

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 April 2003 (24.04.2003)

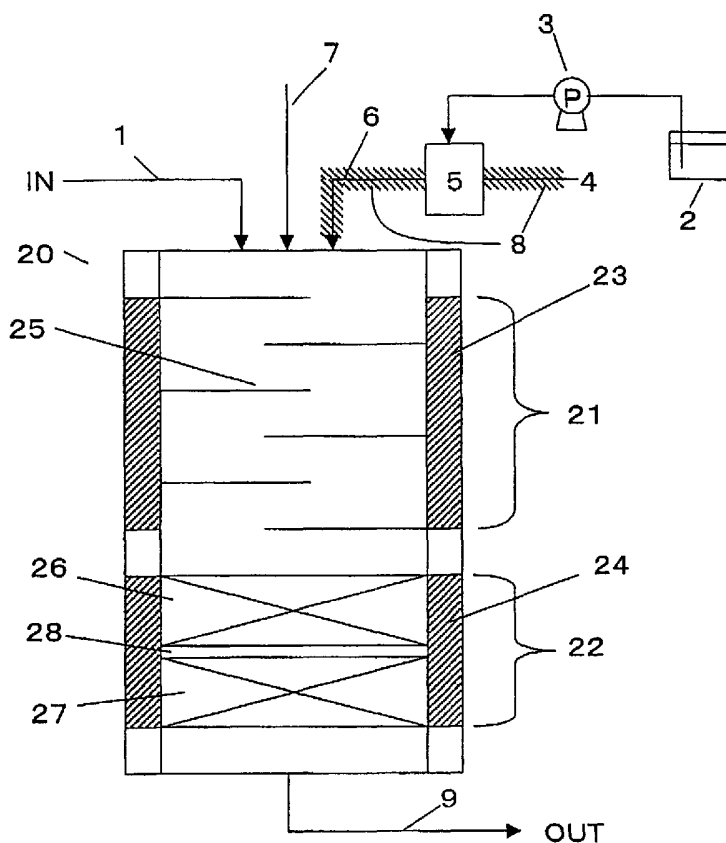
PCT

(10) International Publication Number
WO 03/033116 A1

- (51) International Patent Classification⁷: **B01D 53/86** 1-6-18-B202, Jukkenzaka, Chigasaki-shi, Kanagawa 253-0045 (JP).
- (21) International Application Number: PCT/JP02/10475
- (22) International Filing Date: 9 October 2002 (09.10.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
2001-312565 10 October 2001 (10.10.2001) JP
- (71) Applicant (for all designated States except US): **EBARA CORPORATION** [JP/JP]; 11-1, Haneda Asahi-cho, Ohta-ku, Tokyo 144-8510 (JP).
- (74) Agent: **HOSOKAWA, Shinya**; YUASA AND HARA, Section 206, New Ohtemachi Bldg., 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo 100-0004 (JP).
- (81) Designated States (national): KR, US.
- (84) Designated States (regional): European patent (DE, FR, GB).
- Published:**
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- (72) Inventor; and
(75) Inventor/Applicant (for US only): **MORI, Yoichi** [JP/JP];

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD AND APPARATUS FOR TREATING EXHAUST GASES CONTAINING FLUORINE-CONTAINING COMPOUNDS



(57) Abstract: A method for treating exhaust gases containing fluorine-containing compounds which comprises the steps of bringing an exhaust gas containing fluorine-containing compounds into contact with a metal catalyst carrying a tungsten oxide on an alumina-zirconium composite oxide and then bringing the emission into contact with a γ -alumina catalyst.



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DESCRIPTION

METHOD AND APPARATUS FOR TREATING EXHAUST GASES CONTAINING
FLUORINE-CONTAINING COMPOUNDS

BACKGROUND OF THE INVENTION

5 This invention relates to treating of exhaust gases containing fluorine-containing compounds. More particularly, the invention relates to a method and apparatus for treating exhaust gases containing fluorine-containing compounds that are discharged in the semiconductor industry from the step of dry
10 cleaning the inner surfaces and the like of semiconductor fabrication equipment and from the step of etching a variety of films including oxide films.

