An economic, commercial process for

Detoxifying PCB-Contaminated Transformer and Heat-Transfer Fluids

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SAFE disposal of highly toxic polychlorinated biphenyl (PCB) transformer and heat-transfer fluids long a perplexing problem for plant engineers (see section "The PCB Disposal Dilemma")—is now feasible, using a recently developed chemical treatment process. The treatment, which is also applicable to other halogenated contaminants such as polybrominated biphenyls and DDT tetrachlorobenzodioxin pesticides and herbicides, extracts the toxic ingredients and converts them into a nontoxic residue that can be safely incinerated in conventional equipment. The contaminant-free fluids can be recovered for reuse.

The process has been successfully used on a large scale at a Goodyear plant. Batches of PCB-contaminated heat-transfer fluids, ranging in size from 100 to 2000 gal, have been converted to environmentally acceptable substances. Typically, PCB content has been reduced from 82 ppm to less than 10 ppm—well below the Environmental Protection Agency's (EPA) 50 ppm maximum permissible limit. The EPA is evaluating the process and patents are pending. When granted, the patents will be dedicated to the public and the process will be made available for widespread use.

Target Goals—The following goals were established when the technique was developed. The process should

- Permit complete, yet selective, conversion of chlorinated substances to nontoxic, easily disposable products
- Be capable of use on plant premises, preferably in existing equipment
- Handle either small or large volumes of materials
- Have relatively low equipment and operating costs.

Major steps in the process are shown in Fig. 1. The method used to convert the PCB-contaminated fluids consists essentially of causing the fluids to react with an organosodium reagent, sodium naphtha-

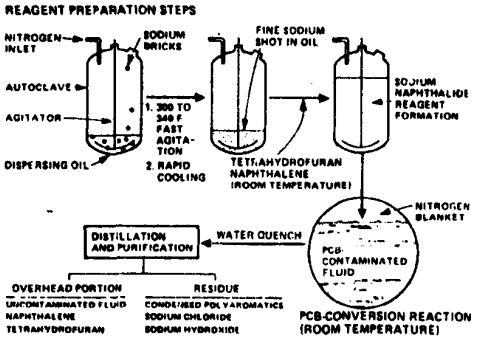

Fig. 1. Batch process converts PCB-contaminated heat-transfer fluids into nontoxic residue capable of being safely incinerated by conventional equipment. Contaminant-free fluids are recovered for reuse.

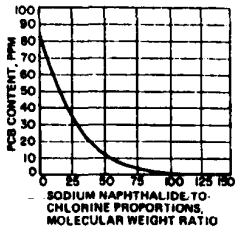

Fig. 2. A minimum 50-to-100 gram molecular weight ratio of sodium naphthalide to chlorine is needed to remove 98 percent of PCB from standard heat-transfer fluid containing 82 ppm of PCB.

MONS 009252

"The reaction destroys the chemical bonds that previously held the PCBs together and created the toxic effects."

The PCB Disposal Dilemma

The ideal fluid for electrical equipment and heat-transfer systems has excellent heat stability, a non-flammable nature, low volatility, and good viscosity characteristics at operating temperatures. These properties are characteristics of some chlorinated aromatic compounds that have found widespread use as a family of related materials known as Aroclors and askarels.

However, subsequent events have demonstrated that coupled with their desirable properties, these materials (collectively known as polychlorinated biphenyls or PCBs) also have undesirable properties that can cause health problems. The chemical stability and environmental persistence of PCBs, coupled with their widespread use in the 1960s and 1970s, indicated the possibility of a potential health hazard to the public.

Their manufacture was discontinued and EPA regulations were issued under the authority of the Toxic Substances Control Act to control the materials currently in use in the U.S. The regulations became effective July 1, 1980. They define any material containing 50 ppm or more of a mono- or polychlorinated biphenyl as a PCB and regulate its use and disposition. Currently, the only permissible disposal of a PCB is by incineration in an EPA-approved incinerator (none exist) or by burial in an EPA-approved landfill.

Either method requires transportation from the point of use to the disposal site, thereby increasing the chances of inadvertent release into the environment. Furthermore, the siting of incinerators to burn PCBs has met strong opposition from local residents of areas under consideration. Consequently, the chemical conversion of PCBs to environmentally acceptable by-products is a most desirable solution.

MATERIAL COSTS FOR TREATING HEAT-TRANSFER FLUID CONTAINING 82 PPM OF PCBs

Material	Amount required to treat 100 lb of oil, lb	Cost/lb, dollars*	Cost/100 lb of oil, dollars
Sodium	0.1098	0.60	0.0747
Heat-transfer oil (PCB contaminated)	1.0994	-----	-----
Naphthalene	0.7029	0.36	0.2530
Tetrahydrofuran	1.9525	0.86	1.6792
Total			2.0069

*Prices listed in *Chemical Marketing Reporter*, February 18, 1980. Unit cost depends on quantities purchased.

lide. The reaction destroys the chemical bonds that previously held the PCBs together and created the toxic effects.

The reaction takes less than 5 min under an inert atmosphere (nitrogen) at room temperature in glass or steel vessels. A minimum mole ratio of sodium naphthalide to chlorine of 50 to 100 is required to remove 98 percent of PCBs from a standard heat-transfer fluid containing 82 ppm of PCBs, Fig. 2.

Only small amounts of heat are generated when the reagent is mixed with the heat-transfer fluid and when the reaction is taking place. Although the reaction is essentially completed in a matter of minutes, the mixture is held in the reactor for several hours to ensure complete reaction. Following this holding time, the solution is quenched with water and distilled under vacuum to recover the reagent and the contaminant-free heat-transfer fluid. The residue remaining after distillation consists of non-halogenated polyphenyls and sodium chloride that can be safely incinerated.

Reagent Preparation—The procedure for preparing the reagent is relatively simple but requires careful control. Approximately 150 to 400 mL of either fresh or contaminated heat-transfer fluid per gram-atom of metallic sodium pieces are charged to the reagent preparation vessel. The mixture is then vigorously stirred at 300 to 340 F for 5 to 10 minutes under an inert (nitrogen) atmosphere.

The treatment produces highly reactive, finely dispersed, liquid-sodium droplets. Agitation is continued while the mixture is rapidly cooled to room temperature. Cooling causes the sodium droplets to solidify into fine, bright spheres.

A tetrahydrofuran solution of naphthalene is then added to the mixture. The addition instantly begins to produce the organo-sodium reagent, sodium naphthalide, as evidenced by the formation of a characteristic greenish-black color. Gentle, additional stirring for 1 to 4 hours completes the preparation of the reagent, which is then ready for use. At this point, the reagent solution is homogeneous.

However, it is imperative that extreme caution be taken with all reactions involving metallic sodium. Rapid generation of hydrogen occurs when sodium makes contact with water. For this reason, care must be taken to ensure that no metallic sodium enters the PCB-conversion-reaction vessel. Also, during the water quench step, the water must be added in small amounts over a long period to minimize possible hydrogen release. Nitrogen or a similar inert gas is used as a blanket to prevent the formation of potentially explosive hydrogen/oxygen mixtures.

Economics—Chemical material costs for the PCB treatment process are about $0.02 per pound of recovered heat-transfer fluid, compared to $1 per lb for newly purchased fluid. The cost does not include savings realized from naphthalene and tetrahydrofuran recovery, which can be significant in large-scale operations. Data for large scale treatment of heat-transfer fluid contaminated with 82 ppm of PCBs are shown in the accompanying table.

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