment where the fish live.[56]

PCB Toxicity

Only recently have the toxic effects of PCBs been carefully researched. PCBs have been shown to interefere with the reporductive processes of fish, birds, and mammals.[57] Eggshells produced by birds that ingested PCBs are often thinner.[58] Rats fed PCBs at 100 ppm for 21 months got large numbers of malignant liver tumors.[59]

At the University of Wisconsin-Madison, Pathologist James Allen has been studying the effects of low PCB doses (2.5 and 5.0 ppm) on Rhesus monkeys. Even though the 2.5 ppm dose is one-half that permitted in human food, toxic symptoms developed in the monkeys in two months. The monkeys' skin showed a characteristic acne, their eyes became swollen, and they lost some hair. Female monkeys had trouble conceiving. Only 12.5 per cent of those monkeys fed a diet with 5.0 ppm of PCBs conceived, and 37.5 fed a 2.5 ppm dose conceived. But 90 per cent of those fed no PCBs conceived.[60]

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[55] Ibid.

[56] Ibid., p. 2.

[57] Ahmed, Testimony, p. 3.

[58] Ibid.

[59] Ibid., p. 4.

[60] Allen, p. 1677

PCB Control

As a result of the environmental and toxicological findings over the past decade, many government agencies have set up controls on the use of PCBs. In 1971, Norway required that PCB uses be authorized by the Ministry of Social Affairs. In 1972, Sweden required users to obtain authorization from the country's Environmental Protection Board. Finland and the Netherlands banned PCB use in copy paper, and following the rice-oil incident, Japan banned all PCB manufacture in 1972.[61]

In the United States, control action came not from government, but from the industry that manufactures PCBs. Monsanto voluntarily curtailed PCB sales to all companies using PCBs in open system products.[62] In addition, Monsanto incinerates used PCBs for closed system users.[63]

While not yet making any laws banning PCB manufacture, sale, or use, the United States Environmental Protection Agency eventually hopes to eliminate production of PCBs and PCB-containing products.[64] Monsanto has also agreed to stop manufacturing PCBs when an adequate substitute is developed, either by Monsanto or another company.[65]

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[61]OECD, p. 38.

[62]Monsanto, p. 5.

[63]PCBs can be destroyed only by burning at temperatures above 2500° Fahrenheit--requiring a special incinerator.

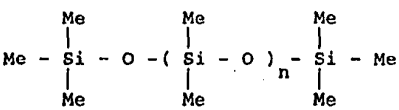
[64]Train, p. 3.

[65]Monsanto Company, Press Release, January 26, 1976, p. 1.

The Wisconsin Department of Natural Resources recently set a ruling limiting PCB effluents to 10 ppm.[66] And a bill recently passed by the Wisconsin Assembly bans manufacture, sale, and purchase of PCBs or any PCB-containing product by February 1, 1977, for all uses except as a dielectric or for research purposes. The bill also exempts paper recyclers who have no way of recognizing or separating old carbonless copy paper from the waste they buy. The electrical use exemption can be lifted by the DNR when it determines there is an adequate substitute for PCBs.[67]

Possible Substitutes

Few substitutes for PCBs in electrical equipment have been proposed. One possible compound that might be used is polydimethysiloxane fluid. Dow Chemical Company researchers



claim the chemical has low toxicity, but they do not know whether or not it accumulates in the food chain.[68]

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[66]Boller, p. 2.

[67]State of Wisconsin, *1975 Assembly Bill 1342, Assembly Substitute Amendment #1*, pp. 1-4.

[68]Dow Corning Company, (Report on PCB Substitute), August 29, 1975.

CONCLUSION

It is generally agreed that while PCBs are an environmental problem and their use should be banned in open system applications, they as yet have no ideal replacements for use in electrical equipment. With care in handling, their escape to the environment can most likely be minimized. As soon as an alternative to PCBs can be found, Monsanto has agreed to stop manufacturing them, and their overall use will probably be banned by government agencies.

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