 In the semiconductor industry, a great variety of harmful gases are used during the semiconductor fabrication process and
15 those gases, if simply discharged into the environment, may potentially pollute it. Particularly in the step of cleaning the inner surfaces of semiconductor fabrication equipment and in the etching or CVD step, fluorine-containing compounds including hydrofluorocarbons such as CHF_3 and perfluorocarbons
20 (PFCs) such as CF_4 , C_2F_6 , C_3F_8 , C_4F_6 , C_4F_8 , C_5F_8 , SF_6 and NF_3 are employed; the fluorine-containing compounds contained in exhaust gases from those steps are global warming gases and there is an urgent need for developing an effective system to remove them.

25 With a view to removing PFCs from PFC containing gases, the present inventors previously invented a method for thermally cracking PFC in the presence of both O_2 and H_2O using a γ -alumina catalyst having a specified crystalline structure and applied for a patent on the method (Japanese Patent
30 Application No. 2000-110668). A method has also been proposed

for treating non-PFC flon gases by cracking flons with a cracking catalyst carrying a tungsten oxide on an alumina-zirconium composite oxide in the presence of a hydrocarbon such as n-butane and O₂ being used as cracking assist gases.

5 When the γ -alumina catalyst having the specified crystalline structure was used in PFC treatment according to the proposal made by the present inventors, the γ -alumina showed high enough cracking activity to achieve complete (100%) PFC removal, with no CO generated as a by-product. In spite of
10 this high efficiency in treatment, the present inventors found by later studies that the γ -alumina gradually deteriorated as the passage of gas was prolonged and that the percentage of gas removal dropped within a shorter time than it was initially desired.

15 As for the metal catalyst carrying a tungsten oxide on an alumina-zirconium composite oxide, its use in the treatment of flon gases (e.g. flon-115) has been proposed but no review has been made about its applicability to refractory PFCs (CF₄, for example, must be cracked by heating to at least 1200°C). In
20 the proposed method, a hydrocarbon and O₂ are used as cracking assist gases but no review has been made about using H₂O in place of the hydrocarbon. Hence, the metal catalyst carrying a tungsten oxide on an alumina-zirconium composite oxide has not been studied at all from the viewpoint of its activity in
25 cracking PFCs in the presence of H₂O and O₂.

SUMMARY OF THE INVENTION

Under these circumstances, the present inventors reviewed the activity of said metal catalyst in cracking PFCs and succeeded in providing a method for treating exhaust gases
30 containing fluorine-containing compounds by which PFCs could be

removed completely without concomitant generation of CO as a by-product and which could achieve high treatment efficiency over an extended period of time.

BRIEF DESCRIPTION OF THE DRAWING

5 Fig. 1 shows in conceptual form an apparatus for treating exhaust gases containing CF_4 according to one aspect of the invention.

DETAILED DESCRIPTION OF THE INVENTION

According to one aspect of the present invention, there is
10 provided a method for treating exhaust gases containing fluorine-containing compounds which comprises the steps of bringing an exhaust gas containing fluorine-containing compounds into contact with a metal catalyst carrying a tungsten oxide on an alumina-zirconium composite oxide and then
15 bringing the emission into contact with a γ -alumina catalyst.

In the method of the invention, an exhaust gas containing PFC and other fluorine-containing compounds (hereunder collectively referred to as PFCs) is passed through a bed of metal catalyst carrying a tungsten oxide on an alumina-
20 zirconium composite oxide and then passed through a γ -alumina catalyst bed.

