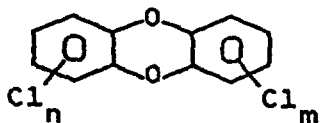
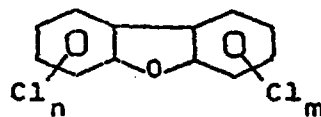


## Description

This invention relates to a process for the degradation of highly toxic halogenated organic compounds, in particular polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF), contained in SO<sub>2</sub>-free gases, wherein the highly toxic compounds are removed from the gas by oxidative degradation. The gases may in particular be waste gases from chemical processes as well as waste gases from refuse incinerators, wherein the gases may additionally contain other pollutants, such as NO<sub>x</sub>, but contain no sulphur dioxide.

Increasing significance is being attached both in public debate and generally in terms of process optimisation to the reduction of emissions of highly toxic halogenated organic compounds, such as in particular PCDDs and PCDFs, as may be contained in the gases arising from chemical and incineration processes. The content of highly toxic PCDDs and PCDFs in such gases may be in the range of some tenths of a ng TE/Nm<sup>3</sup> to approximately 30 ng TE/Nm<sup>3</sup>. (ng TE/Nm<sup>3</sup> = nanogram toxic equivalent per normal cubic metre). In the 17th implementing regulations of the German Federal immission control law, legislators have provided a limit value of 0.1 ng TE/Nm<sup>3</sup> from 1996, so improved processes for the removal or degradation of pollutants are consequently required to achieve the legal limit value.

The highly toxic halogenated organic compounds are in particular PCDDs and PCDFs of varying degrees of chlorination (n and m in the formula denote an integer from 1 to 8), which occur in numerous isomers or congeners of varying toxicities



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polychlorodibenzo-p-  
dioxins (PCDD)

polychlorodibenzo-  
furans (PCDF)

The above-mentioned TE value is calculated by multiplying  
10 the concentrations of the individual PCDDs and PCDFs by the  
appropriate NATO-CCMS toxic equivalent factor and by adding  
the results together. The particularly highly toxic  
2,3,7,8-tetrachlorodibenzodioxin has a TE factor of 1:  
other TE factors are mentioned by way of example,  
15 1,2,3,7,8-pentaCDD 0.5; 1,2,3,4,7,8-hexaCDD 0.1;  
2,3,7,8-tetraCDF 0.1; 2,3,4,7,8-pentaCDF 0.5;  
1,2,3,4,7,8-hexaCDF 0.1.

Hitherto, those pollutants of the PCDD or PCDF type  
20 contained in gases such as flue gases from incineration  
processes have been removed by passing the gases over  
adsorbents. Adsorption processes using a moving or fixed  
bed with open hearth coke and entrained-bed processes with  
added lime/activated charcoal are known. Adsorption  
25 processes have the disadvantage that a waste gas problem  
becomes a solid waste problem, because the pollutant-laden  
adsorbent must either be expensively regenerated or  
disposed of as special waste. Moreover safety hazards are  
associated with plants with adsorbers filled with activated  
30 charcoal due to CO formation in "hot spots" or even  
combustion, which makes expensive safety measures  
necessary.

According to the process in DE-OS 40 01 305, dioxins and  
35 furans may be removed from flue gases by treating the flue  
gases, after a wet scrubbing stage, with UV radiation of a  
wavelength of below 310 nm, preferably of below 245 nm in

the presence of added hydrogen peroxide. According to the examples in the stated document, residual dioxin/furan contents of only 1 ng TE/m<sup>3</sup> are obtained. This process is clearly not suitable for achieving the residual contents pursuant to the future legal limit value of 0.1 ng TE/m<sup>3</sup>. Additionally, there are costly technical difficulties related to the use of the necessary energy in the form of UV radiation.

10 International patent application WO 92/19364 discloses a process for the purification of flue gases containing condensable organic pollutants by wet scrubbing using a recirculable scrubbing liquid. The scrubbing liquid contains a finely divided solid, such as activated carbon, 15 or an oxide of titanium, aluminium, iron or silicon and may additionally contain an oxidising agent, such as hydrogen peroxide. Halogenated dibenzodioxins and dibenzofurans are cited among the pollutants which may be separated according to this processes. The extent to which these substances 20 may be separated and/or chemically degraded cannot be learnt from this document.

