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(54) **A process to remove polychloro-bi-phenyls from mineral oils**

(57) Poly-chloride-bi-phenyls are removed from mineral oils by means of a hydro-dehalogenation reaction in a multi-phase system by means of a process which takes place in a reactor at temperatures between 10 and 150°C and at a pressure less than 5 Atm and the mineral oil containing poly-chloro-bi-phenyls is put in contact and made to react with a multi-phase system comprising an alkali water solution, a hydrogenation catalyst, a phase transfer catalyst and a source of hydrogen.

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Description

The present invention concerns a process to remove poly-chloro-bi-phenyls from mineral oils, especially from di-electric oils contaminated within electrical appliances.

In the description herein the poly-chloride-bi-phenyls will be defined as - PCBs - and the process to remove the PCBs from mineral oils shall be defined as - decontamination -.

The mineral oils from electric transformers may contain PCBs; because PCBs are toxic for animal and vegetal organisms, and are not bio-degradable, these mineral oils must be decontaminated.

The problem of decontaminating these mineral oils has been faced by many with diverse methods; it is understood that only chemical methods may provide satisfactory results in the decontamination of large quantities of mineral oils.

A number of methods for decontamination are known, with the use of ultra-violet radiation or treatment with strongly oxidizing substances or with alkali metals or with powerful nucleophiles.

According to the U.S. patent N° 4,144,152, the dioxines are broken down in a methanol solution and in presence of ultra-violet radiation. Following the disclosures in this patent the decontamination has been performed in the presence of a semi-conductor (TiO_2), both in suspension (Chemosphere 1985, 14, 195), and immobilized on membranes (U.S. 4,806,514); in the latter case the penta-chloro-phenol was made to react. Some photo-chemical methods for the reduction of PCBs use ultra-violet radiation for the production of ozone. A pilot plant that operates in this way has been described as treating up to 40,000 gallons of contaminated oil per day (35th Annual Purdue Industrial Waste Conference, May 1990).

It is known that in nature the decomposition of PCBs takes place owing to $\text{Fe}_2^+ + \text{H}_2\text{O}_2$ (Environ. Sci. Technol, 1991, 25, 1419).

A number of processes have long since been known that use the super-oxide ion as an oxidizer, also generated by electro-chemistry (Journal of Am. Chem. Soc., 1987, 109, 8081, e Environ.Sci. Technol, 1988, 22, 1182). A demonstration portable plant based on the electro-chemical process has been set up by Resource Engineering Inc. (Chemical Week, April 1, 1987, 13).

Alkaline metals have been used for a long time as means for the decontamination of mineral oils containing PCBs, as in the processes by Chemical Waste Management and Degussa; more recently the use of metallic sodium with sand or inert support has been reported (Jap. Pat. 74, 8, 570 and Can. Pat. 1, 247, 139).

The process by Sunohio is well known (IEEE Trans. Power Appar. Sys., 1983, PAS-102, 3893), called PCBX, that uses metallic sodium together with naphthalene; this process has been employed in the U.S.A.

A number of methods, also industrially developed, are based on nucleo-phile replacement, such as the Vertac process (US. PAT. 4, 327, 368 and US. PAT. 4, 353, 793).

Other methods, all based on these technologies, are still now published and implemented (Eur. PAT. 397, 310 and US. PAT. 4, 663, 027 and US. PAT. 4, 748, 292). The latter methods use and alcolate or potassium hydroxide as a nucleo-phile, in the presence of a solvent (usually PEG) that is able to supply an anionic activation to the aggressive base. The drawbacks of the known processes lie in the low reaction velocity (ultra-violet radiation and super-oxide ion) or in the possibility of explosions (alkali metals) or in the production of sub-products that must in any case be disposed of (an inconvenience present in all the processes described, excluding the ultra-violet reaction).

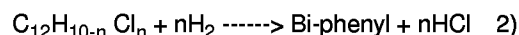
The following reaction (Equation 1):



has long been known, but has yet never been applied to PCBs in mineral oils, because the decomposition requires a lot of time and the catalysts necessary are often very costly.

However its potential application value is very high, because the PCBs would not generate any sub-products (Rylander, P.N.; "Catalytic Hydro-generation in Organic Synthesis"; Academic Press, New York, 1973; pp. 235-248, and Kiebon, Van Rantwick, in "Hydrogenation in Synthetic Organic Chemistry"; Delft University Press, Delft, The Netherlands, 1977).

In fact, the hydro de-chlorination of PCBs with hydrogen or one of its pre-cursors leads to bi-phenyl as the only reaction product (Equation 2):



This last compound may to all purposes be considered a component of mineral oil.

