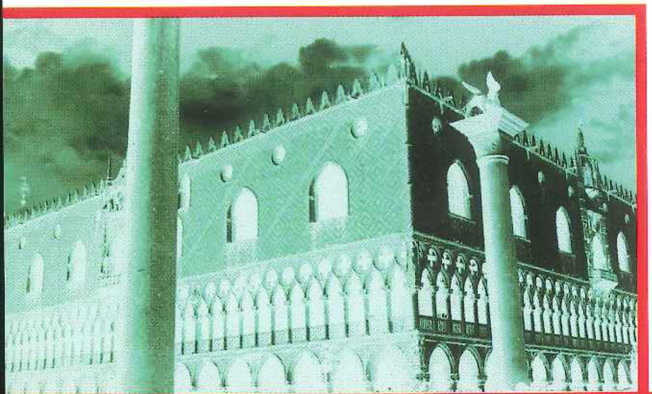
19th International

Symposium

DIOXIN 99



on Halogenated Environmental

Organic Pollutants

and POPs

September 12 - 17, 1999

Venice, Italy

Ecotoxicology-Metabolism-Epidemiology-Remediation Technology

A Continuous Technology for Decontamination of Electrical Equipment through Dechlorination of PCBs/PCTs/PCDFs/PCDDs in Insulating Oil - CDP Process® Applications

W. Tumiatti[1], A.Porciani[1],R.Actis[1], S.Kapila[2] and P.Nam[2]
[1]Sea Marconi Technologies Via Crimea 4- - 10093 Collegno (To) Italy

[2] Center for Environmental Science and Technology
University of Missouri - Rolla , MO 65409 USA

Abstract

The recent European Directive (No. 59/96 issued on 16 Sept. 1996) calls for the protection of the environment and implementation of new limits on the presence of PCBs in fluids and equipment. Under the directive, electrical devices containing insulating oils with PCB (PCBs+PCTs+PCBTs) concentrations in excess of 50 mg/kg are classified as PCB-contaminated devices. The directive sets forth requirements for decontamination of transformers, fluids and equipment. An innovative process has been developed that meets the requirements of the directive. The process relies on a continuous chemical dehalogenation technology that has been termed CDP Process®. This process reduces the concentration of PCBs/PCTs/PCDFs/PCDDs in insulating fluids well below the requirements and thus renders the equipment PCB free. The process also meets other requirements for proximity, self-sufficiency, and resource recovery as set forth in the European directive (Art. 3 "...decontamination and/or disposal shall be affected at the latest by the end of 2010."

Introduction

The recognition of PCBs as an environmental menace is a familiar saga of many synthetic industrial chemicals and spans well over a century (1867 – First lab synthesis by Griefs in Germany). It is characterized by the extraordinary functional features of these chemicals and their wide acceptance in the commercial sector (1927 - first industrial application by Swan USA). The later discovery of their incompatibility with the biosphere led to their designation as environmental pollutants, and the "PCB risk" has been a globally recognized problem for more than a decade (1966 - First identification in the environment by Jensen, Sweden) (1968 - first massive incident in Yusho Japan, involving 31,180 people intoxicated and 26 deaths, as a consequence of rice oil contaminated by PCBs/PCDFs/PCDDs leaking from a heat exchanger).

The risks posed by PCBs to the ecosystem have resulted in the promulgation of several national regulations on the prohibition of production and use of these chemicals (1976 EEC Directive 76/405 and 76/769. USEPA 1979 40 FR Part/961). A number of international agreements aimed at the elimination of these toxic and persistent compounds within an established schedule have also been reached. These include a bilateral agreement between the United States and Canada for the protection of water resources in the Great Lakes Region (18% of global reserves) and several European Directives.[1,2]

The term 'PCB', in Art. 2 of the most recent European Directive No. 59/96 include other halogenated compounds besides the 209 possible congeners. It includes PCTs (8557 possible congeners) and PCBTs (several thousand congeners) equivalents at concentrations beyond the50 mg kg^{-1} limit. These chemicals are collectively classified as dangerous, persistent, and bio-accumulative, causing an unreasonable risk for the environment and human health (i.e. contamination of foods, such as in Belgium, France, Italy in June 1999).[2]

In the event of uncontrolled thermal oxidation during the operation of transformers (hot spots > 150 °C) or in the event of failures (arching of electrical systems) with explosions or fires, significant concentrations of very dangerous compounds are generated, such as PCDFs (135 congeners) and PCDDs (75 congeners).

The use of PCBs as insulating liquid in electrical equipment, particularly capacitors and transformers, led to widespread contamination of the environment. It is estimated that nearly 30 million such units are in use around the world. These devices represent an extremely large volume of contaminated oil; the mass of contaminated oil in OECD countries alone is estimated to be 10 billion kg. The contaminated equipment and materials represent a capital cost of several hundred billions dollars. The task of handling and decontaminating such a large volume of equipment and materials presents costly technical and logistical difficulties.

