



(51) International Patent Classification:

B01D 53/94 (2006.01) **B01J 23/44** (2006.01)
B01J 35/00 (2006.01) **F01N 3/035** (2006.01)
B01J 37/02 (2006.01)

(21) International Application Number:

PCT/JP2017/012865

(22) International Filing Date:

29 March 2017 (29.03.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2016-073878 1 April 2016 (01.04.2016) JP

(71) Applicant: **JOHNSON MATTHEY JAPAN G.K.**
[JP/JP]; 5123-3 Kitsuregawa, Sakura-shi, Tochigi,
3291412 (JP).

(72) Inventors: **SUMIYA Satoshi**; c/o Johnson Matthey Japan
G.K., 5123-3 Kitsuregawa, Sakura-shi, Tochigi, 3291412
(JP). **YOKOTA Daisuke**; c/o Johnson Matthey Japan
G.K., 5123-3 Kitsuregawa, Sakura-shi, Tochigi, 3291412
(JP).

(74) Agent: **SONODA & KOBAYASHI INTELLECTUAL
PROPERTY LAW**; 34th Floor, Shinjuku Mitsui Build-
ing, 1-1, Nishi-Shinjuku 2-chome, Shinjuku-ku, Tokyo,
1630434 (JP).

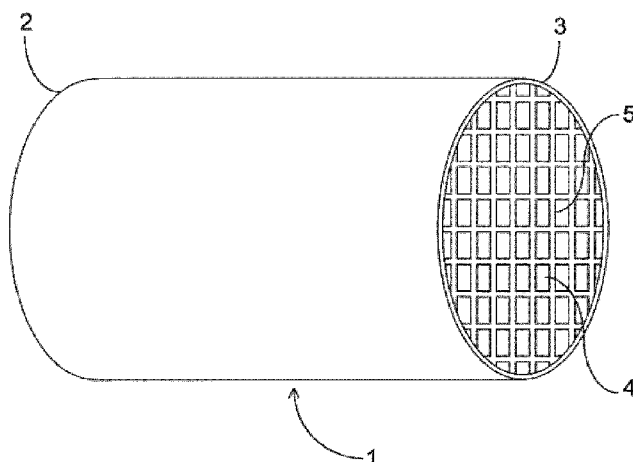
(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN,
KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA,
MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG,
NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS,
RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY,
TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN,
ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: EXHAUST GAS PURIFICATION FILTER



(57) Abstract: The problem addressed by the present invention lies in providing an exhaust gas purification filter which can effi-
ciently treat particulate matter in exhaust gas. The present invention provides an exhaust gas purification filter including a substrate
comprising a plurality of porous partitions, wherein the partitions form an exhaust gas flow path, a porous catalytic layer is provided
on the partitions and the catalytic layer having a thickness of 10 μ m or greater is provided over at least 20% of the total length of the
partitions in the lengthwise direction thereof, and the catalytic layer having a thickness of 10 μ m or greater is not present on the par-
titions 15 mm from an outflow side.

Description

Title of Invention: EXHAUST GAS PURIFICATION FILTER

Technical Field

[0001] The present invention relates to an exhaust gas purification filter.

Background Art

[0002] Particulate matter (PM) is contained in exhaust gas discharged from fuel-burning combustion engines, especially from high-pressure fuel injection internal combustion engines. PM comprises: a component (e.g., a carbon-based substance) including soot and other carbon atoms produced by fuel combustion; a soluble organic component (referred to below, as appropriate, as "SOF") comprising unburned fuel (hydrocarbons) or unburned oil; and trace amounts of sulfates. PM is known as a substance which contaminates the atmosphere and has an adverse effect on plant and animal life, and reducing PM is becoming an important issue in the automotive industry at the present time.

[0003] For this reason, methods for trapping PM by means of a diesel particulate filter (DPF) are currently being developed as methods for reducing PM. However, there are limits to the amount of PM which can be trapped by a DPF, and the trapped PM has to be removed using external energy etc. This is therefore unsuitable for continuous treatment of exhaust gas and requires the installation of an external device, so there are problems in terms of cost and also an increase in the size of an exhaust gas treatment device, among other things.

[0004] Furthermore, a method for treating SOF, hydrocarbons and carbon monoxide in exhaust gas by means of an exhaust gas catalyst (oxidation catalyst) has been proposed. In general, exhaust gas catalysts are prepared for the most part by forming a catalyst component slurry and uniformly soaking a support in this slurry and then baking the support. Consequently, it has been found that when the exhaust gas flows into the catalyst component (catalytic layer) there is a reduction in the gas diffusion properties of the exhaust gas (hydrocarbon gas having a long carbon chain in particular), and as a result the capacity to purify the exhaust gas cannot be adequately demonstrated. Furthermore, a porous structure is generally used for the support for holding the catalytic layer, but the pore size may produce a reduction in the exhaust gas removal rate due to a limitation on exhaust gas diffusion under large space velocity conditions.

[0005] Patent Document 1 and Patent Document 2, for example, propose a NO_x occlusion and reduction catalyst in which the exhaust gas diffusion properties are improved so as to improve the NO_x purification efficiency, by supporting a NO_x occluding agent and

a precious metal on a coating layer comprising a porous structure provided with pores having a specific size.

