PCB REMOVAL FROM TRANSFORMER INSULATING FLUIDS

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Paper No. PCI-81-4

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ABSTRACT

PCB removal techniques differ from PCB destruction techniques in that they seek the reclamation of the electrical insulating fluid as well as the destruction of the PCB contaminants. There are two different approaches to PCB removal; these are chemical decomposition and physical separation. A schematic of the various processes for PCB removal is presented, along with a discussion of each technique.

INTRODUCTION

Polychlorinated biphenyls were first introduced in large quantities in 1929. Their excellent dielectric properties, low flammability, high heat capacity, chemical and thermal stability were recognized almost immediately as having the potential to provide low fire risk indoor type transformers with the inherent advantages of liquid cooled efficiency and reliability. General Electric Company patented the electrical application of these fluids, and they were subsequently marketed as transformer askarels under such trade names as Pyranol (General Electric), Inerteen (Westinghouse), and Chlorextol (Allis-Chalmers).

In the late 1960's, it became apparent that PCB's had entered and contaminated the environment (primarily from non-electrical applications). Investigation into the long range effect of this contamination demonstrated that although the acute toxicity of PCB's was low its resistance to biodegradation and its tendency to bioaccumulate and biomagnify could create situations where PCB levels would be harmful to man and his environment. As a result, manufacturers instituted voluntary restrictions on the sale and use of PCB's except in closed electrical equipment, federal and state agencies took steps to minimize or eliminate the release of additional PCB's into the environment, and users also instituted controls to prevent the further spread of PCB contamination.

Unfortunately, during the first forty years of use the environmental problem with PCB's was not recognized, and a number of activities took place which caused the widespread PCB contamination of conventional oil-filled equipment. Transformer manufacturers used common filling hoses for both PCB's and regular transformer oil, common oil processing equipment, common impregnation equipment, and in some cases actually impregnated transformers with PCB's for electrical testing safety and then subsequently drained and refilled them with conventional transformer oil. Owners of transformers (and contractors servicing them) used common hoses, pumps and filters on both PCB transformers and conventional oil-filled transformers. Oil storage tanks in service shops were sometimes used interchangeably for conventional transformer oil or for PCB's.

As a result of these manufacturing and maintenance practices, there are now millions of gallons of conventional napthenic transformer oil, both in operating transformers and in bulk storage tanks, that are contaminated with relatively low, "less than 500 PPM (of .05%)," PCB levels. There is a much smaller volume of "high fire point" liquids used as transformer insulating fluid in place of the askarel in retrofilled PCB transformers. Due to leaching of the impregnated PCB's out of the cellulose in these transformers, the retrofilled fluids typically become contaminated at relatively high, 5 to 20% (50,000 to 200,000 PPM), PCB levels.

Since there is only one commonly used transformer insulating fluid, this paper will deal primarily with removal of PCB's from conventional napthenic transformer oil; the special case of PCB removal from high fire point liquids will be treated as a separate section.

REVIEW OF BASIC APPROACHES TO PCB REMOVAL

Since the early 1970's when the environmental problems of PCB's were first recognized, two different approaches to PCB removal have received ever increasing attention: CHEMICAL DECOMPOSITION and PHYSICAL SEPARATION. In the first approach, the methods seek the destruction of the PCB molecule itself; since these methods offer a final resolution to PCB contamination, they are being very thoroughly studied by a wide variety of public and private institutions. In the second approach, the methods seek removal and concentration of the PCB contaminants for subsequent disposal; although in many cases this two-step process of isolation and disposal could be economically attractive, these methods have not yet received widespread attention. This may largely be attributed to the fact that until the recent EPA approval of two PCB incinerators, there was no way to dispose of the PCB's; once removed, they could only be stored.

In the paper, "PCB Problems: From Basics to New Innovations for Disposal,"[1] the author differentiates between methods designed for reclamation of contaminated fluids and methods designed primarily for the destruction of PCB liquids. The schematics outlining the various processes are reproduced in Figures 1 and 2. The bottom half of Figure 1 provides a breakdown of the chemical and physical approaches to PCB removal; the remainder of the schematics serves to put these processes into perspective with the many other techniques being developed today.

Regardless of the ultimate disposition of the PCB's themselves, certain performance criteria apply to all potential methods for removing PCB's from transformer insulating fluids:

1. THE SYSTEM MUST BE EFFECTIVE.
Final PCB levels must be well below the EPA defined maximum (currently 50 PPM). Recovery rate of the insulating fluid should be high.