The metal catalyst that can be used in the invention and which carries a tungsten oxide on an alumina-zirconium compound oxide is of an Al_2O_3 - ZrO_2 - WO_3 system and the catalyst disclosed
25 in Japanese Patent No. 2569421 can be used with advantage. In a preferred case, the zirconium content of the alumina-zirconium composite oxide is 0.2-0.8. To mention just one example, an Al_2O_3 - ZrO_2 - WO_3 catalyst in which the molar ratios of Al_2O_3 , ZrO_2 and WO_3 are 0.75, 0.2 and 0.05, respectively, can be
30 used with advantage. In order to secure the largest possible

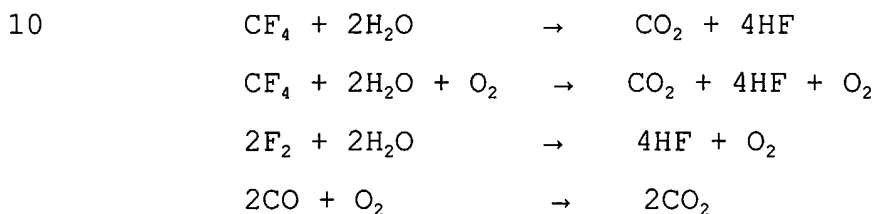
area of contact, the size of the catalyst is preferably as small as possible on the condition that there be no increase in the resistance to the passage of gas. For example, it is preferred to use a generally cylindrical shape of extrusion molding that measures about 0.8-5 mm in diameter and about 5-15 mm in length.

Any γ -alumina that is known to be capable of cracking PFCs can be used as the alumina catalyst in the present invention. Preferred for use is the γ -alumina which the present inventors proposed in Japanese Patent Application No. 2000-110668 and which has such a crystalline structure that a diffraction line with an intensity of 100 or more appears at the following five diffraction angles 2θ measured with an X-ray diffractometer, $33^\circ \pm 1^\circ$, $37^\circ \pm 1^\circ$, $40^\circ \pm 1^\circ$, $46^\circ \pm 1^\circ$ and $67^\circ \pm 1^\circ$. In order to secure the largest possible area of contact, the size of the γ -alumina is preferably as small as possible on the condition that there be no increase in the resistance to the passage of gas. For example, it is preferred to use a particulate shape that measures about 0.8-2.6 mm, more particularly 1.0-2.0 mm, in diameter.

In the method of the invention, the exhaust gas being brought into contact with the metal catalyst bed and the alumina catalyst bed is preferably at a temperature of 600-900°C. It is also preferred to add O_2 and H_2O as cracking assist gases to the exhaust gas before it is brought into contact with the metal catalyst bed and the alumina catalyst. In this case, H_2O is preferably introduced in a gaseous state; to this end, H_2O may be pumped out of a H_2O tank into an evaporator, where it is heated to 100°C and above so that it is all converted to water vapor, which is then forced out by means

of an inert gas such as N₂ and introduced into the reaction system.

If the exhaust gas containing PFCs and other fluorine-containing compounds is passed through the bed of cracking catalyst of the Al₂O₃-ZrO₂-WO₃ system (metal catalyst bed), preferably in the presence of both O₂ and H₂O, and then passed through the γ-alumina bed (alumina catalyst bed), CF₄ which is a PFC gas, an oxidizing gas such as F₂ and other gases such as CO are decomposed into CO₂ and HF by the following reactions:



Thus, CF₄ reacts with H₂O and O₂ to be decomposed into CO₂ and HF whereas the oxidizing gas such as F₂ reacts with H₂O to be decomposed to HF, and CO is oxidized to CO₂.

In the contemplated reactions, O₂ is preferably added in moles which are one more than the minimum number of moles specified above and H₂O is preferably added in 6-10 moles per mole of PFC.

The efficiency of the reaction 2CO + O₂ → 2CO₂ increases with the increasing molar concentration of O₂ because the difference between the molar concentrations of CO and O₂ is so great that O₂ surrounds the CO molecule more easily and their reactivity is increased. Further, due to the collision of individual O₂ molecules in stream, O₂ becomes a radical of higher activity. Therefore, it is preferred to add O₂ in moles at least 5 times the number of moles of CO.

