(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 184 342**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **85308218.8**

(22) Date of filing: **12.11.85**

(51) Int. Cl.^{4}: **A 62 D 3/00**
C 23 G 5/00

(30) Priority: **23.11.84 GB 8429709**

(43) Date of publication of application:
11.06.86 Bulletin 86/24

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

(71) Applicant: **ALCAN INTERNATIONAL LIMITED**
1188 Sherbrooke Street West
Montreal Quebec H3A 3G2(CA)

(72) Inventor: **Ross, Robert Anderson**
Box 45 R.R. No.1 King Pitt Road
Kingston Ontario(CA)

(72) Inventor: **Lemay, Rejean**
7 Bayswater, No. 322
Kingston Ontario(CA)

(74) Representative: **Pennant, Pyers et al,**
Stevens, Hewlett & Perkins 5 Quality Court Chancery Lane
London, WC2A 1HZ(GB)

(54) Destroying halogen containing organic compounds.

(57) Halogen-containing organic compounds e.g. polychlorinated biphenyls (PCB's) are destroyed by being contacted in gaseous form in the absence of oxygen to Al, Mg, Si, Ti or Be having a high specific area, and an area of 0.1 - 65 m^2 of metal surface per gram of organic compound to be destroyed, at temperatures of 450 - 650°C for times up to 50 seconds. The PCB's are generally entrained in an inert carrier gas. The method is suitable for continuous operation. When the metal becomes deactivated by reason of a carbonaceous deposit on the surface, it can be regenerated, e.g. by treatment with sodium hydroxide solution.

Croydon Printing Company Ltd

DESTROYING HALOGEN-CONTAINING ORGANIC COMPOUNDS

Polychlorinated biphenyls (PCB's) is a generic term covering a family of partially or wholly chlorinated isomers of biphenyl. PCB's are non-conductors of electricity and have good resistance to high temperatures, so they are widely used as working fluids in heat exchangers and hydraulic systems and by the electrical industry in transformers and capacitors. PCB's are extremely toxic, but are difficult to destroy on account of their thermal stability and chemical inertness. The standard destruction method involves incineration at temperatures around 1500°C, but suffers from several disadvantages. Operation at these very high temperatures is expensive; and incomplete combustion can give rise to chlorinated dioxins or furans which are even more toxic than PCB's. The present invention provides a method for the destruction of PCB's and related compounds which involves reaction with metal rather than combustion, and operates at much lower temperatures.

C. S. Shultz describes in U.S. Patent 4,469,661 a method for destroying PCB's by contacting them in vapour form with molten aluminium metal. This process, which is not demonstrated by Shultz, is unsatisfactory for several reasons. The use of a body of molten aluminium metal is somewhat hazardous, on account of the risk of explosion, and expensive, on account of the high temperatures involved (aluminium melts at 660°C) and the difficulty of containing molten aluminium which aggressively attacks standard materials such as steel and quartz. It is expected to be more difficult to ensure intimate physical contact of gaseous PCB's with molten aluminium than with aluminium in the solid state; and that the reaction of PCB's with molten aluminium will produce much more $AlCl_3$ than will reaction with aluminium in the solid state.

Shultz discloses as a non preferred embodiment, but does not claim, a process which involves contacting PCB's with a solid aluminium surface. As reported in Examples 1 to 3, his experiments involved heating transformer oils containing PCB's in the presence of aluminium foil at various temperatures, but did not result in complete destruction of the PCB's even over periods as long as 30 minutes.

Japanese Kokai 51-25471 describes a method of decomposing PCB's by heating them to effect partial dissociation to HCl or Cl_2, and passing the mixture over a suitable metal and recovering a chloride salt of the metal by sublimation from the decomposition system. There is no indication that air is excluded; and no evidence that complete decomposition of PCB's is achieved even after several hours reaction.

This invention is based on the discovery that PCB's can be rapidly destroyed by heating in the presence of solid aluminium, but only provided certain critical parameters are observed. The invention thus provides a method of destroying halogen-containing organic compounds by reaction with a metal in the solid state at elevated temperature, characterized by contacting the compounds in gaseous form in the absence of oxygen with a metal selected from Al, Mg, Si, Ti and Be, and alloys thereof having a high specific surface area at a temperature of at least 450°C and a contact time of from 0.5 to 50 seconds.

Tests have established that the method is capable of destroying a wide range of chlorinated organic compounds. We know of no reason why any chlorinated organic compound, which is thermally stable enough to be heated up to the required reaction temperature, should not be destroyed by the method. The invention is also applicable to organic compounds of the other halogens, fluorine, bromine and iodine. However, environmental problems do not exist to the same extent as with chlorine compounds because of the far greater industrial use of the latter. The invention is, of course, of particular value in relation to PCB's and related compounds.

