RESEARCH LABORATORIES
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A SAFE, EFFICIENT CHEMICAL DISPOSAL METHOD FOR POLYCHLORINATED BIPHENYLS - "PCB's"

In the design of electrical equipment and heat transfer systems for various applications, the ideal fluid from a design standpoint is a material having excellent heat stability, a nonflammable nature, low volatility, and good viscosity characteristics at operating temperatures. These properties are characteristics of some chlorinated aromatic compounds and as such, were exploited by the development and widespread use of a family of related materials known as Arochlors or Askarels. Subsequent events have demonstrated, however, that coupled with their desirable properties, these materials, collectively known as polychlorinated biphenyls or PCB's, also can cause serious health problems. The chemical stability and environmental persistence of PCB's coupled with their widespread use in the 1960's and 70's therefore indicated the possibility of a potential health hazard to the public at large. For this reason, their manufacture has been discontinued and regulations have been issued under the authority of the Toxic Substances Control Act (TOSCA) to control the fate of those materials currently in use in the United States.

These EPA regulations, which became effective July 1, 1979, define any material containing 50 ppm or more of a mono- or polychlorinated biphenyl as a "PCB" and regulate closely its use and disposition. Currently, the only permissible disposal of a PCB is by incineration in an EPA approved incinerator (none of which currently exist) or by incorporation in an EPA approved landfill.

Either method requires transportation of the PCB from its present location to the disposal site, thereby increasing the chance of inadvertent release into the environment. Furthermore, the siting of incinerators to burn these materials has met particularly strong opposition from local residents of areas under consideration.

In considering the problems to be faced in meeting the now effective regulation of 50 ppm PCB's, certain criteria necessary for the ideal conversion process were clearly defined. These included:

1. The process adopted should allow for complete yet selective conversion of chlorinated species to non-toxic, easily-disposed-of products.
2. The process should be capable of being performed on-site, preferably in existing equipment.
3. The process should be adaptable to the treatment of very small or quite large volumes of materials.
4. The process should be relatively low in cost.

In an effort to develop a method that would meet the above criteria, screening tests of the application of known macro-scale reactions of halogenated aromatics were applied to a heat-transfer fluid containing micro-quantities (120 ppm) of chlorinated biphenyls. Those methods found to offer significant reductions in PCB levels were further evaluated. Ultimately two approaches were considered

for further work; the catalytic hydrogenolysis of carbon-chlorine bonds over a palladium catalyst and the cleavage of such bonds by the use of sodium or organo-sodium reagents.

Both methods are adaptations of known reactions which are described primarily in analytical methods literature.[1-6] Under the appropriate conditions, both methods have been shown in our laboratories to readily dehalogenate PCB materials, reducing levels from ~120 ppm to less than 10 ppm. The catalytic hydrogenolysis method however, was found to require high temperatures (150-250°C) and moderate pressures (~110 psig hydrogen) thus necessitating special equipment. For this reason, the reaction with sodium or organo-sodium reagents was deemed to be the most likely to succeed in meeting proposed target criteria.

Laboratory experiments demonstrated the ability of sodium metal per se to react with the chlorinated biphenyls under conditions of high temperature and good agitation as shown below.

Quantity of hydrocarbon oil	100 ml
PCB content	76 ppm
Sodium metal	0.10 gm
Time of reaction	6 hrs

Temperature	Remaining PCB Content (ppm) after 6 hrs
200°C	76
250°C	49
300°C	0.9

The reaction was obviously slow, and extremely high temperatures were required. Scale-up of this reaction only intensified the nature of these problems.

Reactions with the organo-sodium reagent, sodium naphthalide, on the other hand, were found to be extremely rapid at ambient temperature. The preparation of this reagent as described in the literature is quite straight forward. Suitable solvents for the preparation of the reagent are dimethyl ether, ethylene glycol dimethyl ether or tetrahydrofuran. Indeed, Japanese authors have recently described the use of this reagent in the gross dechlorination of high concentrations of polychlorinated biphenyls in tetrahydrofuran at 0°C.[7] Under these conditions they claim that only 1.1 to 1.3 moles of sodium naphthalide reagent per gram-atom of chlorine was required to completely remove all the organic chlorine. A similar method was also reported by workers at the University of Waterloo (Canada).[8]

In an attempt to adapt the analytical organo-sodium reagent and Japanese techniques to our problem of low level (ppm) PCB contamination it was discovered that the mole ratios of sodium naphthalide to chlorine in the 1.1 to 1.3 range were ineffective in obtaining any significant reduction in levels. As shown in Figure I, a ratio of approximately 50-100 was found to be the minimum necessary to remove 98% of the PCB's from a heat-transfer oil containing 83 ppm PCB. The reaction was found to proceed very rapidly (<5 minutes) under an inert atmosphere at ambient temperature in either glass or steel vessels.

Initially for small scale laboratory experiments, the sodium naphthalide reagent was prepared by dissolving 1.1 to 1.5 moles of naphthalene per gram-atom of sodium in tetrahydrofuran. Sodium pieces were then added to this solution under an inert atmosphere at room temperature. Stirring for two hours resulted in a deep greenish-black solution of the reagent. During our attempts to scale-up this laboratory preparation, it was noted that the reaction time for the formation of the reagent varied greatly and seemed to be somewhat dependent on the size (surface area) of the sodium pieces. To overcome this problem, a new procedure for reagent preparation was devised.