Another process for reducing the quantity of PCDD/PCDF emissions from the waste gas sections of refuse 25 incinerators is known from European patent application 0 373 312: in this process, superheated steam is either introduced into the waste gas section or superheated steam is generated therein by introducing water. Catalytically active metal salts or oxidising agents, such as hydrogen 30 peroxide, may be added together with the introduced water or steam. The added or formed superheated steam should conveniently have a temperature of at least 200°C.

The as yet unpublished German patent application 35 P 42 10 055.0, which corresponds to EP-A-0 546 314 which is also not a prior publication, discloses a process for the removal of halogenated compounds, such as PCDDs and PCDFs,

- from waste gases optionally containing  $\text{NO}_x$ , wherein the waste gas is optionally passed through a fixed or fluidised bed and is brought into contact with Caro's acid  $\text{H}_2\text{SO}_5$  or a salt thereof. The Caro's acid may be formed *in situ* from
- 5 hydrogen peroxide and sulphuric acid, which is added or produced from the sulphur dioxide present in the waste gas to be treated and  $\text{H}_2\text{O}_2$ . Catalytically active solids mentioned are *inter alia* pyrogenic and precipitated silicas, alumina, titanium dioxide and zeolites.
- 10 DE 42 10 055.0 teaches that Caro's acid plays a decisive part in the oxidation of PCDDs and PCDFs; if the gas to be treated contains no or only a little  $\text{SO}_2$ ,  $\text{SO}_2$  or  $\text{H}_2\text{SO}_4$  must be added. Although the highly toxic dioxins and furans are over 90% degraded on the solid to less toxic products under
- 15 the processing conditions and only a small proportion remains adsorbed on the solid, it must be considered disadvantageous that only gases containing  $\text{SO}_2$  are suitable for the process or that  $\text{SO}_2$  or  $\text{H}_2\text{SO}_4$  must be added.
- 20 The object of the present invention is therefore to provide another process for the degradation of highly toxic halogenated organic compounds, in particular polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF), contained in gases containing no  $\text{SO}_2$ , by treating
- 25 the gases with a peroxy compound, which process avoids the disadvantages of the prior art process. The process should additionally be capable of reliably achieving 0.1 ng TE/ $\text{Nm}^3$ .
- 30 This object is achieved by passing the gas at a temperature in the range from above its dew point to  $180^\circ\text{C}$  in the presence of hydrogen peroxide or of a compound which liberates hydrogen peroxide, with the exception of Caro's acid ( $\text{H}_2\text{SO}_5$ ) or salts thereof, over a substantially
- 35 inorganic solid heterogeneous catalyst from the range comprising precipitated silicas, pyrogenic and surface-modified silicas, silica gel, diatomaceous earth,

natural and synthetic silicates, zeolites, metal oxides, mixed oxides and sintered glasses, supports with oxides of iron, chromium, manganese, vanadium, molybdenum or tungsten on their surface, molybdophosphates and tungstophosphates.

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The subordinate claims relate to preferred embodiments of the process.

The peroxy compounds added to the gas or to the solid are  
10 hydrogen peroxide or compounds releasing hydrogen peroxide, such as peroxides, perborates, percarbonates, persilicates together with alkali metal or alkaline earth metal perphosphates. Salts are added in the form of an aqueous solution or suspension, in fact in such a manner that an  
15 effective quantity of the per compound comes into contact with the solid for the purposes of activation. It has not yet been clarified whether the stated per salts are themselves active, or whether hydrogen peroxide must first be released. Hydrogen peroxide is particularly preferably  
20 used as an aqueous solution of a desired concentration, preferably 30 to 70 wt.%. The aqueous  $H_2O_2$  solution is introduced into the system in an effective quantity. "Effective" means that the quantity is sufficient to be able to oxidise both any readily oxidisable pollutants  
25 which may be present and dioxins and furans. Hydrogen peroxide is conventionally used in excess in relation to the dioxins and furans.

The gas to be treated is passed, in the presence of a  
30 peroxy compound, over a sufficiently catalytically active solid, which is conveniently arranged in the form of a fixed or fluidised bed. Contact time is dependent upon the desired pollutant degradation. Naturally, in the case of the preferred fixed bed, contact time may be increased by  
35 reducing the velocity of the gas and increasing the depth of the fixed bed. Good results may be achieved with gas velocities in the range 0.1 to 5 m/s.