The present invention also provides an apparatus for implementing the above-described method. Thus, according to

its second embodiment, the invention provides an apparatus for treating exhaust gases containing fluorine-containing compounds which comprises a reaction vessel comprising a metal catalyst bed packed with a cracking catalyst carrying a tungsten oxide
5 on an alumina-zirconium composite oxide and an alumina catalyst bed that is placed downstream of the metal catalyst bed and which is packed with γ -alumina, as well as means for introducing an exhaust gas containing fluorine-containing compounds and means for discharging the gas from the reaction
10 vessel.

In the apparatus of the invention, the reaction vessel consists basically of two catalyst beds, one for the first-stage treatment which is a bed of cracking catalyst (of Al_2O_3 - ZrO_2 - WO_3 system) carrying a tungsten oxide on an alumina-
15 zirconium composite oxide (metal catalyst bed) and the other for the second-stage treatment which is a γ -alumina bed (alumina catalyst bed). With this dual-bed arrangement, the catalyst of Al_2O_3 - ZrO_2 - WO_3 system at the first stage achieves partial removal of CF_4 and CO and the γ -alumina at the second
20 stage takes care of the untreated CF_4 and CO. With this design, the service lives of the respective catalysts can be controlled easily and they can be replaced independently of each other, thus leading to effective use of the catalysts.

In the reaction vessel of the invention apparatus, the bed
25 of Al_2O_3 - ZrO_2 - WO_3 catalyst at the first stage and the γ -alumina bed at the second stage are preferably packed into a cylindrical or otherwise shaped container, with a metal screen typically made of stainless steel being placed between the two beds. The dimensions of the reaction vessel to be used in the
30 invention can be determined as appropriate for the limits

imposed by the flow of the gas to be treated and the installation space of the apparatus. Generally, the catalyst of $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-WO}_3$ system in the form of a cylindrical extrusion molded shape which, as already mentioned above, measures about 5 0.8-5 mm in diameter and about 5-15 mm in length may be packed into a cylinder with an inside diameter of 10-20 cm to a height of 25-80 cm; then, γ -alumina particles which, as also mentioned above, measure 0.8-4.5 in diameter are packed downstream of the metal catalyst, with the two catalyst beds being spaced apart 10 by a stainless steel screen which is preferably 0.08-0.16 cm thick. Thus, at each of the first and second stages of treatment in the reaction vessel, layers of the same cracking catalyst are stacked so closely that the zone in which the exhaust gas reacts with H_2O and O_2 can be shortened in the 15 direction of flow; this contributes to reducing not only the unevenness in the reactions that occur in each of the cracking catalyst beds but also the overall size of the apparatus. In the apparatus of the invention, the metal catalyst bed and the γ -alumina bed may be placed within the same column as just 20 described above to construct a reaction vessel of monolithic type; alternatively, the two catalyst beds may be placed in separate columns which are cascaded to construct a reaction vessel of split type.

The apparatus of the invention is preferably equipped with 25 a preheating vessel which performs preliminary heating of the exhaust gas, preferably together with H_2O and O_2 , to a temperature of 600-900°C. By allowing the exhaust gas as well as H_2O and O_2 to pass through the reaction vessel (catalyst beds) after they are heated in the preliminary heating vessel, 30 the uniformity of the cracking catalysts in the reaction vessel

can be retained. If the exhaust gas and the cracking assist gases are introduced into the reaction vessel without preliminary heating, the topmost part of the metal catalyst bed is deprived of thermal energy and cooled upon contact with the exhaust gas. In a preferred embodiment of the invention, the exhaust gas, preferably together with H₂O and O₂, are heated to 600-900°C in the preheating vessel before they are introduced into the catalyst beds, so the cracking catalysts will not be deprived of any heat; in addition, the required heating of the reaction vessel can be held to a minimum level that is sufficient to compensate for the heat of radiation from said vessel and this contributes a lot to cost reduction.