Citation List

Patent Literature

- [0006] PTL 1: JP 2002-191988 A
PTL 2: JP 2002-253968 A

Summary of Invention

- [0007] The inventors of the present invention discovered a configuration for an exhaust gas purification filter which makes it possible to achieve efficient treatment of particulate matter in exhaust gas. The present invention was devised against this background, and the aim thereof lies in providing an exhaust gas purification filter in which pressure loss hysteresis occurring when PM is repeatedly regenerated is improved, and particulate matter in exhaust gas can be efficiently treated. A further aim of the present invention lies in providing the structure of the abovementioned exhaust gas purification filter and a method for producing same.
- [0008] The present invention provides an exhaust gas purification filter including a substrate comprising a plurality of porous partitions, wherein the partitions form an exhaust gas flow path, a porous catalytic layer is provided on the partitions and the catalytic layer having a thickness of 10 μm or greater is provided over at least 20% of the total length of the partitions in the lengthwise direction thereof, and the catalytic layer having a thickness of 10 μm or greater is not present on the partitions 15 mm from an outflow side.
- [0009] According to a mode of the present invention, the application amount of catalyst component forming part of the catalytic layer varies according to the specific gravity of the catalyst component and the pore volume in the catalytic layer.
- [0010] According to a mode of the present invention, the mean diameter of pores formed by an organic pore-forming material in the catalytic layer is between 1 and 5 μm .
- [0011] According to a mode of the present invention, the void ratio of the catalytic layer is no greater than 50%.
- [0012] According to a mode of the present invention, a slurry including a catalyst component and an organic pore-forming material is applied in order to form the catalytic layer.
- [0013] According to a mode of the present invention, the mean length/diameter ratio of the organic pore-forming material is 1.5 or less.
- [0014] According to a mode of the present invention, the void ratio of the substrate partitions is between 40% and 60%.
- [0015] According to a mode of the present invention, the mean diameter of the pores in the

substrate partitions is between 10 μm and 20 μm .

[0016] According to a mode of the present invention, the catalyst component may include at least one of platinum and palladium, and may further include at least one of an alkali metal and a rare earth metal.

[0017] According to a mode of the present invention, the thickness of the catalytic layer is between 10 μm and 50 μm .

[0018] A mode of the present invention provides a method for producing the above-mentioned exhaust gas purification filter, comprising a step in which a slurry including a catalyst component and an organic pore-forming material is applied in order to form pores in the catalytic layer.

[0019] According to a mode of the present invention, the mean length/diameter ratio of the organic pore-forming material is 1.5 or less in the method for producing the above-mentioned exhaust gas purification filter.

[0020] The present invention makes it possible to provide a filter that does not impair performance in relation to PM trapping efficiency, and can also maintain CO and HC oxide treatment efficiency by means of a catalyst, while also enabling a shorter drying time when the exhaust gas purification filter is produced.

Brief Description of Drawings

[0021] [fig.1]Fig. 1 is a schematic diagram to illustrate the exhaust gas purification filter according to a mode of embodiment of the present invention; and

[fig.2]Fig. 2 is a graph showing the correlation between void ratio obtained from an SEM image and void ratio obtained from measurement results of a mercury porosimeter.

Description of Embodiments

[0022] A mode of embodiment of the present invention will be described below with reference to the figures but the present invention is obviously not limited by the mode of embodiment.

[0023] (Mode of Embodiment 1)

A feature of the exhaust gas purification filter according to this mode of embodiment lies in the fact that said exhaust gas purification filter includes a substrate comprising a plurality of porous partitions, the partitions form an exhaust gas flow path, a porous catalytic layer formed by an organic pore-forming material is provided on the partitions and the catalytic layer having a thickness of 10 μm or greater is provided over at least 20% of the total length of the partitions in the lengthwise direction thereof, and the catalytic layer having a thickness of 10 μm or greater is not present on a gas inflow-side partition 15 mm from an outflow side.

[0024] The exhaust gas purification filter according to this mode of embodiment restricts

deep PM filtration by virtue of the fact that it is coated (on-wall coated) with a catalytic layer having a constant thickness or greater and comprising a suitable porous structure, and "pressure loss hysteresis" from repeated PM deposition and regeneration can be improved.

[0025] In terms of an exhaust gas purification filter, it is thus possible to restrict increases in pressure loss accompanying PM deposition, and it is also possible to detect a more suitable regeneration timing when increased pressure loss serves as a trigger for deposited PM regeneration treatment.

[0026] As shown in fig. 1, the exhaust gas purification filter according to this mode of embodiment includes a substrate 1, and a catalytic substance (not depicted) provided inside the substrate 1, said substrate 1 comprising a plurality of cells 4 that form a gas (exhaust gas) flow path and have a gas inflow-side end 2 and outflow-side end 3, and a plurality of porous partitions 5 that define the cells 4. A porous catalytic layer (not depicted) is provided on the partitions 5.

[0027] The substrate 1 supports the catalytic substance and serves to form an exhaust gas flow path; the substrate 1 is preferably durable so that as far as possible there is no reduction in combustion efficiency in a connected internal combustion engine caused by pressure loss. There is no particular limitation as to the porous material forming the substrate 1 as long as pores are provided at least in the partitions 5, but a porous ceramic material is preferably used.

[0028] Preferred materials for the substrate 1 include a cordierite ceramic comprising three components, namely aluminium oxide (Al_2O_3 : alumina), silicon dioxide (SiO_2 : silica) and magnesium oxide (MgO); silicon carbide and aluminium titanate. By using these materials together with the organic pore-forming material, it is possible to set the porosity of the partitions 5 etc. in the substrate 1 in a preferred range.

[0029] A honeycomb shape comprising the abovementioned materials is preferred as the substrate 1. A honeycomb-shaped filter includes a plurality of cells forming a gas flow path, but there is no particular limitation as to the cross-sectional shape of the cells and a grid-like mesh is feasible, as shown in fig. 1, or a hexagonal shape is equally feasible, but there is no restriction as to the shape thereof. Alternatively, what is known as an asymmetrical cell structure having cells of different sizes at an inlet and outlet may be used.

[0030] There is no limitation as to the structure of the substrate 1 in the exhaust gas purification filter according to this mode of embodiment, but the substrate 1 comprises at least the gas inflow-side end 2 and outflow-side end 3. Furthermore, the substrate 1 comprises at least the plurality of cells 4 forming the gas flow path, and the plurality of porous partitions 5 defining said cells 4.