Note that as yet the hydro-de-halogenation of PCBs in mineral oils has never been reported. Recently it has been disclosed that a multi-phasic system comprising a highly alkaline water solution and a hydrogenation catalyst, is able to hydro-dehalogenate aromatic polyhalogens, present in an organic solvent, if a phase transfer catalyst is present (Journal. Chem. Soc. Perkin Trans. I, 1993, pag. 529) in which, however, no reactions on PCBs are reported nor is mineral oil used as a solvent.

Now, we have found that, surprisingly, mineral oils contaminated by PCBs can be rapidly decontaminated when the hydro-de-halogenation process is conducted in the presence of: an alkaline water solution, a hydrogenation catalyst, preferably carbon supported Palladium, Nickel-Raney, or a hydrogenation catalyst based on Rutenium or Rhodium, using molecular hydrogen as a source of hydrogen, or sodium hypo-phosphate or hydrazine and, should the reactions be conducted in the presence of a phase transfer catalyst, preferably in the presence of Aliquat 336 (Tri-caprilil Methyl Ammonia Chloride).

It is known that phase transfer catalysts are insoluble in the two phases, oil and water solution, or else they are absorbed onto the surface of the hydrogenation catalyst.

The reaction is very fast, so much so that, as described in Example 2, operating at only 50°C, the contamination of the mineral oil dropped from 550 ppm to 23 ppm after only 2.0 hours of reaction.

Similarly, starting at 5000 ppm, as in Example 1, the concentration dropped to 100 ppm operating at 50°C for 8 hours.

It should be noted that, if one operates without the Aliquat 336 as described in the example 2 process, no reaction takes place.

The main advantages of the invention are given by:

a) the possibility of operating on the mineral oil with no previous treatments and at low temperatures, b) the absence of noxious process by-products, c) by the fast reaction velocity.

Other advantages are: the treated mineral oil still features high di-electric characteristics and, after having removed humidity and gases present, can again be used in an electric transformer; the process is versatile because molecular hydrogen or one of its precursors can be used as a source of hydrogen; the hydrogenation catalysts can be re-cycled both using a batch decontamination process and setting up a continuous system, such as a CSTR (continuous stirred tank reactor).

Below some examples to describe the hydro-de-halogenation of PCBs in mineral oils are provided.

The formulation of the PCBs used in the examples described herein where Arochlor® 1254, Apirolio® 1488 and Arochlor® 1260.

The initial concentration of PCBs in the oils was between 5000 and 105 ppm.

The phase transfer catalyst was generally Aliquat 336, although good results were also provided by hexa-decil-tri-butyl-phosphone chloride, tri-butyl-ammonium chloride, phenyl-tri-butyl-ammonium chloride and tetra-ethyl-ammonium chloride.

The temperatures were between 50°C and 80°C in all the examples described.

The following were used:

- various hydrogenation catalysts, but we found that the best results in terms of effectiveness were obtained by using catalysts with Palladium supported on carbon, Nickel-Raney, with Ruthenium base and with Rhodium base.
- various hydrogen sources, such as, for example, molecular hydrogen, ammonium formate or sodium hypo-phosphite or hydrazine;
- bases such as NaOH, KOH or K₂CO₃
- various di-electric oils containing PCBs.

EXAMPLES

Example n°1

In a double-neck 25 ml conical glass thermo-stat controlled at 50°C and magnetically agitated, 7 ml of oil contaminated with 5000 ppm of Arochlor® 1260, 5 ml of KOH 50% p/v, 50 mg of Pd/C 5%, 100 mg of Aliquat 336 with hydrogen at atmospheric pressure were placed for reaction. After 8 hours of reaction the gas-chromatography with ECD detector highlighted a 98% degrading yield. The oil contained 100 ppm of mono-, di-, and tri-chloride-bi-phenyls.

Example n°1a

Operating in the same conditions as in Example 1, excepting the reduction agent (2.65 g of sodium bi-hydrate hypo-phosphone instead of gaseous hydrogen) and of the phase transfer agent (0.49 g of hexa-decil-tri-butyl-phosphonium chloride instead of the Aliquat 336) after 30 hours a low decontamination rate was observed (35%) although the quality profile showed a drop in high-chloride congeners.

The same mixture as in example 1, excepting the Aliquat 336, showed a very slow reaction, so much so that after 6 days the yield reached around 14%, with a drop of a few high-chloride congeners.

Example n°2

In a double-neck 25 ml conical glass thermo-stat controlled at 50°C and magnetically agitated, 7 ml of oil contaminated with 550 ppm of Arochlor® 1254, 5 ml of KOH 50% (p/v), 50 mg of Pd/C 5%, 100 mg of Aliquat 336 with hydrogen at atmospheric pressure were placed for reaction. After 2 hours of reaction the gas-chromatography with ECD detector highlighted a 96% degrading yield. The oil contained 23 ppm of mono-, di-, and tri-chloride-bi-phenyls.