Fig. 1 shows in conceptual form an apparatus for treating exhaust gases containing fluorine-containing compounds in accordance with a preferred embodiment of the invention. The apparatus of the invention for treating fluorine-containing compounds (which are hereunder referred to as PFC exhaust gas) has a reaction unit 20. The reaction unit 20 is divided into a preheating vessel 21 at the first stage and a catalytic reaction vessel 22 at the second stage. The preheating vessel 21 and the catalytic reaction vessel 22 are equipped with heating jackets 23 and 24, respectively, for heating the gas atmospheres in the respective vessels to predetermined temperatures and holding those temperatures. In the apparatus of the design shown in Fig. 1, the preheating vessel 21 is positioned above the catalytic reaction vessel 22 so as to provide such a fluid communication that the exhaust gas to be treated runs down the preheating vessel 21 to flow into the catalytic reaction vessel 22. In the embodiment under consideration, cylindrical containers of identical size are

used as the preheating vessel 21 and the catalytic reaction vessel 22.

Provided at the top of the preheating vessel 21 are an exhaust gas supply line 1 through which the exhaust gas containing PFCs and other fluorine-containing compounds is introduced into the reaction unit 20, an O₂ supply line 7 through which an assist O₂ gas is introduced into the reaction unit 20 and a H₂O supply line 6 through which an assist H₂O gas is introduced into the reaction unit 20. The exhaust gas supply line 1 is connected via piping to a PFC exhaust gas supply source (not shown) such as an exhaust gas line in a semiconductor fabrication apparatus. The O₂ supply line 7 is connected to an O₂ supply source (not shown) via piping. The H₂O supply line 6 is connected to an evaporator 5 via piping around which a band heater 8 is wound. The evaporator 5 is connected to a H₂O (liquid) tank 2 via piping fitted with a storage pump 3; the evaporator 5 is also connected to an inert gas (N₂) supply source 4 via piping.

The preheating vessel 21 has a hollow internal space into which the PFC exhaust gas, O₂ and H₂O are introduced through the respective supply lines 1, 6 and 7 and the introduced gases are preliminarily heated at 600-900°C in the preheating vessel. The preheating vessel 21 may optionally be provided with a plurality of deflectors 25 for promoting the heating of the PFC emission gas. The deflectors 25 are plates or fins that are slightly longer than the inner radius of the preheating vessel 21 and they may be provided on the inner surface of the preheating vessel 21 either spirally or in such a way that they alternate radially to face each other. In order to measure the temperature in the preheating vessel 21, thermocouples (not

shown) may be provided within the preheating vessel 21.

Deflectors of other shapes may be employed as the means for promoting the heating of the exhaust gas; alternatively, in place of or in combination with the deflectors, layers of filler material causing small pressure loss may be installed within the preheating vessel.

Downstream of the preheating vessel 21 (in the lower part of the apparatus of the design shown in Fig. 1), the catalytic reaction vessel 22 is provided to provide fluid communication with the preheating vessel 21. The catalytic reaction vessel 22 is further divided into two beds and a bed 26 at the first stage is filled with a catalyst of Al_2O_3 - ZrO_2 - WO_3 system and a bed 27 at the second stage is filled with γ -alumina. The two catalyst beds 26 and 27 are separated by a stainless steel screen 28.

A jacket 24 for heating γ -alumina at 600-900°C is preferably provided on the outer circumference of the catalytic reaction vessel 22. In order to measure the temperature in the catalytic reaction vessel 22, thermocouples (not shown) may be provided in its interior.

The PFC exhaust gas to be treated by the method of the invention and O_2 as a cracking assist gas are introduced into the preheating vessel via the lines 1 and 7. As for the other cracking assist gas H_2O , water (liquid) is supplied from the water tank 2 into the evaporator 5 by means of the pump 3 and the water vapor generated in the evaporator 5 is introduced into the preheating vessel 21 through the line 6 as carried by N_2 supplied through the line 4. The exhaust gas and the cracking assist gases as introduced into the preheating vessel 21 are heated to 600-900°C. The heated gas mixture is then

introduced into the catalytic reaction vessel 22 where it is held at a temperature of 600-900°C as the PFCs and other fluorine-containing compounds are subjected to progressive cracking reactions by means of the catalyst of Al₂O₃-ZrO₂-WO₃ system at the first stage and the γ-alumina at the second stage. The treated gas containing cracked PFCs and other fluorine-containing compounds is discharged out of the system via an emission line 9.