It is necessary that the compounds should be in the gas phase, for reaction of liquid compounds with solid metal has not proved effective. The compounds are preferably entrained in an inert carrier gas, for example argon or other gas in group 0 of the periodic table. High purity nitrogen may also be used, and is regarded for this purpose as an inert gas. However, its use is not preferred, for nitrogen is known to form highly toxic compounds with PCB's but the concentrations so far observed of these are insignificant.

There is no critical upper limit of concentration of the compounds in carrier gas. The method works without a carrier gas, provided that sufficient metal surface area is available for reaction, but would only be safe with a completely closed reaction vessel. In industrial practice, safety considerations determine an upper limit of concentration. There is no critical lower limit of concentration, but a practical lower limit is generally determined by economic factors. The concentration of halogen-containing organic compounds in carrier gas is preferably from 10 ppm up to 10%.

It is at all events necessary that oxygen, and compounds that might generate oxygen in situ, be substantially absent. If the method is performed in the presence of significant quantities of oxygen, then destruction of PCB's is incomplete and there is the risk of formation of chlorinated dioxins or furans.

As metals that can be used for reaction with the compounds, are specified Al, Mg, Si, Ti and Be, and alloys of these metals with each other or with minor proportions of other metals. The five named metals have two characteristics in common: they form oxides having electrically insulating properties; and the oxides have high thermal and chemical stability. Berylium presents a toxicity problem in itself, and is on that account the least preferred. The most preferred metals are magnesium and, particularly, aluminium. The metals can be used in the natural state, i.e. without the need to remove any oxide film that may be present. Aluminium can be used having an anodic oxide film which may contain minor proportions of oxides of other metals such as Co, Ni, Sn, Cu etc., in the pores. It is not known with certainty whether any oxide film remains during operation of the method, or whether it is removed by reaction with halogen-containing organic compounds.

The metal can be used in any physical form in which it has a high specific surface area. Suitable forms include a packed bed of spheres, chips or granules, a fluidized bed of powder, honeycomb, wire mesh or wire wool. Our presently preferred material is scrap aluminium and alloys thereof in granulated form, because this is cheap and readily obtainable. Sufficient metal surface area should be provided to ensure rapid and complete destruction of the halogen-containing organic compounds. This is generally 0.1 to 65 m^2, preferably from 1 to 20 m^2, of active metal surface (not necessarily bare metal surface, but surface not coated with e.g. inactivating carbonaceous deposits) per gram, of compound to be destroyed.

To achieve sufficiently rapid reaction, the reaction temperature needs to be at least 450°C. An upper limit on temperature is set by the melting point of the metal being used. One of the advantages of the method of this invention is the low temperatures required, and it is preferred not to use higher temperatures than are necessary in order to achieve reaction at the desired rate. Depending on other conditions, preferred reaction temperatures are likely to lie in the range 550°C to 650°C.

Provided the above reaction conditions: absence of oxygen; state of the metal; temperature of the metal, are maintained as described above, destruction of halogen-containing organic compounds are achieved at short contact times. We specify a range of up to 50 seconds, preferably 0.5 to 30 seconds contact time. In a continuous system, this is the average residence time of gas in the region of the active metal surface. Clearly reaction time is related to the total surface area of metal per unit of halogen-containing organic compounds, and to the reaction temperature. Adjustment of gas flow to ensure complete destruction of the compounds is achieved by routine trial and error.

Reaction products resulting from the method appear to be metal halide (e.g. aluminium chloride), low-boiling hydrocarbons, halogen, (e.g. chlorine) and carbon deposited on the metal substrate. As a result of this deposition, the substrate gradually becomes inactive. When this happens, the substrate can be regenerated. With aluminium, this can be achieved by subjecting the metal to sodium hydroxide solution, or less preferably, by heating the metal in air to burn off the carbon deposits. Other treatments for regenerating aluminium involve exposing the carbonised surface:-

(a) at 580°C to oxygen for 30 minutes followed by chlorine for 1 minute.

(b) hydrogen for 30 minutes at 550°C followed by oxygen for 30 minutes.

(c) oxygen for 30 minutes at 550-580°C followed by a steam/oxygen mixture at 125-175°C.

Hydrogen and chlorine may be diluted with flowing argon. Of the above, treatment (a) is preferred. It seems possible that the regenerated surface is in some way "re-activated" by the chlorine. Using this treatment, a 79.7% recovery of usable surface was obtained. Treatment (b) is more preferred than (c). Other metal substrates can similarly be regenerated by removing the carbon deposits under conditions in which the substrate is not affected.

The following examples illustrate the invention.