2. THE SYSTEM MUST MAINTAIN THE INTEGRITY OF THE INSULATING FLUID.
The fundamental composition of the fluid should not be altered; the process should not preferentially remove any significant components of the fluid, and no new chemicals should be added as a result of the process. The electrical, chemical, physical, and aging characteristics of the processed fluid should be as close to new fluid as possible.

3. THE SYSTEM MUST BE COMMERCIALLY VIABLE.
It must be economical, non-polluting, easy to use, and must use readily available chemicals and equipment. The system should be applicable to bulk storage tanks and to in-service transformers.

CHEMICAL DECOMPOSITION

In the book, "The Chemistry of PCB's,"[2] the authors state "one of the main reasons for the usefulness of PCB as industrial compounds is their low reactivity. For instance, PCB's are stable to conditions of hydrolysis and oxidation encountered in industrial use." "The most important reactions known to occur with chlorobiphenyls" are discussed in the chapter "Chemical Reactions of Chlorobiphenyls." These reactions pertinent to PCB removal are: oxidation, reduction (reductive dechlorination), reaction with alkanide, and reaction with amines. All of the current systems for the chemical decomposition of PCB's employ one of these methods.

The chemical decomposition of PCB's while they are dissolved in a potentially recyclable fluid is a difficult process. Any method that seeks the destruction of the PCB molecule must necessarily involve very strong reactants, very harsh processing conditions, or both. The problem, therefore, is to find a chemical process that specifically attacks the carbon-chlorine bond of the PCB molecule and yet does not damage the remaining fluid. A variety of chemical, biological, and radiation-induced PCB decomposition methods are referenced in the annotated bibliography, "Degradation of Chemical Carcinogens."[3] Most of these, however, have not been tested for use with conventional transformer oil.

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The oldest [illegible] "petroleum naphtha" [illegible] is covered [illegible] Whistler's book "Insecticide Chemistry: Their Uses, Manufacture, and Properties."[4] Chlorinated naphthenic transformer oils contain a large percentage of cycloparaffins (naphthenes), often with alkyl substituents. There is a moderate percentage of regular (straight and branched chain) paraffins, and a small percentage of aromatics. Extensive refining processes are used for the production of transformer oil. "Severe hydrogenation, also called 'hydrofining,' is used to reduce the total unsaturated ring compounds; for example, aromatic to napthene and paraffin hydrocarbons." "In producing electrical oils particular attention is paid to producing an oil with good electrical properties, oxidation stability and, where required, gas-absorbing properties. This calls for a low sulphur and nitrogen content, but an optimum aromatic content."[4]

Whereas new transformer oil *essentially* contains only paraffins, napthenes, and aromatics, aged transformer oil is a very complex mixture that also contains water (primarily from the thermal and chemical degradation of the cellulose in the transformer), esters, ketones, organic acids, alcohols, and sludge products (from condensation and polymerization reactions). Due to arcing, partial discharges, and thermal degradation there will also be dissolved gases such as hydrogen, methane, ethane, ethylene, and acetylene. Other contaminants include metallic salts (of iron, copper, aluminum) and various other ionic and polar compounds depending upon the method of refining, the composition of the initial crude petroleum, and the materials used in the construction of the transformer (wire insulation, etc.).

Since many of the contaminants in aged oil either will participate in any reaction involving PCB's or will inhibit or catalyze the reaction, the development of a particular chemical decomposition method becomes very difficult indeed. Several methods are, however, being commercially developed, such as the Acurex, PCBX (SunOhio), and NaPEG (Franklin Institute) systems.

Chemically Induced Decomposition

"Alkali metals such as sodium (and potassium and lithium) happen to be both very aggressive chemically and very specific (within the range of compounds found in most PCB contaminated liquids) toward the carbon-chlorine bond. Therefore, most of the chemical destruction processes for PCB's employ sodium as the active compound. Since sodium metal is quite dangerous to work with, virtually all of these techniques first react sodium to some organic compound to create a new organo-metallic compound that is then used as the reagent to decompose the PCB's. This intermediate step allows the sodium to be processed at a central plant, producing a reagent that is easier to transport and safer to use."[1]

In the Goodyear process,[3] for example, napthalene is dissolved in tetrahydrofuran and then reacted with sodium shot to form sodium napthalide. The sodium napthalide mixture is then used as a reagent to strip the chlorines off of the PCB molecules. The end products are a polymerized mass of biphenyl units, salt, and any secondary reaction products. The sodium napthalide must be used in a 100:1 stoichiometric excess at low PCB levels to ensure complete reaction, and the excess reagent is destroyed with a water quench. The resulting napthalene (and tetrahydrofuran) remain in the fluid, also. Acurex Corporation has modified the Goodyear process to use a new intermediate compound rather than napthalene, since napthalene is presently a Priority 1 pollutant.[5]

Other techniques such as reductive dechlorination using hydrogen over a nickel catalyst[6] and voltammetric reduction[7] are being explored, but it is not known at this time whether or not these techniques will be applicable to the reclamation of oil as well as the destruction of the PCB's. Researchers at the British Columbia Hydroelectric Utility in Vancouver, have developed a process that can use lithium or potassium as well as sodium; the chemistry of the process has not been specified, however.