Example n°2a

In the same conditions as in example 2 but without the Aliquat 336 and at 80°C, after 6 hours of reaction no decontamination yield was recognized; the addition of 0.1 g of hexa-decil-tri-butyl-phosphone chloride instead, after 4 hours of reaction at 80°C, provided a yield equal to 94% with a concentration of low-chloride PCBs equal to 34 ppm.

The substitution of the base (NaOH instead of KOH) allowed to achieve 96% yield after only 1 hour of reaction, with a concentration of low-chloride PCBs at 22 ppm.

The use of 0.1 ml of hydrated hydrazine at 98% instead of hydrogen provided a decontamination yield after 2 hours equal to 92%, with residual PCBs amounting to 42 ppm.

Example n°3

In a double-neck 50 ml conical glass thermo-stat controlled at 60°C and magnetically agitated, 20 ml of oil contaminated with 550 ppm of Arochlor® 1254, 5 ml of KOH 50% (p/v), 50 mg of Pd/C 5%, 100 mg of Aliquat 336 with hydrogen at atmospheric pressure were placed for reaction. After 2 hours of reaction the decontamination yield was 80%, while after 4 hours 96% was reached with a concentration of low-chlorinated PCBs of 22 ppm.

Example n°4

In a double-neck 50 ml conical glass thermo-stat controlled at 50°C and magnetically agitated, 10 ml of oil contaminated with 465 ppm of Arochlor® 1260, 5 ml of KOH 50% (p/v), 50 mg of Pd/C 5%, 100 mg of Aliquat 336 with 0.1 ml of hydrated hydrazine 98% were placed for reaction. After 4 hours of reaction the gas-chromatography with ECD detector highlighted a decontamination yield at 90%. The oil contained 46 ppm of mono-, di- and tri-chloro-bi-phenyls.

Example n°5

In a double-neck 50 ml conical glass thermo-stat controlled at 60°C and magnetically agitated, 20 ml of oil contaminated with 580 ppm of Apirolio® 1488 T, 10 ml of KOH 50% (p/v), 50 mg of Pd/C 5%, 100 mg of Aliquat 336 with 0.2 ml of hydrated hydrazine 98% were placed for reaction. After 4 hours of reaction the gas-chromatography with ECD detector highlighted a decontamination yield at 82%. The oil contained 102 ppm of PCBs, that, after a further 4 hours of reaction dropped to 35 ppm of mono- and di-chloro-bi-phenyls (yield 94%).

Example n°6

In a double-neck 50 ml conical glass thermo-stat controlled at 60°C and magnetically agitated, 25 ml of oil contaminated with 648 ppm of Apirolio® 1488 T, 10 ml of KOH 50% (p/v), 75 mg of Pd/C 5%, 178 mg of Aliquat 336 with hydrogen at atmospheric pressure were placed for reaction. After 4 hours of reaction the gas-chromatography with ECD detector highlighted a decontamination yield at 90%; while after a further 4 hours the oil contained 26 ppm of low-chlorinated PCBs (96%).

Example n°7

In a double-neck 50 ml conical glass thermo-stat controlled at 60°C and magnetically agitated, 20 ml of oil contaminated with 105 ppm of Apirolio® 1488 T, 10 ml of KOH 50% (p/v), 73 mg of Pd/C 5%, 174 mg of Aliquat 336 with hydrogen at atmospheric pressure were placed for reaction. After 2 hours of reaction the gas-chromatography with ECD detector highlighted a decontamination yield at 90%. The oil contained 10 ppm of mono- and di-chloro-bi-phenyls.

Example n°8

In a five-neck 5 litre reactor, thermo-stat controlled at 60°C and mechanically agitated, 1850 ml of oil contaminated with 750 ppm of Apirolio® 1488 T, 350 ml of KOH 50% (p/v), 2.8 g of Pd/C 5%, 7.4 g of Aliquat 336 and hydrogen at atmospheric pressure were placed for reaction. After 8 hours of reaction the gas-chromatography with ECD detector highlighted a decontamination yield at 70%. After 24 hours the oil contained 30 ppm of mono- and di-chloro-bi-phenyls (96%).

Example n°9

In a five-neck 5 litre reactor, thermo-stat controlled at 60°C and mechanically agitated, 1900 ml of oil contaminated with 750 ppm of Apirolio® 1488 T, 360 ml of KOH 50% (p/v), 2 g of Pd/C 5%, 7.4 g of Aliquat 336 with hydrated hydrazine 98% were placed for reaction. After 8 hours of reaction the gas-chromatography with ECD detector highlighted a decontamination yield at 58%. After a further 12 hours of reaction the oil contained 145 ppm of mono- and di-chloro-bi-phenyls (81%).