Example 1

The metal used was 1100 aluminium alloy chips (0.5 x 0.5 x 0.1 cm). A bed about 27 cm long of these chips was positioned in a vertical quartz tube 1.8 cm outside diameter, and maintained at a nominal temperature of 580°C. A vessel containing the reactant was positioned in the quartz tube below the bed, and was surrounded by a separate tube furnace whose temperature was raised from ambient to 600°C over a period of 60 minutes. The lower end of the quartz tube was closed except for an inlet port through which argon carrier gas was passed at a flow rate of 87.7 ml/min (NTP). As the reactant heated up it vapourized and became entrained in the carrier gas. The flow rate was such that the residence time of the gas in the bed of aluminium chips was about 15 seconds. The temperature profile of the bed of chips was measured as 366°C at 0 cm up from the bottom; 473°C at 5 cm; 563°C at 9 cm; 601°C at 16 cm and 600°C at 27 cm. The top end of the quartz tube was closed except for a gas outlet, and the reaction products were condensed. After the experiment, any remaining reactant, the material in the bed of aluminium chips and the reaction products were all analysed for halogen-containing organic compounds.

In one experiment, the reactant was 0.0078 g of decachlorobiphenyl. The destruction efficiency was 99.9999%. The section from 14 to 24 cm (measured from the bottom) of the aluminium bed became black.

In other experiments, the rate of heating of the reactant sample was varied so that the concentration of decachlorobiphenyl in carrier argon gas ranged from 166 ppm to 3048 ppm. In all cases, the destruction efficiency was at least 99.999%.

After one experiment, dry air was passed through the bed of aluminium chips at 580°C. The bed, a section of which had been blackened by carbon deposition, was partially regenerated by contact with air. Only very little black colour remained on the aluminium surface.

Comparative experiments were run under the same conditions but with an empty bed, i.e. without the aluminium chips. Destruction efficiency was of the order of 0 to 5%. This demonstrates the excellent high temperature stability of decachlorobiphenyl under normal circumstances, and the dramatic effect produced by the bed of aluminium chips.

Example 2

Other halogen-containing organic compound reactants were destroyed by the laboratory method described in Example 1. Destruction efficiency was not measured with the same accuracy as in Example 1, because of the lack of analytical techniques for measuring small amounts of different halogenated organic compounds.

a) The reactant was 0.5 ml of carbontetrachloride, injected at ambient temperature into the carrier gas. The bed of aluminium chips was one that had been regenerated by air as described in Example 1. The destruction efficiency was not measured accurately, but was high.

b) The reactant was 0.2 ml of ethylene dichloride, injected at ambient temperature into the carrier gas. The destruction efficiency was greater than 90%.

c) The reactant was 1.0 ml of Freon-113, injected into the carrier gas. The destruction efficiency was greater than 90%.

d) The reactant was 0.0052 g of "Vitar" fluorocarbon. This was all decomposed in the sample vial and did not reach the bed of aluminium chips.

e) The reactant was 0.0613 g of iodobenzene. The destruction efficiency was 99.6%.

f) The reactant was 0.0185 g of pyranol transformer oil containing 60% by weight of pentachlorobiphenyl. The concentration of reactant in the argon carrier gas was 1000 to 2000 ppm. The destruction efficiency was 98%.

Example 3

This example demonstrates the use of different metal substrates in the laboratory method generally described in Example 1.

a) A bed of aluminium alloy chips was used (as described in Example 1). The bed had been previously used and had been regenerated by treatment with an aqueous solution containing about 5 g of sodium hydroxide per litre which was effective to remove all the carbon residues. The reactant was 0.0261 g of pentachlorophenol. The destruction efficiency was greater than 95%.

b) The bed comprised anodized aluminium chips made from a sheet of 5252 alloy with a 7.5 micron anodic oxide film which had been coloured electrically with cobalt. The size of the chips was 0.5 x 0.5 x 0.1 cm. Both sides of the chips were coloured black with cobalt but the periphery was bare 5252 alloy. The reactant was 0.0049 g of decachlorobiphenyl. The destruction efficiency was 99.999%.

c) The bed was composed of aluminium fines, that is to say particles which passed through a 20 mesh sieve (opening 0.84 mm). The reactant was 0.06 g of pyranol transformer oil. The destruction efficiency was 99.99%.

d) The bed was of 70 to 80 mesh (about 0.2 mm opening) magnesium metal powder. The reactant was 0.009 g of decachlorobiphenyl. The destruction efficiency was 99.999%.