The most widely publicized chemical destruction process for PCB's is undoubtedly the PCBX process developed by Sun-Ohio Corporation. While the operation of the prototype mobile unit was presented recently,[8] the actual chemistry of the process has never been revealed to the general public. It appears, however, that this process uses sodium metal, reacted with an amine, to accomplish the dechlorination of PCB's. It is known, for example, that sodamide (formed from sodium plus ammonia) will, if dissolved in liquid ammonia, rapidly dechlorinate PCB's. When the information finally is released, it will be interesting to learn the chemistry of the actual process employed by PCBX. The by-products of the PCB destruction are a polymerized chain of biphenyl molecules and "naturally occurring chlorides."[1]

Another sodium based process has been developed by the Franklin Institute. Unlike the other processes, however, the NaPEG (Sodium, Na + Polyethylene Glycol, PEG) reagent employed in this process is an alkoxide rather than a simple metal-organic compound. "Chemically, it is insensitive to moisture or air and precautions to exclude these simple substances are therefore unnecessary."[9] When the NaPEG is reacted with PCB's, the PCB molecules are oxidized rather than [illegible] and the PCB decomposition products [illegible] pounds. "The reaction products are: purified oil, [illegible] sodium chloride — ordinary table salt. The treated oil is easily cleaned up by water washing, drying and returning to service. If desired. The washings and other reaction products are treated simply and discharged to municipal sewage systems, biodegraded, or drummed for disposal in an ordinary landfill."[9]

Radiation Induced Decomposition

In the book, "Degradation of Chemical Carcinogens,"[2] both photodecomposition and ionizing radiation methods are referenced, these include the use of Cobalt-60, ultraviolet light, and sunlight. The only system being explored commercially, however, seems to be that of Atlantic Research Corporation,[6] which uses hydrogen gas as a reducing agent, and employs ultraviolet light to excite the PCB molecules and make them more reactive.

Biologically Induced Decomposition

Although many studies have been carried out using various microbes[2,3], the success of these attempts has been limited, and there are as yet no commercial ventures using this technique. The great specificity of the biological systems is a drawback in this case; heavily chlorinated biphenyls are either not attacked at all, or only very slowly. Furthermore, the position of the chlorine atoms on the two rings is critical to the stereochemistry of the enzymes.

PHYSICAL SEPARATION OF PCB'S

Physical processing techniques provide a promising means for reduction of PCB's in transformer oils. Physical processing can reduce PCB's from 500 PPM (or more) to less than 50 PPM and provide a greatly reduced volume of material which must be disposed of. Although physical methods do not destroy PCB's, the much smaller volume of material which contains the PCB's can be easily stored and can be easily shipped to PCB incineration facilities. Furthermore, physical processing methods are less likely to result in detrimental changes to the properties of transformer oils than are chemical destruction methods.

The greatest problem in the physical separation of PCB's from transformer oil is the fact that neither fluid is a single, simple compound; both fluids are complex mixtures of various molecular weight compounds having similar properties. As a result, both PCB's and transformer oil have very broad distillation ranges. Even a gas chromatograph column used for PCB detection cannot normally separate the PCB's from the oil; because the peaks overlap so much, special chlorine sensitive detectors are used so that the interference from the oil will be minimized. Despite the problems associated with physical separation, however, some successful methods have been developed, such as a proprietary azeotropic distillation process for hydraulic fluid (Battelle-Columbus Laboratories), and a chemisorption process for transformer oils (EPAC System, RTE Corporation).

Distillation

Distillation is used to separate solutions into higher and lower boiling constituents. Vacuum distillation refers to distillation at pressures below atmospheric. Vacuum is used to reduce the vapor pressure requirements, and thus the temperature of the system; distilling at atmospheric pressure would result in temperatures which would probably decompose the transformer oils. Since vapor pressure is not a constant function of temperature for all materials, it is often possible to find an optimum pressure range for the separation of two materials.