[0031] The plurality of cells 4 in the exhaust gas purification filter according to this mode of

embodiment are alternately sealed at the inlets/outlets thereof at the ends of at least some of the cells 4. By adopting this kind of configuration, exhaust gas can pass efficiently through the flow path and particulate matter in the exhaust gas can be efficiently treated.

[0032] The exhaust gas purification filter according to this mode of embodiment more preferably employs a substrate having a configuration such as that described above, but the substrate supporting the catalytic substance is not limited to the abovementioned configurations.

[0033] The porous catalytic layer is provided on the partitions of the exhaust gas purification filter according to this mode of embodiment, said catalytic layer having a thickness of 10 μm or greater being provided over at least 20% of the total length of the partitions in the lengthwise direction thereof, while the catalytic layer having a thickness of 10 μm or greater is not present on the gas inflow-side partitions 15 mm from the outflow side.

[0034] The catalytic layer having a thickness of 10 μm or greater more preferably constitutes at least 50% (excluding 15 mm from the outlet) of the total length of the partitions in the lengthwise direction thereof, from the point of view of reducing pressure loss hysteresis. Furthermore, it is preferable for a high-concentration precious metal component also to be present from the inlet portion in an amount of less than 50%, from the point of view of improving catalyst oxidation activity.

[0035] More preferably, the catalytic layer having a thickness of 10 μm or greater is not present on the gas inflow-side partitions of the inlet cells within 15 mm of the outflow side. Furthermore, the thickness of the catalytic layer on the partitions 15 mm from the outflow side is more preferably either between 10 and 40 μm or distributed in an in-wall state.

For example, when a range of 10 mm from the outflow side is used for sealing plugs, the catalytic layer is preferably not provided in a range of less than 5 mm from the ends of the plugs.

[0036] Coating 100% of the total length of the catalytic layer having a constant thickness is intrinsically advantageous in view of a DPF function, but this advantage can still be maintained to a certain extent if a partially uncoated portion is present. Furthermore, if an on-wall layer formed using a wet slurry is shortened, it is possible to shorten the time taken to dry moisture filling the pores in the partitions, which makes it possible to improve producibility. It is also possible to reduce pressure loss in terms of air circulation.

[0037] For example, if the total length (100%) of the partitions is coated with wet slurry, moisture fills the inside of the partitions, so ventilated drying is not possible until a water film has ruptured, so the drying time increases and this is a problem in terms of

producibility. With the exhaust gas purification filter according to this mode of embodiment, however, the catalytic layer having a thickness of 10 μm or greater is not applied over the total length of 100%, so ventilated drying is possible directly after coating and it is possible to resolve said problem.

[0038] The exhaust gas purification filter according to this mode of embodiment has the configuration described above, and therefore it is possible to overcome production drawbacks while imparting the effect of an on-wall catalytic layer.

[0039] Furthermore, it is possible to enhance the gas dispersibility of the exhaust gas by virtue of the fact that the catalytic layer has pores formed by means of the organic pore-forming material, and as a result it is possible for the exhaust gas catalyst to perform efficient oxidation treatment of gaseous components such as CO and HC.

[0040] "Pores formed by means of the organic pore-forming material" as referred to in the exhaust gas purification filter according to this mode of embodiment indicate that voids are present inside, on the surface of, and at the interface etc. of the catalytic layer and the partitions. There is no particular limitation as to the shape of the "pores", and a hole shape, spherical shape, elliptical shape, prism shape, through-path or any similar shape is feasible, but preferably $L/D < 1.5$.

[0041] The thickness of the catalytic layer in the portion of the exhaust gas purification filter according to this mode of embodiment having a thickness of 10 μm or greater is between 10 μm and 50 μm . The thickness of the catalytic layer in the portion having a thickness of 10 μm or greater is more preferably between 10 and 20 μm .

[0042] That is to say, a catalytic layer having a thickness of between 10 and 20 μm is preferred for reasons of reduced pressure loss and formation of an on-wall PM-trapping layer, and 50% or more (excluding a range of 15 mm from the outflow-side end) of the total length of the partitions in the lengthwise direction thereof is preferably coated from the point of view of reducing pressure loss hysteresis. Furthermore, less than 50% from the inflow-side end is preferably coated from the point of view of improving catalyst oxidation activity.

[0043] Specifically, the catalytic layer preferably includes a precious metal component such as platinum or palladium; a metal oxide such as alumina, silica or titania or a composite oxide thereof, or a component in which a rare earth element has been added thereto, such as ceria; and a Ba, Mn, Cu or OSC material and/or an alkali metal such as K or Cs serving as an auxiliary catalyst.

More preferably, the catalytic layer comprises a precious metal, a composite oxide having alumina as the main component serving as a support material for the precious metal, and an OSC (oxygen storage) material serving as a PM combustion catalyst.

[0044] The catalyst component which is used has the feature of catalysing the combustion of particulate matter and oxygen in the exhaust gas, and also of catalysing nitric oxide in

the exhaust gas to nitrogen dioxide, catalysing carbon monoxide to carbon dioxide, and catalysing hydrocarbons to carbon dioxide and water. Specific examples of this kind of catalyst component which may be cited are those selected from the group consisting of alkali metals, alkaline earth metals, transition elements and elements from groups 10 to 12 of the extended periodic table of the elements, and mixtures thereof.