Example n°10

In a 150 litre reactor, thermo-stat controlled at 70°C and mechanically agitated, 54 litres of oil contaminated with 500 ppm of Apirolio® 1488 T, 28 litres of KOH 50% (p/v), 100 g of Pd/C 5%, 250 g of Aliquat 336 with hydrogen at atmospheric pressure were placed for reaction. After 16 hours of reaction the gas-chromatography with ECD detector highlighted a decontamination yield at 72%. After a further 12 hours of reaction a yield of 85% was reached and the oil contained 75 ppm of mono-, di-, and tri-chloro-bi-phenyls (81%).

Example n°11

In a 150 litre reactor, thermo-stat controlled at 70°C and mechanically agitated, 51 litres of oil contaminated with 750 ppm of Apirolio® 1488 T, 26.5 litres of KOH 50% (p/v), 100 g of Pd/C 5%, 520 g of Aliquat 336 with hydrogen at atmospheric pressure were placed for reaction. After 20 hours of reaction the gas-chromatography with ECD detector highlighted a decontamination yield at 97%, equal to a contamination in the oil of 22.5 ppm of mono- and di-chloro-bi-phenyls.

Example n°12

In a 150 litre reactor, thermo-stat controlled at 70°C and mechanically agitated, 48 litres of oil contaminated with 185 ppm of Apirolio® 1488 T, 33.5 litres of KOH 50% (p/v), 100 g of Pd/C 5%, 480 g of Aliquat 336 with hydrogen at atmospheric pressure were placed for reaction. After 8 hours of reaction the gas-chromatography with ECD detector highlighted a decontamination yield at

92%; the oil contained only 16.7 ppm of mono- and di-chloro-bi-phenyls.

Claims

1. A process to remove poly-chloride-bi-phenyls from mineral oils by means of a hydro-dehalogenation reaction in a multi-phase system characterized in that it takes place in a reactor at temperatures between 10 and 150°C and at a pressure less than 5 Atm in which the mineral oil containing poly-chloro-bi-phenyls is put in contact and made to react with a multi-phase system that comprises an alkali water solution, a hydrogenation catalyst, a phase transfer catalyst and a source of hydrogen.

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2. A process according to Claim 1 characterized in that the base used to form said alkali water solution is potassium hydroxide or sodium hydroxide or a carbonate of alkali metals or calcium hydroxide or magnesium hydroxide.

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3. A process according to Claim 1 characterized in that the hydrogenation catalyst is Palladium on a carbon support or Nickel-Raney or a Rutenium or Rhodium based hydrogenation catalyst.

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4. A process according to Claims 1, 2, and 3 characterized in that the phase transfer catalyst is tri-capril-methyl-ammonium chloride.

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5. A process according to Claims 1, 2, and 3 characterized in that the phase transfer catalyst is hexadecil-tri-butyl-phosphone chloride.

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6. A process according to Claims 1, 2, and 3 characterized in that the phase transfer catalyst is tri-benzyl-ethyl-ammonium chloride.

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7. A process according to Claims 1, 2, and 3 characterized in that the phase transfer catalyst is phenyl-tri-butyl-ammonium chloride.

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8. A process according to Claims 1, 2, and 3 characterized in that the phase transfer catalyst is tetra-ethyl-ammonium chloride.

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9. A process according to Claim 1 characterized in that the source of hydrogen is molecular hydrogen or hydrazine or sodium hypo-phosphite.

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10. A process according to Claim 1 characterized in that it is applicable to mineral oils containing poly-chloride-bi-phenyls in concentrations included between 50,000 and 5 ppm.

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11. A process according to Claim 1 characterized in that it takes place in a reactor bath or CSTR.



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EUROPEAN SEARCH REPORT

Application Number
EP 95 11 6723

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	JOURNAL CHEM. SOC. PERKIN TRANS. I, 1993 page 529-533 XP 000565551 C.A. MARQUES ET AL. 'hydrodehalogenation of polychlorinated aromatic halides ...' * the whole document *	1-11	A62D3/00
A	US-A-5 093 011 (FRIEDMAN ARTHUR J ET AL) 3 March 1992		
A	US-A-4 410 422 (BRUNELLE DANIEL J) 18 October 1983		
A	J. ORG. CHEM., vol. 58, no. 19, 10 September 1993 page 5256-5260 XP 000565639 C.A.MARQUES ET AL. 'Facile hydrodehalogenation with hydrogen and pd/c catalyst under multiphase conditions'	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			A62D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		13 March 1996	Dalkafouki, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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