The peroxy compound is either directly added to the gas to be treated or is applied to the solid heterogeneous catalyst, for example by soaking the solid or by spraying it with an aqueous solution of the peroxy compound.

- 5 Preferably, an aqueous hydrogen peroxide solution is added directly to the gas, which generally has to be treated as a continuous stream. Addition is preferably performed by spraying an aqueous  $\text{H}_2\text{O}_2$  solution into the gas stream or by introducing  $\text{H}_2\text{O}_2$  vapour into the gas stream.

10

Treatment of the gas containing no  $\text{SO}_2$  is preferably performed at above the dew point of the gas, so as to avoid condensation on the solid heterogeneous catalyst. A temperature in the range from above the dew point, in particular at least  $5^\circ\text{C}$  above the dew point, and up to  $180^\circ\text{C}$ , preferably  $120^\circ\text{C}$ , is particularly suitable. Since the dew point of combustion gases is frequently between  $40$  and  $60^\circ\text{C}$ , treatment is preferably performed in such cases in the range from  $80^\circ\text{C}$  to  $120^\circ\text{C}$ . If salts are used as the peroxy compound, it may be convenient to cause condensation at least temporarily by reducing the temperature below the dew point, in order to wash off any salts deposited on the fixed bed with the condensate, in order to maintain activity of the heterogeneous catalyst.

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The following solid heterogeneous catalysts may be used, either individually or mixed together, in finely divided form, shaped as pellets, tablets or any other shapes, including honeycombs, or applied onto shaped supports:

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- silica gels, diatomaceous earth, precipitated silicas, pyrogenic silicas, silicas which have been surface-modified, for example rendered hydrophobic;

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- natural and synthetic silicates, including calcium and aluminium silicates, phyllosilicates;

- zeolites, such as mordenite, ZSM-5 zeolites, dealuminated Y-zeolites;
- 5       - metal oxides, such as gamma and alpha  $\text{Al}_2\text{O}_3$  and titanium dioxide and mixed oxide and sintered glasses;
- 10       - above-stated materials and other supports having on their surface oxides of the elements iron, chromium, manganese, vanadium, molybdenum or tungsten,
- 15       - heteropolyacids of the molybdophosphate and tungstophosphate series.

Some of the solid heterogeneous catalysts have very different activities, as they adsorb the PCDDs and PCDFs and catalyse the oxidation reaction to a variable extent. Silicas have proved to be particularly preferred solid  
20 heterogeneous catalysts, as adsorption and catalysis appear to be optimally balanced in terms of their use for pollutant degradation according to the invention: at a degradation rate of over 90%, only small quantities of pollutants remain adsorbed on the heterogeneous catalyst,  
25 wherein the adsorbed quantity scarcely increases even during continuous operation, such that activity does not deteriorate even after several months' continuous operation. In contrast, the tested 12-ring zeolites (mordenite and dealuminated Y-zeolite) proved to adsorb  
30 well but were less catalytically active, although a residual content of less than 0.1 ng TE/Nm<sup>3</sup> in the treated gas is also achieved here.

The particularly preferred solid heterogeneous catalysts,  
35 pyrogenic amorphous silicas with a specific surface area (BET) of 100 or 380 m<sup>2</sup>/g were used as tablets (6 x 5.5 mm), precipitated silicas as extrudate (7 x 6 mm).

The process according to the invention may be integrated into known gas purification processes.

- It has been found that neither hydrogen peroxide alone,  
5 i.e. in the absence of a solid heterogeneous catalyst, nor the solid heterogeneous catalyst alone, i.e. without added hydrogen peroxide, is capable of degrading the highly toxic halogenated organic compounds. It is instead the combination of the solid heterogeneous catalyst and  
10 hydrogen peroxide which is required not only to remove practically 100% of the pollutants from the gas, but simultaneously substantially to degrade the pollutants to less toxic substances.
- 15 The process according to the invention is characterised by its elevated efficiency while simultaneously being easy to handle and requiring low investment in the necessary plant and equipment. Residual values of below  $0.1 \text{ ng TE/Nm}^3$  may be achieved without problem and in fact generally at a  
20 degradation rate of over 90%. The solid heterogeneous catalyst is incombustible and has an extended service life; in the case of the particularly preferred solid heterogeneous catalyst, there was no fall in activity even after several months' operation. In contrast with the  
25 teaching of DE-P 42 10 055.0, it surprisingly proved unnecessary to add  $\text{SO}_2$  or  $\text{H}_2\text{SO}_4$  to gases containing no  $\text{SO}_2$  in order to form Caro's acid.