- [0045] Alkali metals which may be cited are selected from the group consisting of sodium (Na), potassium (K), caesium (Cs) and mixtures thereof, with potassium and caesium and mixtures thereof being preferred. Alkaline earth metals which may be cited are selected from the group consisting of magnesium, calcium, barium and mixtures thereof, with magnesium, barium and mixtures thereof being preferred.
- [0046] Transition elements which may be cited are selected from the group consisting of zirconium, lanthanum, cerium, platinum, rhodium, ruthenium, palladium, iron, silver and mixtures thereof, with cerium, platinum, iron and mixtures thereof being preferred. Zinc may be cited as an element from group 12 of the extended periodic table of the elements. Elements from group 13 of the extended periodic table of the elements which may be cited are selected from the group consisting of aluminium, gallium, indium and mixtures thereof, with aluminium being preferred.
- [0047] The catalyst component preferably also brings a function of oxidizing gaseous components in the exhaust gas. Catalyst components of this kind which may be cited belong to the precious metals and the base metals from among those mentioned above.
- [0048] The catalyst component in the exhaust gas purification filter according to this mode of embodiment more preferably includes at least one of platinum and palladium, and at least one of an alkali metal and a rare earth element.
- [0049] The weight ratio of platinum and palladium is more preferably at least 1:1 for the catalytic substance. By this means, it is possible to achieve an effect enabling restriction of thermal sintering (agglomeration) of a precious metal, in particular platinum, under an oxidizing atmosphere. Furthermore, platinum and palladium are preferably included at a ratio of between 2:1 and 5:1 from the point of view of sulfur tolerance.
- [0050] The exhaust gas purification filter according to this mode of embodiment more preferably further includes, as a catalyst auxiliary, at least one material selected from the group consisting of an OSC material, an alkali metal and a perovskite material. The further inclusion of a PM combustion catalyst comprising this kind of transition metal group makes it possible to achieve an effect of promoting combustion of carbon-based substances.
- [0051] Examples of oxygen storage materials which may be cited include materials comprising Ce, Pr, Zr and Nd. Among these, Ce is particularly preferably used for reasons of promoting combustion. Examples of alkali metals which may be cited

include K, Cs and Mg. Among these, K and Cs are particularly preferably used for reasons of promoting combustion. Examples of perovskite materials which may be cited include $\text{Bi}_4\text{Ti}_3\text{O}_4$ (JP 2010-69471 A) and $\text{Ce}_{0.5}\text{Bi}_{0.1}\text{Pr}_{0.4}$ (JP 2009-112907 A).

[0052] The application amount of the catalyst component forming part of the catalytic layer of the exhaust gas purification filter according to this mode of embodiment is more preferably set at 40 g/L or less, taking the catalyst component as γ -alumina. The amount of catalyst applied is related to the actual formation of an on-wall catalytic layer, and also affects pressure loss characteristics. 40 g/L may be converted to approximately 0.7 g/in³.

[0053] Furthermore, an on-wall layer cannot be adequately formed when the material used in order to impart the catalytic function is applied at 10 g/L or less. The amount of catalyst component applied is more preferably 30 g/L or less for reasons of being able to limit a large increase in pressure loss, but the minimum amount is also affected by the specific gravity and pore volume of the material used. For example, when γ -alumina having a pore volume of 0.7 ml/g is used, an application amount of 40 g/L or less is preferred, and when cerium oxide having a pore volume of 0.21 ml/g is applied, an application amount of approximately 200 g/L is preferred. These show that the optimum application amount varies according to the material forming the slurry.

[0054] A further catalyst auxiliary may be added to the exhaust gas purification filter according to this mode of embodiment. Specific examples of catalyst auxiliaries are selected from the group consisting of aluminium oxide, cerium oxide, titanium oxide, zirconium oxide, silicon oxide, magnesium oxide and mixtures thereof, with magnesium oxide, cerium oxide, titanium oxide, zirconium oxide and silicon oxide being preferred. The catalyst auxiliary is added in an amount of 50-99% with respect to the total weight of the components forming the catalytic layer.

[0055] The mean diameter of the pores in the catalytic layer in the exhaust gas purification filter according to this mode of embodiment is more preferably between 1 and 5 μm . The mean diameter of the pores in the catalytic layer is more preferably between 2 and 5 μm for reasons of a balance between pressure loss and restricting deep filtration of PM particles.

[0056] The void ratio of the catalytic layer in the exhaust gas purification filter according to this mode of embodiment is more preferably no greater than 50%. The void ratio of the catalytic layer is more preferably between 50 and 30% for reasons of pressure loss and of maintaining the mechanical strength of the on-wall layer.

[0057] The slurry including the catalyst component and the organic pore-forming material is more preferably mixed and applied in order to form the catalytic layer as an on-wall structure and in order to form pores in the catalytic layer of the exhaust gas purification filter according to this mode of embodiment.

- [0058] There are several methods for on-wall coating of the catalyst. One such method employs solid particles which are larger than the pores in the partitions. It is possible to restrict the penetration of catalyst particles into the pores in the partitions by means of a pore-forming material having large particles which also serves as the catalyst solid content. Furthermore, this pore-forming material also contributes to reducing pressure loss in the on-wall catalytic layer.
- [0059] The particle size of the pore-forming material is preferably between 1 and 5 μm , and more preferably between 2 and 5 μm in order to prevent deep filtration in the actual voids formed.
- [0060] Specific examples of means for providing voids in the catalytic layer which may be cited include a means by which an exhaust gas catalyst component and a pore-forming material are added to and stirred in a medium (e.g., water) to prepare a slurry which is then supported on a support and baked in order to combust and decompose the forming agent. The forming agent can therefore preferably be removed by combustion during the baking process.
- [0061] Any type of forming agent can be used provided that it causes the formation of voids, and materials having the same or different shapes, types or sizes etc. can be used. A forming material which is spherical or cylindrical etc. and can be thermally decomposed or combusted is preferred. An organic pore-forming material is more preferably used as the forming agent.
- [0062] An organic pore-forming material can be advantageously used provided that it is a combustible material having a specific gravity at the same level as that of a slurry aqueous solution. This is because the organic pore-forming material does not readily form a uniform dispersed state with other materials in the aqueous solution if the specific gravity thereof is excessively low or excessively high.
- [0063] Specific examples of this kind of forming agent which may be cited include: foaming agents, surfactants, foamable synthetic resins, activated carbon, graphite powder and pulp powder. Specific examples of foaming agents which may be cited include $\text{La}_2(\text{CO}_3)_3$, $\text{Al}_2(\text{CO}_3)_3$, and $\text{Ce}_2(\text{CO}_3)_3$, and the same elements as in the exhaust gas catalyst component are preferably included. Specific examples of surfactants which may be cited include anionic surfactants such as sulfonic acid surfactants and carbonic acid surfactants; cationic surfactants such as amine surfactants; and amphoteric surfactants such as fatty acid ester surfactants. Foamable synthetic resins and the like which may be cited include polyurethane-based, polystyrene-based (e.g., polystyrene), polyethylene-based, polyester-based, and polyacrylic-based (e.g., polymethyl methacrylate) synthetic resins.
- [0064] When the organic pore-forming material is used, the mean length/diameter ratio of the organic pore-forming material is preferably 1.5 or less. The spheres of spherical