By using approximately 150-400 ml of either fresh or contaminated heat-transfer fluid per gram-atom of sodium, a very reactive (high surface area) form of sodium containing a minimum surface oxide coating could be generated. This was accomplished by heating any size piece(s) of sodium in the heat-transfer fluid under an inert atmosphere to 150-170°C for 5-10 minutes with vigorous stirring. This produces finely dispersed liquid sodium droplets. By rapidly cooling to ambient temperatures while stirring, the sodium droplets solidify into fine bright spheres. Addition of a tetrahydrofuran solution of naphthalene to the sodium sand in the heat-transfer fluid at ambient temperature instantly begins to produce the reagent as evidenced by the formation of its characteristic greenish-black color. One hour with gentle stirring is sufficient to complete the reagent formation. This procedure was found to be very effective on either small or very large scale. The reagent prepared by this method could be added in either a normal or inverse manner to a

large amount of additional contaminated heat-transfer fluid, with the amount of reagent adjusted to give a minimum reagent/chlorine ratio of 50 to 100. Only very slight exotherms were encountered during large scale mixing of the reagent and the contaminated heat-transfer fluid. The reaction proceeds very rapidly at room temperature. After approximately one hour, the excess reagent was quenched by adding at least a stoichiometric amount of water. Again only a slight exotherm was noted. The quenched fluid was then vacuum stripped to recover tetrahydrofuran and naphthalene for possible recycling. The residue was then subjected to further vacuum distillation. Almost pure heat-transfer fluid containing less than 1 ppm PCB's was recovered. The pot residues from this second distillation consist of non-halogenated polyphenyls, which may be safely burned, and sodium chloride.

Further experiments to determine minimum amounts of tetrahydrofuran to accomplish successful formation of the sodium naphthalide reagent were conducted in laboratory glassware, then verified in 5-gallon stainless steel reactors. The following quantities of materials were recommended for the reagent preparation and in the large scale treatment of a heat-transfer fluid contaminated with 87 ppm of chlorinated biphenyls: Quantities are given per 100 lbs of fluid to be treated. Prices indicated are those given in "Chemical Marketing Reporter", April 2, 1979.

	Lbs	$/Lb*	$/100 Lbs Oil
Sodium Metal	0.1098	0.64	0.0703
Heat-transfer Oil	1.0994		
Napthalene	0.7029	0.36	0.2530
Tetrahydrofuran	1.9525	0.86	1.6792
			2.0025

*Unit costs will depend on quantities purchased.

This procedure has been adopted for use on a commercial scale successfully. Significant amounts of material have been treated with the reagent to reduce chlorinated biphenyl content from 130 ppm to less than 10 ppm. Materials cost for this treatment, because of smaller quantities purchased approximated $0.03/lb, vs a heat-transfer oil original cost of greater than $1.00/lb. No credit for the recovery of naphthalene or tetrahydrofuran was considered in establishing material costs, though with large scale application of this technique such a recovery may be economically justified.

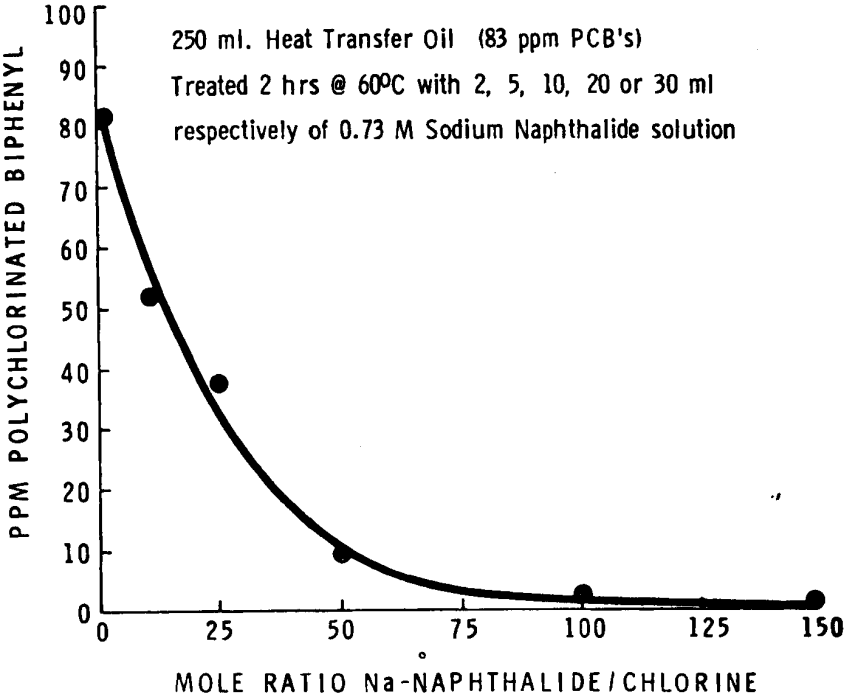
In conclusion, this technique can also be used to treat other halogenated contaminates such as polybrominated biphenyls (PBB's) and halogenated pesticides and herbicides like DDT and tetrachlorobenzodioxin. Additionally, the four criteria we originally established for an ideal process have been met. The process is selective, can be performed on-site in existing equipment, is adaptable to small or large scale operation and is relatively low in cost.

*Quantitative analyses for PCB's were performed on a Hewlett-Packard 5840A gas chromatograph with an EC-Ni^{63} electron capture detector.

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FIGURE 1



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