A typical scenario of a European Country (i.e. France) regarding just generation, transportation, distribution electrical transformers of electric power with insulating liquids (average life 30 ÷ 40 years and costing 10,000 US$ per MVA to replace them) shows the following level of contamination ≥ 50 mg/kg of PCBs + PCTs+PCBTs: about 40 % of the distribution transformers, out of a population of about 1.2 million units (average weight 1000 kg each); 28 % of the generation a transportation transformers out of a population of about 15,000 units (average weight 80,000 kg each); similar situations for the transformers and equipment used by industries and services (instrument, tap changers, reactors, rectifiers, furnaces etc.).
During the past 20 years, several methods for the decontamination and destruction of PCBs and related compounds have been developed and used on an industrial scale. These include incineration, photolysis, radiolysis, chemical dehalogenation, biochemical transformations, and deposition in secured landfills.[3-9]Among these techniques, chemical dehalogenation is of particular interest because it allows for the protection of machines in operation while conserving valuable resources.

This abstract describes the performance and operational characteristics of a chemical dehalogenation process, designated the CDP Process.® The efficiency of the process has been successfully demonstrated through laboratory experiments and field applications for the dehalogenation of PCBs/PCTs/PCDFs/PCDDs.

CDP Process®

The uniqueness of the CDP Process® lies in the reagent composition, which permits its use in both batch mode and continuos mode. The reagent is comprised of a mixture of non-alkali metal catalyst, a polyalkyleneglycol or Nixolen, an alkali metal hydroxide or an alcoholate. Several combinations of nonalkali metal catalysts were evaluated, including iron, magnesium, aluminium, palladium, nickel, zinc and titanium. The catalysts were used in neat form or coated on suitable adsorbents. Polyalkyleneglycols of different molecular weights were used with different alkali metal and /or alkaline earth metal hydroxides.

The dechlorination of PCBs/PCTs/PCBTs/PCDFs/PCDDs in mineral oil was carried out in either batch or continuous mode. For the latter, the reagents were formulated on an appropriate particulate support to obtain a "solid reagent - S/CDP". This reagent was dry packed into flow-through columns. The columns are jacketed to permit operation at low temperatures (80-100°C). The flow-through reagent columns, pumps and ancillary valves and control circuitry were assembled into modular units. The modular units are suitable for on-site operation as the decontamination mobile units (DMUs). The DMUs in continuous mode are operated in a closed loop arrangement and controlled through a Controlled Logic Programmer (CLP) that continuously monitors vital parameters such as temperature, pressure, and flow. The CLP also permits three-levels of manual or automated intervention in case of a malfunction. These features facilitate and simplify on-site, on-line decontamination of operations with maximum safety considerations.[9,10]

Analysis of PCBs/PCTs/PCBTs/PCDFs/PCDDs

The level of PCBs contamination in treated and untreated oils were determined through the congener specific analysis. The PCB congener specific analyses were carried out with a high-resolution gas chromatograph HRGC (Model 6890, Hewlett Packard Instr.) interfaced to an electron capture detector (ECD) in accordance with method IEC/CENELEC 61619-97-04.11. The determination of PCBs and related compounds (PCTs/PCBTs) were performed in accordance with method pr. EN 12766 (Part 1, Part 2, Part 3) Version August 1998. Analyses of selected samples were carried out with a high-resolution gas chromatograph interfaced to a quadruple mass spectrometer (Model 5972, Hewlett Packard Instr. All measurements were made in accordance with USEPA protocol 8268 Good Laboratory Practices (GLP) guidelines were followed to ensure the validity of the analytical results and USEPA method 8280 Rev. 1 – Dec. 1996 (for PCDFs/PCDDs).

RESULTS

The efficiency of the CDP Process® was evaluated with oil and solid matrices contaminated by PCBs/PCTs/PCBTs/PCDFs/PCDDs. The PCB concentrations in the matrices ranged from 25-50,000 mg/kg (25-50,000 ppm). Dehalogenation rates obtained with the process were found to be considerably superior to the rates reported in literature for processes based on the traditional KOH/PEG reagents.[4-6] This was attributed to the presence of catalysts and hydrogen donors which enhanced hydro dechlorination of PCBs. The characterization of the CDP Process reaction products indicated that the overall process involves both hydro dechlorination and nucleophilic substitution reaction mechanisms. The process was also found to be more effective than the dimethyl sulfoxide (DMSO) reagent based process described by Peterson.[7] The efficiency of the process was improved significantly with the application of ultrasound. In one experiment the PCB concentration in insulating was reduced from 2,000 mg/kg to 2 mg/kg in one tenth of the time required for reaction carried out without the ultrasound.