particles generally make point contact and although this is believed to produce poor void communication, results up until now show that the advantages can be maintained. It is believed that setting L/D close to spherical facilitates predicting the amount of penetration into the pores in the partitions due to differences in the orientation of the pore-forming material, enabling the usage amount to be set more reliably.

[0065] A more preferred example of an organic pore-forming material is a polymer such as a polylactic acid polymer.

[0066] The void ratio of the pores in the partitions in the exhaust gas purification filter according to this mode of embodiment is preferably between 40% and 60%. The void ratio of the pores in the partitions is more preferably between 40 and 55% from the point of view of compatibility between reducing pressure loss and PM trapping performance.

[0067] The mean diameter of the pores in the partitions in the exhaust gas purification filter according to this mode of embodiment is preferably between 10 μm and 20 μm . The mean diameter of the pores in the partitions is preferably 10 μm or greater from the point of view of DPF pressure loss and is preferably 20 μm or less because this provides a high PM trapping efficiency from the outset. The mean diameter of the pores is more preferably between 10 and 15 μm .

[0068] The form of the pores and the void ratio of the catalytic substance in the above-mentioned mode of embodiment can be obtained using an SEM (scanning electron microscope)/EPMA (electron probe microanalyser). For example, the pore area (A) of the substrate before application of the catalytic substance can be obtained by image processing in a field of view magnified between 150 and 500 times by means of an SEM/EPMA. Furthermore, the pore area (B) after application of the catalyst can also be obtained by the same method. Furthermore, the area of the substrate portion is obtained by means of image processing using the same two-dimensional method, which makes it possible to calculate the relative ratio of the pore area of holes in the substrate 1 and the occupied area ratio.

[0069] Furthermore, the mercury intrusion method is generally used as the method for measuring the three-dimensional pore structure volume, and the result of the correlation between that method and the abovementioned image processing method is as shown in fig. 2; there is a correlation between the two-dimensional void ratio (ratio of occupied area) obtained from the SEM image and the void occupation volume ratio obtained from the measurement results using a mercury porosimeter, which constitutes three-dimensional data.

[0070] A compositional image at a magnification of 150 to 200 times is preferably used here in the SEM/EPMA method, and the occupied area can be obtained by separating the areas occupied by the substrate and the catalyst into individual colours using the RGB

method, for example.

When the occupied area is obtained by image processing in the exhaust gas purification filter according to this mode of embodiment, the image is preferably binarized and a calculation is preferably made using an automatic mode or the like in order to prevent human error.

[0071] The exhaust gas purification filter according to the abovementioned mode of embodiment is used to purify exhaust gas and a device employing the exhaust gas purification filter according to the abovementioned mode of embodiment is preferably used in an exhaust system of an internal combustion engine, in particular a spark-ignition engine (e.g., a petrol engine) or a compression-ignition engine (e.g., a diesel engine).

[0072] Furthermore, these engines may be engines which burn fuel by adjusting the air-fuel ratio, and preferred specific examples thereof which may be cited include lean-burn engines, direct-injection engines, and preferably an engine combining these (i.e., a direct-injection lean-burn engine). A direct-ignition engine employs a fuel supply system which enables a higher compression ratio, improved combustion efficiency and also a reduction in exhaust gas. By combining this with a lean-burn engine, it is therefore possible to further improve combustion efficiency and reduce exhaust gas.

[0073] The exhaust gas purification filter according to this mode of embodiment is preferably used in an exhaust system of an internal combustion engine mounted in a conveyance vehicle or a machine etc. Specific examples of conveyance vehicles and machines which may be cited include: transportation vehicles such as motor vehicles, buses, trucks, dumper cars, diesel railcars, motorcycles, motorized bicycles, ships, tankers, motorboats, and aircraft; agricultural machines such as cultivators, tractors, combine harvesters, chainsaws, and timber carriers; aquatic and fishing machines such as fishing boats; timber working machines such as tank lorries, cranes, compressors, and excavators; and generators.

[0074] The exhaust gas purification filter according to this mode of embodiment may be installed for a start catalyst, an underfloor catalyst, or a manifold converter in a vehicle exhaust system, for example.

Exemplary Embodiments

[0075] Exemplary embodiments according to the present invention will be described below. The content of the present invention should not be interpreted as being limited by these exemplary embodiments.

[0076] (Example of production of an exhaust gas purification filter having a catalytic layer for trapping PM on partitions)

The DPF which was used was an SD082 produced by IBIDEN: diameter 143.8 mm × length 150.2 mm, mean pore size 12 μm, porosity 42%.

[0077] A wash coat (referred to below as a “WC”) in which an organic pore-forming material was kneaded with a slurry containing alumina as the main component and also platinum and palladium was prepared and coated on the DPF by means of a filter coating apparatus in such a way that the amount of catalyst was 20 g/L. After drying at 100°C, the coated filter was baked for 1 hour at 500°C. Here, the organic pore-forming material which was used was a spherical material having an aspect ratio of 1:1 and comprising a polylactic acid polymer which was Landy PL-1000 (produced by Miyoshi Oil & Fat Co., Ltd.).