#### Example

- 30 Dross furnace waste gas containing no sulphur dioxide ( $\text{SO}_2$ ) contained PCDDs and PCDFs in a quantity of  $12.6 \text{ ng TE/Nm}^3$ . The objective was to reduce the PCDD/PCDF content to below  $0.1 \text{ ng TE/Nm}^3$ , wherein the contaminated gas was combined  
35 with hydrogen peroxide and the gas mixture was passed over a solid heterogeneous catalyst arranged in a fixed bed.

The tubular reactor for the solid heterogeneous catalyst contained 65 g of SiO<sub>2</sub> tablets, produced from pyrogenic silicon dioxide with a BET surface area of 200 m<sup>2</sup>/g; reactor temperature 80°C; isothermal operation achieved by silver sheathing of reactor. Dew point of gas 55°C. Using an automatic metering device, a 50 wt.% aqueous H<sub>2</sub>O<sub>2</sub> solution was fed at a rate of 0.01 ml/min into a heat exchanger, the temperature of which was held constant at 90°C, vaporised and mixed into the waste gas stream. The volumetric flow rate of the waste gas (crude gas) was 1 Nm<sup>3</sup>/h.

The gas mixture containing H<sub>2</sub>O<sub>2</sub> was passed over the fixed bed heterogeneous catalyst for 6 hours. Both the crude gas and the pure gas leaving the heterogeneous catalyst were analysed for their PCDD and PCDF content in accordance with VDI guideline 3499, sheet 1 E (03/90 edition); the toxic equivalents (TE) were calculated in accordance with the internationally recognised NATO-CCMS toxic equivalent factor list. Sampling was performed with XAD-z cartridges with a C 1234-tetraCDD standard, dioxin/furan determination by GC-MS. The quantity of PCDD/PCDF adsorbed onto the heterogeneous catalyst after 6 hours' operation was also analysed.

The following results were obtained:

|                         |                            |
|-------------------------|----------------------------|
| Crude gas:              | 12.6 ng TE/Nm <sup>3</sup> |
| Pure gas:               | 0.05 ng TE/Nm <sup>3</sup> |
| Heterogeneous catalyst: | 0.04 ng TE/g               |

The dioxins and furans contained in the crude gas are thus practically entirely degraded; only traces of dioxins/furans remain on the heterogeneous catalyst at the end of the test. These substances do not, however, accumulate on the heterogeneous catalyst even after longer testing.



# Patent Claims

1. Process for the degradation of highly toxic halogenated organic compounds, in particular polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF), contained in SO<sub>2</sub>-free gases by treating the gas with a peroxy compound, characterised in that the gas is passed at a temperature in the range from above its dew point to 180°C in the presence of hydrogen peroxide or of a compound which liberates hydrogen peroxide, with the exception of Caro's acid (H<sub>2</sub>SO<sub>5</sub>) or salts thereof, over a substantially inorganic solid heterogeneous catalyst from the range comprising precipitated silicas, pyrogenic and surface-modified silicas, silica gel, diatomaceous earth, natural and synthetic silicates, zeolites, metal oxides, mixed oxides and sintered glasses, supports with oxides of iron, chromium, manganese, vanadium, molybdenum or tungsten on their surface, molybdophosphates and tungstophosphates.
2. Process according to claim 1, characterised in that treatment is performed at a temperature in the range between at least 5°C above the dew point and 120°C.
3. Process according to claim 1 or 2, characterised in that an effective quantity of hydrogen peroxide is added to the gas to be treated and the resultant gas mixture is passed over the solid heterogeneous catalyst.
4. Process according to one or more of claims 1 to 3, characterised in that



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the solid heterogeneous catalyst is arranged in the form of a fixed bed or fluidised bed, preferably as a fixed bed.

- 5 5. Process according to one or more of claims 1 to 4, characterised in that the solid heterogeneous catalyst used is one from the range comprising precipitated silicas and pyrogenic silicas together with aluminium silicate.

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6. Process according to claim 5, characterised in that the solid heterogeneous catalyst is used in pellet or tablet form.