In theory, any two components can be separated by distillation as long as their boiling points are not identical. In practice, as the boiling points approach each other, the separation becomes more and more difficult and more and more costly. If PCB's were lower boiling than the oil they were to be separated from, the PCB's could be easily and economically removed as an overhead product. However, the PCB's are higher boiling than most of the oil they are to be separated from; the PCB's could therefore be removed as the "bottoms" but the process would be less energy effective since the bulk (over 95 percent) of the material would have to be taken off overhead. Since a portion of the PCB's and the oil that they are to be separated from boil at about the same temperature, separation is difficult and other means, such as azeotropic separation, would be more effective.

An alternative to vacuum distillation would be steam stripping. The presence of steam reduces the vapor pressure (and thus temperature) required for a material undergoing distillation. Separations can thus be achieved at atmospheric pressure without thermally damaging the materials being separated. Steam stripping may also be carried out at pressures above or below atmospheric. This technique, however, is still subject to the problems of overlapping boiling ranges.

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In azeotropic separation, a substance not normally present in the mixture is added to effect separation by changing the relative volatility of the most difficultly separable component. The added substance (azeotrope former or entrainer) forms a weak chemical bond with the component and the combination is referred to as an azeotrope. Usually, when the azeotrope appears in the overhead during distillation, the process is referred to as azeotropic distillation. When the azeotrope leaves the column with the bottoms products, the process is referred to as extractive distillation.

It would be desirable for the entrainer to form a low boiling azeotrope with PCB since the separation could then be accomplished by distilling over the small quantity of the azeotrope rather than the large quantity of transformer oil. In addition to forming a low-boiling azeotrope, the entrainer should be soluble in the transformer oil, and it should be easily separable from both the PCB mixture and the transformer oil. (The easiest separation would occur if the entrainer and the PCB's were immiscible.)

These various distillation (or "stripping") techniques are being investigated, and appear to work very well, for the removal of PCB's from simple compounds such as solvents or synthetic hydraulic and heat transfer fluids. It is unlikely that the problem of the broad boiling ranges of transformer oils and PCB's can be overcome, so these techniques probably will not become commercially viable for insulating fluids.

Extraction

Liquid-liquid extraction of PCB's from transformer oil materials can in theory be a very simple method of PCB removal. To successfully extract PCB's a solvent system must be found in which the PCB's are more soluble than the other transformer oil components. The alternative situation in which the PCB's are not as soluble as the other transformer oil components is probably not practical because of the small amounts of PCB's present and the almost universal solubility of PCB's in nonaqueous solvents. In practice, PCB's are soluble in almost every nonaqueous solvent and even to some extent in alcohol-water systems. The solubilities of the other transformer oil components will vary somewhat with the type of transformer oil. In general, however, the solubility of PCB's in hydrocarbons is greater than in virtually all other common solvents.[3]

Although several companies are now experimenting with extraction techniques, the strong affinity of the hydrocarbons for the PCB's and the fact that the oil is a mixture of aromatics and aliphatics will make commercialization of this technique very difficult.

Adsorption

In adsorption processes, one or more constituents of a complex mixture are preferentially adsorbed onto a solid phase thereby bringing about a separation between the constituents of the mixture. The primary objective in the development of a process for adsorbing PCB's from transformer oil would be to find an adsorbent which preferentially removes PCB from the oil. Depending on how tightly the PCB's are bonded to the solid phase, adsorption processes could be developed that are batch-oriented, semi-batch, or continuous in operation.

There are two filtration systems in use today for removal of PCB's from contaminated fluids: the EPAC system for hydrocarbons, and activated charcoal for silicones. The EPAC filtration system developed by RTE Corporation employs a chemisorption process, and was originally intended to remove high level (up to 10 percent or 100,000 ppm) PCB contamination from RTEmp fluid in retrofilled askarel transformers. (RTEmp fluid is a high fire-point liquid dielectric coolant that is produced from paraffinic hydrocarbons, and many of its characteristics are quite similar to conventional naphtenic transformer oil.) The predominant use today for EPAC systems is to remove relatively low level (below 2,000 PPM or .2 percent) PCB contamination from conventional transformer oil, either in bulk storage tanks or in operating transformers.[10]

HIGH FIRE POINT LIQUIDS

High fire point dielectric fluids are required by NEC 450-23 to have a fire point in excess of 300° C.[11] Although their primary use is to provide extra safety in critical applications of new transformers, they are also being used as replacement fluids in existing askarel filled transformers ("retrofilling" of transformers). Although there are several high fire point fluids being marketed, including synthetic esters and chlorinated benzenes, there are only two fluids that are being used in significant volumes: high molecular weight hydrocarbons and polydimethylsiloxanes (silicones).