[0078] (Exemplary Embodiment 1 and Comparative Examples 1 and 2)

As shown in Table 1, exhaust gas purification filters were produced with different lengths of catalytic layer on the partitions. The WC containing the organic pore-forming material was applied in such a way that the length thereof was 15 mm, 76 mm and 150 mm, and these lengths correspond to Exemplary Embodiment 1 and Comparative Examples 1 and 2, respectively. The location which was not coated with the WC containing the organic pore-forming material were coated using a WC that did not contain an organic pore-forming material. The amounts of platinum, palladium and WC per exhaust gas purification filter were the same.

[0079] It was clear that an exhaust gas purification filter in which the catalytic layer having a thickness of 10 μm or greater was applied over at least 20% of the total length of the partitions in the lengthwise direction thereof, and the catalytic layer having a thickness of 10 μm or greater was not present at a position 15 mm from the outflow side, dried in a shorter time in the slurry drying process, which is a consideration in mass production, and also had superior performance in terms of CO 50% conversion efficiency temperature, and also PM deposition pressure loss and PM deposition pressure loss hysteresis. The PM deposition pressure loss was measured under soot generation conditions of a gas flow rate of 240 kg/hr and a gas temperature of 250°C.

[0080]

[Table 1]

	Length of application of on-wall catalytic layer having a thickness of 10 μm or greater [mm]	Catalytic layer having a thickness of 10 μm or greater at a position 15 mm from outflow side	Time of slurry drying process [min]	CO 50% conversion efficiency temperature [$^{\circ}\text{C}$]	PM deposition pressure loss [kPa]	PM deposition pressure loss hysteresis (pressure loss difference with the same amount of soot accumulation after soot regeneration treatment) [kPa]
Ex. Emb. 2	76	Not present	10-15	240	7.0	0.1 or less
Comp. Ex. 1	15	Not present	5-10	255	7.4	0.6
Comp. Ex. 2	152	Present	90-100	245	7.2	0.1 or less

[0081] (Exemplary Embodiments 3-5)

Exhaust gas purification filters were produced in accordance with Exemplary Embodiment 1 with catalyst component application amounts of 35 g/L, 55 g/L and 5 g/L, and these correspond to Exemplary Embodiments 3, 4 and 5.

[0082] When the amount of catalyst component applied exceeded 40 g/L, as in Exemplary Embodiment 4, the thickness of the catalytic layer and the partitions increased and there was a deterioration in PM deposition pressure loss. Furthermore, when the amount of catalyst component applied was 10 g/L or less, as in Exemplary Embodiment 5, the thickness of the catalytic layer on the partitions decreased and the effect as an on-wall layer could not be demonstrated.

[0083]

[Table 2]

	Length of application of on-wall catalytic layer having a thickness of 10 μ m or greater [mm]	Catalytic layer having a thickness of 10 μ m or greater at a position 15 mm from outflow side	Amount of catalyst component applied [g/L]	Mean thickness of on-wall layer [μ m]	PM deposition pressure loss [kPa]
Ex. Emb. 2	76	Not present	20	13	7.0
Ex. Emb. 3	76	Not present	35	21	7.4
Ex. Emb. 4	76	Not present	55	40	8.4
Ex. Emb. 5	76	Not present	5	3	7.9

[0084] (Exemplary Embodiments 6 and 7)

In accordance with Exemplary Embodiment 2, irregular particles (corn starch) which were not spherical were used as the type (shape) of the organic pore-forming material in Exemplary Embodiment 6, and a melamine polymer (MC6000 (produced by Nissan Chemical Industries, Ltd.), spherical, L/D = 1) was used in Exemplary Embodiment 7. A satisfactory catalytic layer could not be obtained on the partitions in either Exemplary Embodiment 6 or 7.

[0085] [Table 3]

	Length of application of on-wall catalytic layer having a thickness of 10 μ m or greater [mm]	Catalytic layer having a thickness of 10 μ m or greater at a position 15 mm from outflow side	Type of organic pore-forming material	Shape/aspect ratio of organic pore-forming material	Formation of on-wall layer
Ex. Emb. 2	76	Not present	Polylactic acid polymer	Spherical/1:1	Satisfactory
Ex. Emb. 6	76	Not present	Acrylic polymer	Elliptical/3:1	Some of WC entered partitions
Ex. Emb. 7	76	Not present	Melamine polymer	Spherical/1:1	Could not be dispersed in slurry, uneven layer formed after coating

[0086] (Exemplary Embodiments 8 and 9)

In accordance with Exemplary Embodiment 2, exhaust gas purification filters in which the amount of organic pore-forming material added was changed to 4 g/L and 15 g/L were produced, and these correspond to Exemplary Embodiments 8 and 9. In Table 4, the amount of organic pore-forming material added (g/L) is converted to the volume fraction (%) of the organic pore-forming material in the WC. A satisfactory catalytic layer could not be obtained on the partitions in either Exemplary Embodiment 8 or 9, and a state in which the void ratio could be defined was not achieved.

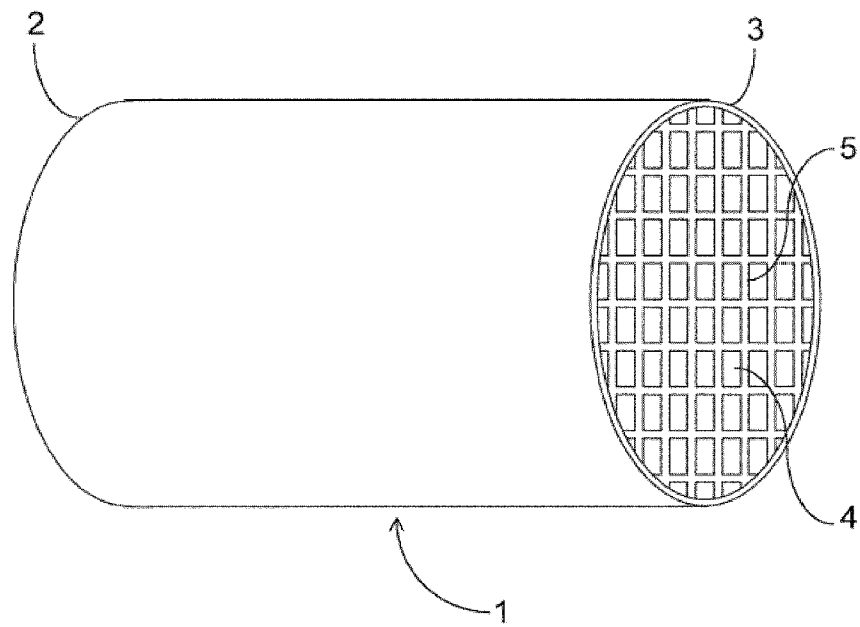
[0087] [Table 4]