The following examples are provided for further illustrating the present invention but are in no way to be taken as limiting.

Example 1

An experiment was run to treat a PFC exhaust gas according to the method of the invention. A stainless steel mini-column having an inside diameter of 27 mm and a length of 500 mm was packed with a catalyst of Al₂O₃-ZrO₂-WO₃ system and γ-alumina. As the catalyst of Al₂O₃-ZrO₂-WO₃ system, one having a compositional ratio (molar ratio) of 0.75 Al₂O₃, 0.2 ZrO₂ and 0.05 WO₃ and which was manufactured by Süd-Chemie Catalysis AG as a trial (in the form of particles 2 mm in diameter and 5 mm long) was used and packed to a bed height of 50 mm (at a loading of 29 mL). As γ-alumina, NEOBEAD GB-08 (the trade name of Mizusawa Industrial Chemicals, Ltd.; in the form of particles with Na₂O content ≤ 0.01 wt% and a size of 0.8 mm) which had such a crystalline structure that a diffraction line with an intensity of 100 or more would appear at the following five diffraction angles 2θ measured with an X-ray diffractometer, 33°±1°, 37°±1°, 40°±1°, 46°±1° and 67°±1° was packed to a bed height of 50 mm (at a loading of 29 mL). The two catalyst beds were spaced apart by a 20-mesh stainless

steel screen having a thickness of 0.8 mm. Thermocouples were installed in the column to measure its internal temperature and it was fitted within a ceramic tubular electric furnace, with the catalyst bed of $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-WO}_3$ system being in the upper part.

5 The catalyst bed of $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-WO}_3$ system and the γ -alumina catalyst bed were heated at 750°C as N_2 -diluted CF_4 and more than equivalent amounts of assist gases O_2 and H_2O were introduced into the column from the top. The total gas flow was 410 sccm with CF_4 and O_2 being flowed at respective
10 concentrations of 1.0% and 5.0% and H_2O supplied at 0.059 mL/min.

The concentrations of CF_4 and CO in the exit gas from the column were measured with a gas chromatograph fitted with a mass analyzer (AGS-7000U, product of ANELVA Corporation); the
15 results are shown in Table 1. Throughout the period of 280 hours from the start of the experiment, CF_4 and CO were undetectable. According to the invention, complete removal of CF_4 was possible without generating CO as a by-product.

Comparative Example 1

20 An experiment was run to treat a PFC exhaust gas using only γ -alumina. The procedure was the same as in Example 1 except that the stainless steel mini-column was packed with γ -alumina to a bed height of 100 mm (at a loading of 58 mL). The results are shown in Table 1; the CO level was invariably lower
25 than the detection limit but the percent removal of CF_4 gradually decreased with time (it remained 100% for 60 hours but dropped to 98% after the lapse of 90 hours).

Comparative Example 2

30 An experiment was run to treat a PFC exhaust gas using only a catalyst of $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-WO}_3$ system. The procedure was the

same as in Example 1 except that the stainless steel mini-column was packed with the catalyst of interest to a bed height of 100 mm (at a loading of 58 mL). The results are shown in Table 1; CF₄ started to leak out in small quantities in a
5 comparatively short time, making its complete removal impossible; however, the percent removal of CF₄ was more than 98% even after the lapse of 90 hours. Nevertheless, CO was discharged in amounts exceeding the tolerable 25 ppm {TLV-TWA value (Threshold Limit Value-Time Weighted Average
10 Concentration) set by the American Conference of Governmental Industrial Hygienists)}.