When a "retrofilled" transformer is placed back into service, the new, clean fluid gradually becomes contaminated as the residual PCB's leach out of the cellulose. "If the transformer has been properly drained and flushed, with removal of the bottom residual fluid at each step, the initial concentration in the new dielectric fluid should be less than 1 percent PCB. However, due to the large quantity of oil-laden in a typical transformer, between 4 and 6 percent of the total original volume of askarel will still be contained in the windings of the transformer. This impregnated askarel cannot be removed by a simple flushing process. Once the transformer is energized, the internal heat generated in the coils will promote diffusion of the PCB's from the paper out into the oil."[12]

In order to remove the PCB's that diffuse out into the new dielectric fluid, RTE Corporation has developed the EPAC Filtration System for RTEmp fluid[10], and silicone fluid retrofill contractors have developed an activated charcoal filter. The EPAC system is designed to be attached to the transformer and performs a continuous filtration of the RTEmp fluid; the activated charcoal filter for silicone units is hooked up to the transformer for a few hours about every six months. In either case, the limiting factor in achieving a permanently low level of PCB contamination is the availability of the PCB's in the fluid; neither filter can remove PCB's any faster than the leaching rate makes them available. For this reason, both systems will necessarily be equivalent in terms of overall length of time required.

So far, only physical separation techniques have been developed for removal of PCBs from the high fire point fluids. Since the volume of contaminated conventional oil is so much greater, virtually all of the work on chemical decomposition methods have concentrated specifically on that fluid.

CONCLUSIONS

Many new techniques for the removal of PCB's from transformer insulating fluids are currently being developed. The most promising approaches are chemical decomposition (PCBX, NaPEG, Actinex) and adsorption (EPAC).

Chemical decomposition techniques must be very aggressive toward PCB's and yet very gentle toward the insulating fluid; furthermore, they must contend with a wide variety of additional types of contamination in aged oils.

Physical separation techniques are hampered by the broad, overlapping boiling ranges of PCB's and of conventional transformer oil, and by the fact that both fluids are complex mixtures of many compounds.

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DISPOSAL OF PCB CONTAMINATED LIQUID

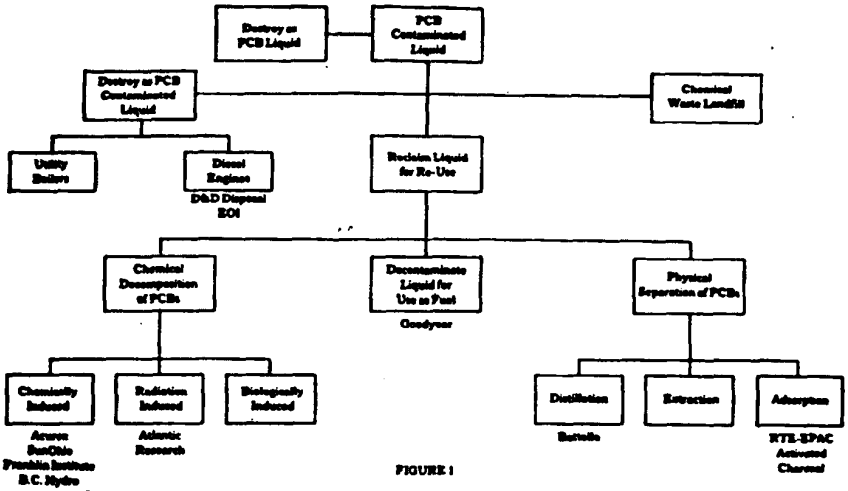

FIGURE 1

Na + PCB
⇓
NaCl + [illegible]

DISPOSAL OF PCB LIQUID

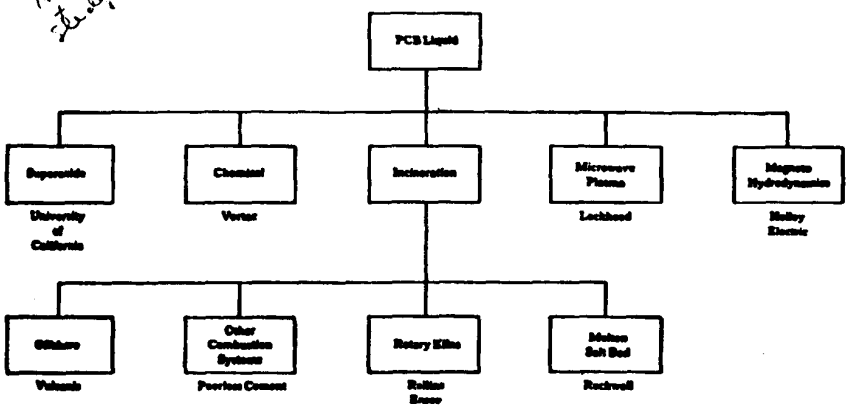

FIGURE 2