	Length of application of on-wall catalytic layer having a thickness of 10 μ m or greater at a position 15 mm from outflow side [mm]	Catalytic layer having a thickness of 10 μ m or greater at a position 15 mm from outflow side	Type of organic pore-forming material	Volume fraction of organic pore-forming material in WC [%]	Void ratio of on-wall catalytic layer [%]	PM deposition pressure loss [kPa]
Ex. Emb. 2	76	Not present	A	46	48	7.0
Ex. Emb. 8	76	Not present	A	24	Could not be defined	7.4
Ex. Emb. 9	76	Not present	A	66	Could not be defined	8.4

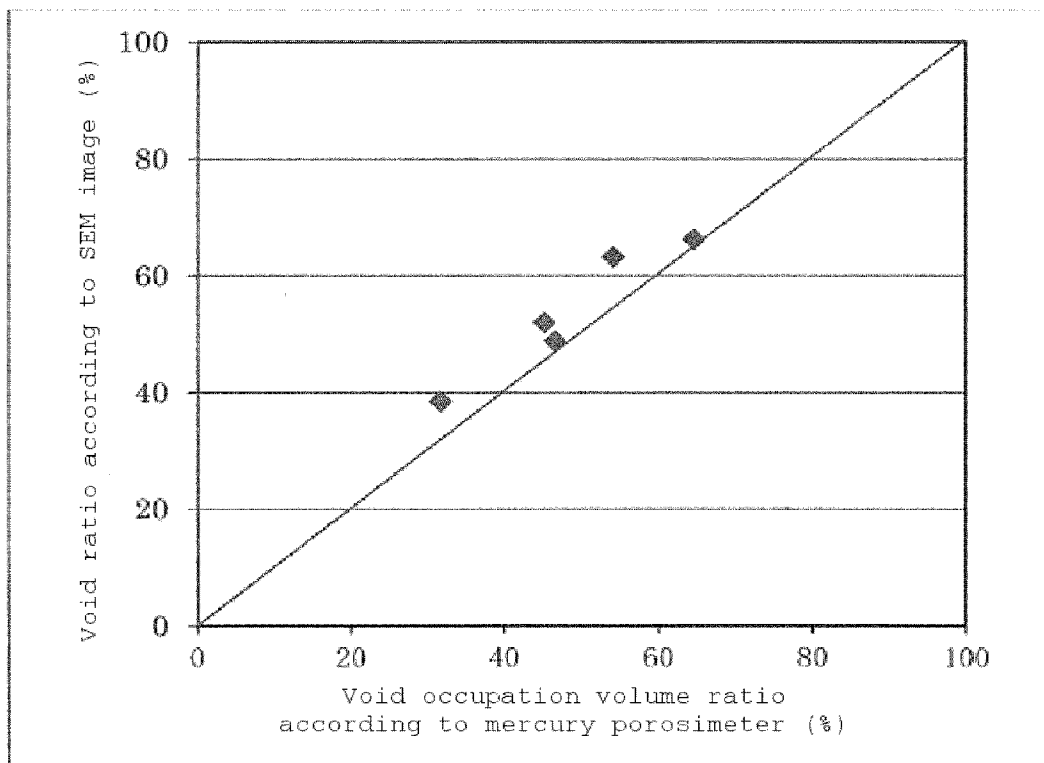
Claims

- [Claim 1] Exhaust gas purification filter including a substrate comprising a plurality of porous partitions,
wherein the partitions form an exhaust gas flow path,
a porous catalytic layer is provided on the partitions and the catalytic layer having a thickness of 10 μm or greater is provided over at least 20% of the total length of the partitions in the lengthwise direction thereof, and
the catalytic layer having a thickness of 10 μm or greater is not present on the partitions 15 mm from an outflow side.
- [Claim 2] Exhaust gas purification filter according to claim 1, wherein the application amount of catalyst component forming part of the catalytic layer varies according to the specific gravity of the catalyst component and the pore volume in the catalytic layer.
- [Claim 3] Exhaust gas purification filter according to claim 1 or 2, wherein the mean diameter of the pores in the catalytic layer is between 1 and 5 μm .
- [Claim 4] Exhaust gas purification filter according to any one of claims 1 to 3, wherein the void ratio of the catalytic layer is no greater than 50%.
- [Claim 5] Exhaust gas purification filter according to any one of claims 1 to 4, wherein the void ratio of the partitions is between 40% and 60%.
- [Claim 6] Exhaust gas purification filter according to any one of claims 1 to 5, wherein the mean diameter of the pores in the partitions is between 10 μm and 20 μm .
- [Claim 7] Exhaust gas purification filter according to any one of claims 1 to 6, wherein the catalyst component may include at least one of platinum and palladium, and at least one of an alkali metal and a rare earth metal.
- [Claim 8] Exhaust gas purification filter according to any one of claims 1 to 7, wherein the thickness of the catalytic layer is between 10 μm and 50 μm .
- [Claim 9] Method for producing an exhaust gas purification filter according to any one of claims 1 to 8, comprising a step in which a slurry including a catalyst component and an organic pore-forming material is applied in order to form pores in a catalytic layer.
- [Claim 10] Method for producing an exhaust gas purification filter according to claim 9, wherein the mean length/diameter ratio of the organic pore-forming material is 1.5 or less.