Example 4

This example demonstrates how the carrier gas can be altered or omitted. Where not otherwise stated, conditions were as described above in Example 1.

a) The bed was of super pure aluminium fines of a particle size to pass through a 20 mesh sieve (opening 0.84 mm). The reactant was about 0.0078 g of decachlorobiphenyl. No carrier gas was used. The reactant was heated from ambient temperature to 580°C in 15 minutes and maintained at 580°C for a further 15 minutes. The destruction efficiency was 99.999%. The amount of aluminium used was 146 grams per gram of decachloro-biphenyl, but further experiments demonstrated that less than 100 grams per gram were equally effective. While it is not meaningful to talk about a contact time bewtween reactant and substrate in a laboratory experiment of this kind, in commercial operation there would always be a flow of gas over the substrate bed.

b) The bed was of aluminium alloy chips as used in Example 1. Instead of argon, pre-purified nitrogen was used as the carrier gas at a flow rate of 87.7 ml/min (NTP). The reactant was 0.0065 g of decachlorobiphenyl, and the destruction efficiency was 99.999%.

In a comparative experiment, extra dry air was used as the carrier gas in place of nitrogen. The destruction efficiency was less than 80%, and unidentified and possibly toxic produces were found in the effluent gas.

CLAIMS

1. A method of destroying halogen-containing organic compounds by reaction with a metal in the solid state at elevated temperature, characterized by contacting the compounds in gaseous form in the absence of oxygen with a metal selected from Al, Mg, Si, Ti and Be, and alloys thereof having a high specific surface area at a temperature of at least 450°C and a contact time of up to 50 seconds.

2. A method as claimed in claim 1, wherein the organic compounds are chlorinated hydrocarbons.

3. A method of destroying chlorinated hydrocarbons by the steps of:-

i) bringing the chlorinated hydrocarbons in the gas phase and in the absence of oxygen into contact with a metal selected from Al, Mg, Si, Ti and Be and alloys thereof at a temperature of 450_{o}C and a contact time of 0.1 - 50 seconds, the metal having a high specific area, whereby the chlorinated hydrocarbons are destroyed and a deactivating carbonaceous deposit is formed on the surface of the metal,

ii) regenerating the metal by removing the carbonaceous deposit from the surface thereof, and

iii) re-using the regenerated metal to destroy more chlorinated hydrocarbons.

4. A method as claimed in any one of claims 1 to 3, wherein the compounds are entrained in gaseous form in an inert carrier gas.

5. A method as claimed in any one of claims 1 to 4, wherein the metal having a high specific surface area is aluminium alloy chips.

6. A method as claimed in any one of claims 1 to 5, wherein the contact temperature is from 550°C to 650°C.

7. A method as claimed in any one of claims 1 to 6, wherein there is provided from 1 to 20 m^2 of active

metal surface per gram of compound to be destroyed.

8. A method as claimed in claim 3, wherein the metal is regenerated by treatment with sodium hydroxide solution.

9. A method as claimed in claim 3, wherein the metal is regenerated by exposure at elevated temperature to oxygen followed by chlorine.

EUROPEAN SEARCH REPORT

0184342
Application number

EP 85 30 8218

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 4)
D,X	CHEMICAL ABSTRACTS, vol. 85, no. 12, 20th September 1976, page 324, abstract no. 82963h, Columbus, Ohio, US; & JP - A - 76 25 471 (ARITA RESEARCH INSTITUTE CO., LTD.) 02-03-1976 * Abstract *	1,2,6	A 62 D 3/00 C 23 G 5/00
A	IDEM	4,5	
D,X	US-A-4 469 661 (C.G. SCHULTZ) * Column 1, lines 40-68; column 2, lines 57-66; column 3, lines 13-30; examples 1-3; claims *	1,2,6	
A	US-A-3 343 911 (D.H. EISENLOHR) * Column 7, lines 11-44; claims 1,3,4 *	1,2,6	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)**
A	CHEMICAL ABSTRACTS, vol. 87, no. 24, 12th December 1977, page 270, abstract no. 188873k, Columbus, Ohio, US; E. OTA et al.: "Decomposition of polychlorinated biphenyls into carbon and hydrogen chloride using molten salt", & NIPPON KAGAKU KAISHI 1977, (9), 1407-9 * Last sentence of abstract *	1,2,5	A 62 D C 22 B B 01 J C 23 G
	--- -/-		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18-02-1986	FLETCHER A.S.

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

European Patent
Office

EUROPEAN SEARCH REPORT

0184842

Application number

EP 85 30 8218

Page 2

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 4)
A	US-A-2 977 323 (P.H. JOHNSON et al.) * Claims *	3,9	
A	DE-B-1 100 023 (PECHINEY COMPAGNIE DE PRODUITS) * Column 3, lines 6-52 *	3,9	
A	GB-A-1 160 945 (AMCHEM PRODUCTS INC.) * Claims 1,4,8,13-16 *	3,8	
A	US-A-2 346 562 (H.K. DE LONG) * Claims *	3,8	
	-----		TECHNICAL FIELDS SEARCHED (Int. Cl 4)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18-02-1986	FLETCHER A.S.

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