Table 1. Example 1 vs. Comparative Examples 1 and 2

Time of gas passage hr	Ex. 1		Comp. Ex. 1		Comp. Ex. 2	
	CF ₄ ppm	CO ppm	CF ₄ ppm	CO ppm	CF ₄ ppm	CO ppm
10	<1	<2	<1	<2	4.4	20
20	<1	<2	<1	<2	11	20
30	<1	<2	<1	<2	17	25
40	<1	<2	<1	<2	26	25
50	<1	<2	<1	<2	31	25
60	<1	<2	<1	<2	40	25
63	<1	<2	1.3	<2	37	25
66	<1	<2	2.7	<2	56	25
69	<1	<2	10	<2	37	25
72	<1	<2	25	<2	45	25
75	<1	<2	36	<2	49	25
78	<1	<2	54	<2	57	25
81	<1	<2	70	<2	54	25
84	<1	<2	100	<2	50	35
87	<1	<2	160	<2	43	35
90	<1	<2	200	<2	48	35
100	<1	<2	-	-	49	35
120	<1	<2	-	-	54	35
140	<1	<2	-	-	70	35
160	<1	<2	-	-	81	35
180	<1	<2	-	-	83	35
200	<1	<2	-	-	94	35
220	<1	<2	-	-	98	35
240	<1	<2	-	-	90	35
260	<1	<2	-	-	95	35
280	<1	<2	-	-	91	35

According to the invention, exhaust gases containing PFCs and other fluorine-containing compounds can be totally freed of PFCs and other fluorine-containing compounds without causing undue generation of CO as a by-product; the effectiveness of the invention lasts for a very long time.

CLAIMS

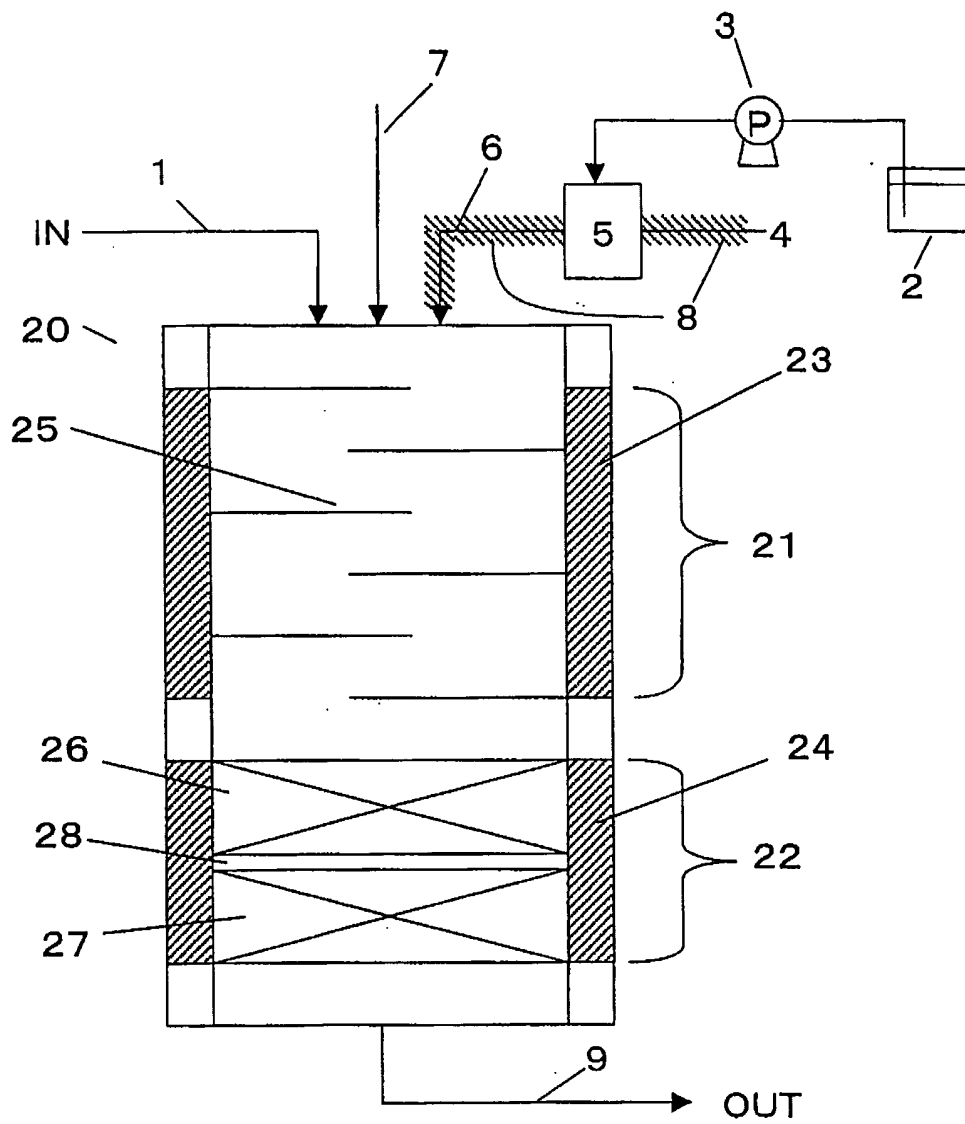
1. A method for treating exhaust gases containing fluorine-containing compounds which comprises the steps of bringing an exhaust gas containing fluorine-containing compounds into contact with a metal catalyst carrying a tungsten oxide on an alumina-zirconium composite oxide and then bringing the emission into contact with a γ -alumina catalyst.
2. The method according to claim 1, wherein contact of the exhaust gas with the metal catalyst and the alumina catalyst is performed at a temperature of 600-900°C.
3. The method according to claim 1 or 2, wherein O₂ and H₂O are added as cracking assist gases to the exhaust gas before it is brought into contact with the metal catalyst and the alumina gas.
4. The method according to any one of claims 1-3, wherein the γ -alumina has such a crystalline structure that a diffraction line with an intensity of 100 or more appears at the following five diffraction angles 2θ measured with an X-ray diffractometer, $33^{\circ}\pm 1^{\circ}$, $37^{\circ}\pm 1^{\circ}$, $40^{\circ}\pm 1^{\circ}$, $46^{\circ}\pm 1^{\circ}$ and $67^{\circ}\pm 1^{\circ}$.
5. An apparatus for treating exhaust gases containing fluorine-containing compounds which comprises a reaction vessel comprising a metal catalyst bed packed with a cracking catalyst carrying a tungsten oxide on an alumina-zirconium composite oxide and an alumina catalyst bed that is placed downstream of the metal catalyst bed and which is packed with γ -alumina, as well as means for introducing an exhaust gas containing fluorine-containing compounds and means for discharging the gas from the reaction vessel.