[Fig. 1]



[Fig. 2]



INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2017/012865

A. CLASSIFICATION OF SUBJECT MATTER INV. B01D53/94 B01J35/00 B01J37/02 B01J23/44 F01N3/035 ADD.																	
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) B01D B01J F01N																	
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 practicable, search terms used) EPO-Internal, WPI Data																	
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>EP 3 001 000 A1 (MITSUI MINING & SMELTING CO [JP]) 30 March 2016 (2016-03-30)</td> <td>1,2,5-8</td> </tr> <tr> <td>Y</td> <td>paragraphs [0021], [0023] - [0026], [0034] - [0036], [0041], [0042], [0053] example 1</td> <td>9,10</td> </tr> <tr> <td>X</td> <td>EP 1 657 410 A2 (CATALER CORP [JP]) 17 May 2006 (2006-05-17) paragraphs [0010] - [0012], [0018], [0019], [0023], [0025] - [0027], [0031], [0032] figure 2 example 1</td> <td>1,2,6,8</td> </tr> <tr> <td></td> <td>----- -/--</td> <td></td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	EP 3 001 000 A1 (MITSUI MINING & SMELTING CO [JP]) 30 March 2016 (2016-03-30)	1,2,5-8	Y	paragraphs [0021], [0023] - [0026], [0034] - [0036], [0041], [0042], [0053] example 1	9,10	X	EP 1 657 410 A2 (CATALER CORP [JP]) 17 May 2006 (2006-05-17) paragraphs [0010] - [0012], [0018], [0019], [0023], [0025] - [0027], [0031], [0032] figure 2 example 1	1,2,6,8		----- -/--	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.															
X	EP 3 001 000 A1 (MITSUI MINING & SMELTING CO [JP]) 30 March 2016 (2016-03-30)	1,2,5-8															
Y	paragraphs [0021], [0023] - [0026], [0034] - [0036], [0041], [0042], [0053] example 1	9,10															
X	EP 1 657 410 A2 (CATALER CORP [JP]) 17 May 2006 (2006-05-17) paragraphs [0010] - [0012], [0018], [0019], [0023], [0025] - [0027], [0031], [0032] figure 2 example 1	1,2,6,8															
	----- -/--																
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.																	
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family																	
Date of the actual completion of the international search		Date of mailing of the international search report															
29 June 2017		06/07/2017															
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Hackenberg, Stefan															

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2017/012865

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2010 227743 A (NGK INSULATORS LTD) 14 October 2010 (2010-10-14) paragraphs [0020], [0027], [0028], [0038], [0047], [0054] - [0058], [0076] figures 3,4a-4c examples 1,8 -----	1-5,7
Y	EP 2 108 447 A2 (NGK INSULATORS LTD [JP]) 14 October 2009 (2009-10-14) paragraph [0079] -----	9,10
A	EP 2 339 135 A1 (NGK INSULATORS LTD [JP]) 29 June 2011 (2011-06-29) paragraphs [0001], [0020], [0021], [0029] - [0031], [0036] - [0046], [0062] - [0067] figure 3 table 1 -----	1-10
A	DE 102 47 946 A1 (BOSCH GMBH ROBERT [DE]) 29 April 2004 (2004-04-29) paragraphs [0013] - [0015] figure 1 -----	1-8
A	EP 2 239 036 A1 (NGK INSULATORS LTD [JP]) 13 October 2010 (2010-10-13) paragraphs [0006] - [0011], [0018] - [0020], [0025] figure 2 example 1 -----	1-8
A,P	WO 2017/001829 A1 (JOHNSON MATTHEY PLC [GB]) 5 January 2017 (2017-01-05) page 4, line 27 - page 5, line 21 page 6, lines 33-37 page 8, line 26 - page 11, line 6 figures 3a, 3b -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2017/012865

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 3001000	A1	30-03-2016	CN 105143620 A 09-12-2015
		EP 3001000 A1	30-03-2016
		JP 5993009 B2	14-09-2016
		JP WO2014189115 A1	23-02-2017
		US 2016115835 A1	28-04-2016
		WO 2014189115 A1	27-11-2014
EP 1657410	A2	17-05-2006	EP 1657410 A2 17-05-2006
		JP 4907860 B2	04-04-2012
		JP 2006136784 A	01-06-2006
		US 2006100101 A1	11-05-2006
JP 2010227743	A	14-10-2010	JP 5349108 B2 20-11-2013
		JP 2010227743 A	14-10-2010
EP 2108447	A2	14-10-2009	EP 2108447 A2 14-10-2009
		JP 5604046 B2	08-10-2014
		JP 2009255055 A	05-11-2009
		US 2009246453 A1	01-10-2009
EP 2339135	A1	29-06-2011	EP 2339135 A1 29-06-2011
		JP 5649945 B2	07-01-2015
		JP 2011147931 A	04-08-2011
		US 2011212831 A1	01-09-2011
DE 10247946	A1	29-04-2004	CN 1688799 A 26-10-2005
		DE 10247946 A1	29-04-2004
		EP 1554473 A1	20-07-2005
		JP 2006502842 A	26-01-2006
		KR 20050059260 A	17-06-2005
		US 2006008396 A1	12-01-2006
		WO 2004036003 A1	29-04-2004
EP 2239036	A1	13-10-2010	EP 2239036 A1 13-10-2010
		JP 5456353 B2	26-03-2014
		JP 2010234317 A	21-10-2010
		PL 2239036 T3	30-11-2012
		US 2010247400 A1	30-09-2010
WO 2017001829	A1	05-01-2017	DE 102016111766 A1 29-12-2016
		GB 2542654 A	29-03-2017
		US 2016375429 A1	29-12-2016
		WO 2017001829 A1	05-01-2017