The effectiveness of the CDP Process® has been demonstrated on PCDFs/PCDDs deriving from explosions/fires of equipment with PCBs.[8] Starting from 1983, in co-operation with Prof. Tundo – University of Turin, applications were performed with experiments promoted by Ufficio Speciale di Seveso (under Sen. Ing.. L Noé's responsibility) on samples of pure 2,3,7,8 TCDDs By CCR-

EURATOM of Ispra (Prof. S. Facchetti) and on highly contaminated compounds of the A101 reactor of ICMESA Spa – Meda, under the technical/scientific supervision of the Governmental Commission and of Givaudau (Switzerland).
The evaluation of the rheological and toxicological properties of the reaction compounds of the dehalogenation process were performed by the Institute fur Toxicology of Schwevzenbach – Switzerland, directed by Prof. Poiger. The tests on guinea pigs provided the following conclusion: quote " no effects (malformation of organs, weight loss etc.) have been found due to the intake of an equivalent of treated TCDDs equivalent to 600 times their average lethal dose. The innocuously of the reagents and reaction products, combined with the reactivity and versatility of the CDP Process®, make this a safe method in the decontamination and elimination of chemically stable aromatic compounds. [13 14] " unquote.

Field Applications
The capability of the S/CDP technology has been demonstrated successfully through field trials. In these trials, degradation of PCBs in transformer fluids was performed in a "closed loop" with a Decontamination Mobile Unit (DMU). A high degree of degradation was achieved for all PCB constituents (PCBs+PCTs+PCBTs). The decontamination of transformers of different sizes and capacities such as power transformers, distribution transformers, special purpose and industrial transformers, was carried out on-site. Equipment with a capacity of up to 50,000 kg of insulating oil and PCB contamination levels as high as 2,000mg/kg were treated. The PCB concentration was reduced to less than 25mg/kg.
Decontamination of principle transformer components, i.e., the interior metal core and insulating solids (paper), was achieved at >99% efficiency through a single treatment cycle. The process was found to be effective in leaching and dechlorinating PCBs absorbed in the solid (paper) insulators of the transformer core, thus providing long-term decontamination. The concentration of PCBs in insulating oil from the treated transformers was monitored over periods ranging up to 12 months. The results have shown that the concentration of PCBs, once reduced to low levels (~2mg/kg), remained low throughout the 12-month period.

The technology is thus at least 10 times more effective than retrofilling and/or flushing with fresh oil. Furthermore, it allows recovery of essentially all of the insulating oil. The technology also improves the functional and insulating properties of the oil. It lowers moisture content, acidity, and dissolved gases. It is effective in removing sludge and polar oxidation products, thus prolonging the useful life of the electrical transformers. Field trials also demonstrated the applicability of the technology for an entire range of commercial transformers.

REFERENCES

1. EEC Council Directive 96/59/EC-16/09/1996 "Disposal of polychlorinated biphenyls and polychlorinated ter phenyls (PCBs/PCTs)".
2. Virtual Elimination Pilot Project - A JOINT US-CANADIAN PROGRAM for Great Lakes-Ecosystem-1996.
3. Ackerman, D.G. in "Destruction and Disposal of PCBs by thermal and non-thermal methods" Noyes Data Corporation - Park Rodge NJ 1983.

4. Brunelle, D.J. Patent Appl. n. 314,163 (1981) (General Electric Co.)
5. Brunelle' D.J.; Singleton' D.A. Chemosphere, 12, 183 (1983)
6. Pytlesky, L.L.; Krevitz K.; Smith, A.B U.S. Patent Appl. n. 142,865 and 158,359 (1980)
7. Peterson, R.L.; Patent Appl. 501,620 (1983) (Galson Research Corporation)
8. Tundo, P.; Tumiatti, W.; Nobile, G.; "Solving Hazardous Waste Problems" J.M. Exner, Ed. ACS Symposium Senes 338, 1987, pp 376/383.
9. Tumiatti W.; SEA Marconi, European Patent Appl. 0675748 (1997)
10. Tumiatti W.; Kapila S.; SEA Marconi, Patent pending PC T/EP9 6/0 368
11 IEC/CENELEC - E 1619- 1997-04 "Insulating Liquids-Contamination by Polychlorinated Biphenyls (PCBs) - Method of Determination by capillary column gas chromatography ".
12 European Standard pr.EN 12766 (part1, Part2, Part 3) Draft August 1998 "Petroleum products and used oils – Determination of PCBs and related products".
13 Tundo P.; Tumiatti W "Chemical decomposition of polychlorinated biphenils and of 2,3,7,8 tetra chlorinated dibenzodioxin with the CDP Process". Technological response to chemical pollution. UFFICIO SPECIALE DI SEVESO – CONVEGNO 20 – 22 September 1984 – Milano page 243/250
14 Sea Marconi Patents. Tundo P. "Processo per la decomposizione di composti tossici alogenati. (Domanda Brevetto n. 1992 A/82) "Nuovi reagenti e metodi per la distruzione chimica di composti organici alogenati e super tossici e per la decontaminazione di superfici inquinate da tali composti (Domanda Brevetto n. 24443 A/83).