6. The apparatus according to claim 5 which is equipped with means for adding O₂ and H₂O to the exhaust gas as cracking assist gases.

7. The apparatus according to claim 5 or 6 which further has
5 means for heating the exhaust gas.

8. The apparatus according to any one of claims 5-7, wherein the γ -alumina has such a crystalline structure that a diffraction line with an intensity of 100 or more appears at the following five diffraction angles 2θ measured with an X-ray
10 diffractometer, $33^{\circ}\pm 1^{\circ}$, $37^{\circ}\pm 1^{\circ}$, $40^{\circ}\pm 1^{\circ}$, $46^{\circ}\pm 1^{\circ}$ and $67^{\circ}\pm 1^{\circ}$.

Fig. 1



A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/86

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 101 524 A (EBARA CORP) 23 May 2001 (2001-05-23) column 3, paragraph 16 - paragraph 18; claims; figures; examples 3,4 ---	1-8
Y	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 06, 31 July 1995 (1995-07-31) & JP 07 080303 A (KYUSHU UNIV), 28 March 1995 (1995-03-28) abstract ---	1-8
A	EP 1 129 775 A (EBARA CORP) 5 September 2001 (2001-09-05) page 8, paragraphs 84,85; examples --- -/--	1-8

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the international search

7 February 2003

Date of mailing of the international search report

14/02/2003

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European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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Lapeyrere, J

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 02/10475

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 02, 2 April 2002 (2002-04-02) & JP 2001 293335 A (EBARA CORP), 23 October 2001 (2001-10-23) cited in the application abstract	1-8
A	----- DE 197 19 834 A (CS HALBLEITER SOLARTECH) 19 November 1998 (1998-11-19) the whole document -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 02/10475

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